Studies in desulfurization of transportation fuels

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DOCTOR OF PHILOSOPHY

In Engineering Sciences

By

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Thesis Certificate

This is to certify that the work incorporated in this Ph.D. thesis entitled **Studies in desulfurization of transportation fuels** submitted by **Ms. Nalinee B. Suryawanshi** to Academy of Scientific and Innovative Research (AcSIR) in fulfillment of the requirements for the award of the Degree of **Doctor of Philosophy**, embodies original research work under my guidance. I further certify that this work has not been submitted to any other University or Institution in part or full for the award of any degree or diploma. Research material obtained from other sources has been duly acknowledged in the thesis. Any text, illustration, table etc., used in the thesis from other sources, have been duly cited and acknowledged.

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Declaration by the Candidate

I, Nalinee B. Suryawanshi, hereby declare that this Ph.D. thesis entitled "**Studies in desulfurization of transportation fuels**" is carried out by me for the degree of **Doctor of Philosophy** in **Engineering Sciences** under the guidance and supervision of **Dr. Vinay M. Bhandari**, CSIR-National Chemical Laboratory, Pune, India.

I confirm that thesis work is done wholly by me while in candidature for a research degree at this institution. No part of this thesis has been previously submitted for a degree or any other qualification at this institution or any other institution. Interpretations put forth are based on my reading and understanding of the original articles and all sources have been dually acknowledged.

Nalinee B. Suryawanshi
Student

GururBrahma GururVishnu:
GururDevo Maheshwara: |
Guru Saakshaat ParaBrahma:
Tasmai Sri Gurave Namaha:||

Teacher is a Brahma, Teacher is a Vishnu:
Teacher is Shiva:|
the God of gods:
Teacher is verily the supreme Brahman:
Salutation to teacher:||

Dedicated to

My dear Father and beloved Husband

Shri. Bhatu Suryawanshi

Shri. Darshan Patil

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ABSTRACT

The harmful impact on environment due to SO_x emissions from fuels and increasingly stricter norms over the years worldwide, have amplified deep desulfurization challenges, consequently demanding greater attention on sulfur removal using various newer technologies as well as modifications in existing methods such as adsorptive separations. The present work explores metal modifications of sulfur specific carbon adsorbents- both commercial (Shirasagi TAC and SRCx 4/6) and newer adsorbents derived from *Cassia fistula* biomass (CFP-450) and its impact on sulfur removal behaviour and selectivity. Single and double metal modifications were made using zinc, cobalt, nickel and copper. An attempt was made to investigate further improvements in sulfur removal using process intensification - acoustic cavitation coupled with adsorption. The removal of three refractory sulfur compounds *viz*. thiophene, benzothiophene, dibenzothiophene was studied using the newer adsorbents and the performance was compared with commercial TAC and SRCx 4/6 for both single and double metal impregnation and process intensification. The commercial carbon adsorbent TAC have high capacity for sulfur removal, up to 23mgS/g especially, for dibenzothiophene. In case of TAC, process intensification using cavitation coupled with adsorption improved sulfur removal to the extent of 100% for thiophene and for Ni-Cu modified TAC, capacity increase up to 38mgS/g for dibenzothiophene was obtained. The results indicate that combined effect of metal modification and process intensification can substantially improve the sulfur removal efficiency of carbon adsorbents.

In the next part of work, a novel approach is developed for desulfurization of fuels or organics without use of catalyst. In this process, organic and aqueous phases are mixed in a predefined manner under ambient conditions and passed through a cavitating device. Vapor cavities formed in the cavitating device are then collapsed which generate (*in-situ*) oxidizing species which react with the sulfur moiety resulting in the removal of sulfur from the organic phase. In this work, vortex diode and orifice were used as cavitating devices. Three organic solvents (n-octane, toluene and n-octanol) containing known amount of a model sulfur compound (thiophene) up to initial concentrations of 500ppm were used to verify the proposed method. A very high removal of sulfur content to the extent of 100% was demonstrated. The nature of organic phase and the ratio of aqueous to organic phase were found to be the most important process parameters. The results were also verified and

substantiated using commercial diesel as a solvent. The developed process has great potential for deep desulfurization of various organics, in general, and for transportation fuels, in particular.

It also describes the efficacy of the cavitation process and compares the cavitation yield for two types of cavitation devices-one employing linear flow for the generation of cavities and other employing vortex flow. The cavitation yield is significantly higher for vortex diode compared to the orifice. The process has potential to provide a green approach for desulfurization of fuels or organics without the use of catalyst or external chemicals/reagents apart from newer engineering configurations for effective implementation of hydrodynamic cavitation in industrial practice and also appears to be economically sustainable.

Present study clearly highlights newer developments in the existing deep desulfurization processes such as adsorptive deep desulfurization and also presents a newer technology based on hydrodynamic cavitation for the deep desulfurization of transportation fuels. The analysis provided clearly indicates techno-economic feasibility for the implementation of the developed methodologies.

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Lab	**CSIR-National Chemical Laboratory, Pune**

1. Introduction

Deep desulfurization, in general and transportation fuels, in particular, is a demanding but essential operation, especially from pollution point of view. Euro-VI norms now demand sulfur concentration in diesel and petrol to be less than 10ppm, compared to earlier norms of 350 and 500 ppm in diesel and gasoline, subsequently lowered a decade ago to the level of 15 ppm and 30 ppm in diesel and gasoline respectively. For fuel cell applications, the sulfur levels are required to be much lower (less than 1 ppm) to avoid poisoning of the catalyst. For organics such as turpentine, removal of sulfur can be important in organic synthesis such as production of camphor.

Deep desulfurization during petroleum refining operations has been a challenge mainly due to the difficulties associated with removal of refractory sulfur compounds and also due to varying nature of compounds in different fuel fractions. A conventional catalytic process of hydrodesulfurization (HDS) used in refineries, is considered as a satisfactory method for lowering sulfur content up to 350 ppm due to low reactivity of the remaining refractory compounds and increased cost of operation. It employs catalyst such as Co-Mo or Ni-Mo and requires high temperatures and pressures of the order of 450°C, and 20-40 atm respectively. Employing HDS process to meet the new standards is expected to require 3-fold increase in the catalyst volume/reactor size adversely affecting economic viability apart from adversely affecting quality of fuel. A number of alternative processes are being investigated which include adsorptive desulfurization (Bhandari et al., 2006), biodesulfurization (Soleimani et al., 2007) and oxidative desulfurization(Otsuki et al., 2000). Biodesulfurization is not a preferable process for commercialization due to inherent difficulties in maintaining the optimum conditions and huge space. Adsorptive deep desulfurization appears to hold promise and a number of sorbents starting from simple activated carbons to π-complexation adsorbents, where Cu-Y and Ag-Y zeolites were shown to exhibit good capacity for thiophene sulfur removal from benzene and n-octane mixtures (Yang et al., 2003). Adsorption can be an excellent supplementary process in the existing set-up, has potential in meeting ultra-low sulfur levels at low costs and hence newer insight is required on various aspects ranging from adsorbent types to different modifications-material or process. A wide variety of materials starting from activated carbon (AC), silica-based sorbents, zeolites and metal exchanged/ impregnated activated carbon/ zeolites/ mesoporous materials have been reported in the past for adsorption. Carbon based adsorbents are preferred due to their maneuvering capacity with a variety of starting materials for obtaining high surface area, controllable physical texture, high mechanical strength, possible surface modifications apart from availability of various sources such as coal, wood and so on, Though a very large number of carbon materials from ordinary to nanocarbons have been reported, the desulfurization capacity with majority of these materials was substantially low implying necessity for newer materials developments, strategy for material modifications and process modifications. Further, multifunctional adsorbents have not been discussed in detail to exploit higher capacity due to enhanced interactions. It is instructive to evaluate these effects of metal modifications apart from extracting functionalities from newer biomass as a starting material for obtaining high capacity and for obtaining insight into sulfur removal.

In the present study, single and double metal modifications of carbon adsorbents, using four different metals (Zn/Co/Ni/Cu) have been discussed in the context of deep desulfurization of transportation fuels, based on the premise that cations of transition metal ions with vacant d orbitals are likely to improve adsorption capability. Another engineering modification in the form of process intensification using acoustic cavitation (ultrasonication), without oxidizing agent or catalyst, has been investigated in detail for improving adsorptive desulfurization. A newer biomass derived (*Cassia fistula*) adsorbent, was studied in detail for the removal of refractory sulfur compounds - thiophene, benzothiophene and dibenzothiophene and the results have been compared with those from using sulfur specific commercial carbon adsorbent.

Oxidation processes in different forms have been increasingly discussed for desulfurization of fuels which also include processes that combine oxidation and extraction (Extractive and catalytic oxidative desulfurization or ECOD). In these, more thrust is placed on developing/ evaluating various catalysts for oxidation and suitable extractants for removing oxidation products (Otsuki et al., 2000). Cavitation, which is also one form of advanced oxidation process, has also been discussed largely using catalysts for desulfurization. Commonly, ultrasound assisted oxidative desulfurization is reported in presence of various catalysts for different substrates, while hydrodynamic cavitation is rarely used, that too without using catalyst.

In the present study, another main objective is to report systematic studies on hydrodynamic cavitation for deep desulfurization of fuels and organics without employing any catalyst and under mild operating conditions. Such work on the non-catalytic deep desulfurization using hydrodynamic cavitation has not been reported in the literature and is being studied for the first time. A newer form of cavitating device, vortex diode and a conventional cavitation device, orifice were used as a cavitating device and the performance was compared for extent of sulfur removal, efficiency and finally to evaluate techno-economic feasibility. Thiophene was chosen as a model sulfur compound mainly due to the limitations of the conventional oxidation processes in its removal and also for ease of comparison of the different processes in this regard. Cavitational yields have been discussed in different forms of cavitation apart from establishing the applicability of cavitation method based on hydrodynamic cavitation for sulfur removal, especially by obtaining insight into the sulfur removal behavior not just for different cavitating devices, but also for different process parameters, more importantly on the nature of organic phase by evaluating three different solvents viz. n-octanol, n-octane and toluene, apart from real diesel. It is believed that the present route offers a greener and a sustainable approach to deep desulfurization of various fuels with significant ease of operation along with techno-economic feasibility.

2. Statement of Problem and Objectives of Ph.D. work

To study deep desulfurization of transportation fuels

1) Newer materials as adsorbents for deep desulfurization of fuels - Adsorbent development and application studies
2) Material modifications and application development - modifications using metal impregnation, evaluating effect of different single and multiple metal modifications
3) Newer methodologies for deep desulfurization that employ adsorption process - Adsorption coupled with cavitation
4) Newer technologies for sulfur removal - Hydrodynamic cavitation for deep desulfurization, study on effect of different process parameters, different reactor configurations and so on.

3. Methodology and Organization of Thesis

The methodology of the research involves critical review of literature, finding the gaps in the research studies through state of art literature review, developing newer materials for adsorptive deep desulfurization, characterization of the materials and application studies in desulfurization. The methodology also includes development of a new non-catalytic hydrodynamic cavitation process for deep desulfurization, experimental validation of the developed schemes using newer form of cavitation device - vortex diode and also using conventional cavitation device - orifice. The research also includes comparison of various deep desulfurization processes along with cost estimation for techno-economic feasibility evaluation.

Chapter 1: Chapter one provides introduction on desulfurization of fuels, in general. Sources of crude oil and their sulfur content along with general overview of petroleum refinery and petroleum products are discussed. This chapter also elaborates on the current status of fossil fuels consumption and energy utilization in transportation sector. Further, worldwide challenges and difficulties associated with high consumption of fossil fuels is discussed specifically in the light of current environmental pollution control rules and regulation for sulfur content in transportation fuels. Detailed discussion is also provided on refinery challenges, especially in view of future demand for sulfur free fuels.

Chapter 2: A detailed review has been carried out on the state of art information on various methodologies of desulfurization such as hydrodesulfurization, adsorption, extraction, oxidative desulfurization, biodesulfurization and other advanced methods for desulfurization**.** The advantages and limitations of the established methodologies have been specifically discussed to bring out the gaps in terms of efficacy in applying various methods. There have been various methodologies being researched in desulfurization of fuels and are currently at different stages. The aspects pertaining to their level of development and scope of implementation are elaborated to highlight the selection of the subject for this research. On the basis of the critical review, scope of the present study is outlined at the end of this chapter.

Chapter 3: In this chapter, detailed discussion is provided for characterization methods and analytical techniques used in this work. It includes, SEM, EDX, FTIR, XRD, BET and MP-AES characterization of the materials along with description of analytical instruments such as TOC, COD, GC-FPD, pH and sulfur analyzer TNTS-3000.

Chapter 4, 5 and 6: Chapters 4, 5 and 6 discuss mainly experimental studies on adsorptive deep desulfurization, new process development using hydrodynamic cavitation for deep desulfurization and effect of various process parameters. The salient results are provided in the “Results & Interpretation” section below.

Chapter 7: Chapter 7 summarizes the important results and findings of the present research. Both adsorption and hydrodynamic cavitation were found to be highly effective in deep desulfurization of fuels, however, the newer methodology developed using hydrodynamic cavitation appears to be highly promising in terms of real life application. Thus, the chapter highlights newer insights into the adsorption and cavitation processes and also engineering aspects that are to be considered for practical implementation.

Chapter 8: In this chapter, future directions are provided for both the desulfurization process that mainly include, newer methods/materials, material modifications, systematic studies on real fuels, obtaining insights into the mechanism of the process and also systematic studies using newer hydrodynamic cavitation for the removal of refractory compounds such as benzothiophene and dibenzothiophene.

4. Results with Interpretation

In the 4th Chapter, metal modifications of commercial sulfur specific (Shirasagi TAC, SRCx 4/6) and newer carbon adsorbents derived from *Cassia fistula* biomass (CFP-450) and its impact on sulfur removal behavior and selectivity were explored. Single and double metal modifications were studied using metals such as zinc, cobalt, nickel and copper. An attempt was made to evaluate further improvements in the sulfur removal using process intensification - acoustic cavitation coupled with adsorption. The removal of three refractory sulfur compounds *viz*. thiophene, benzothiophene, dibenzothiophene was studied using the newer adsorbents and the performance was compared with commercial activated carbon, Shirasagi TAC and SRCx for both single and double metal impregnation (Zn/Co/Ni/Cu) and process intensification. It was found that the modified carbon adsorbents have high capacity for sulfur removal, in general, and for dibenzothiophene in particular. The adsorbent modification was found to more favorably assist the removal of higher molecular weight refractory sulfur compounds as compared to thiophene. Process intensification in the form of cavitation coupled with adsorption improved sulfur removal and an overall improvement close to 100 % can be observed for the removal of thiophene using modified TAC. The results indicate that combined effect of metal modification and process intensification can substantially improve the sulfur removal efficiency of carbon adsorbents.

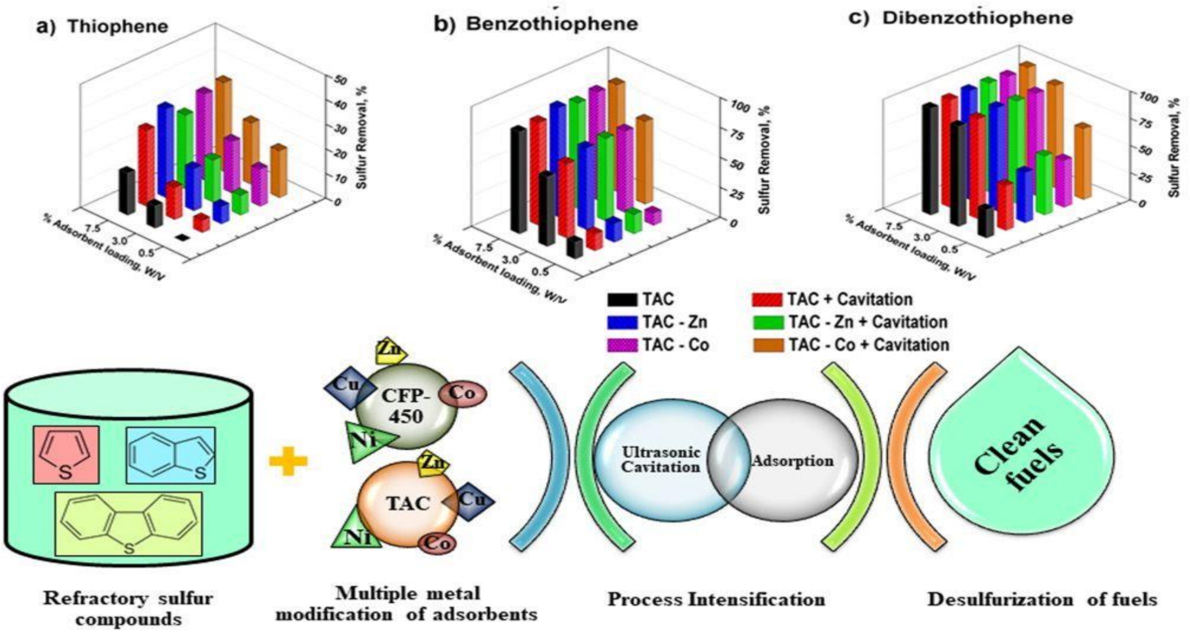

Figure 1: Effect of metal modification and intensification

In the Chapter-5, a novel approach is discussed for desulfurization of fuels or organics without use of catalyst. In this newly developed process, organic and aqueous phases are mixed in a predefined manner under ambient conditions and passed through a cavitating device. Vapor cavities formed in the cavitating device are then collapsed which generate (in-situ) oxidizing species which react with the sulfur moiety resulting in the removal of sulfur from the organic phase. In this work, vortex diode was used as a cavitating device. Three organic solvents (n-octane, toluene and n-octanol) containing known amount of a model sulfur compound (thiophene) up to initial concentrations of 500 ppm were used to verify the proposed method. A very high removal of sulfur content to the extent of 100% was demonstrated. The nature of organic phase and the ratio of aqueous to organic phase were found to be the most important process parameters. The results were also verified and substantiated using commercial diesel as a solvent. The developed process has great potential for deep desulfurization of various organics, in general, and for transportation fuels, in particular (Suryawanshi et al., 2016).

In Chapter-6, a green approach is discussed for desulfurization of fuels or organics without the use of catalyst or external chemicals/reagents using a simple methodology of hydrodynamic cavitation having conventional cavitating device, orifice. The process involves pre-programmed mixing of the organic and aqueous phases, and can be carried out using simple mechanical cavitating devices such as orifice. The process essentially exploits *in situ* generation of oxidizing agents such as hydroxyl radicals for oxidative removal of sulfur. The present work describes the efficacy of the cavitation process and compares the cavitation yield for two types of cavitation devices - one employing linear flow for the generation of cavities and another employing vortex flow. The efficiency of the process is strongly dependent on the nature of device apart from the nature of the organic phase. The effect of various process parameters and engineering designs have been established for three organic solvents (n-octane, toluene, n-octanol) for model sulfur compound - thiophene. A very high removal to the extent of 95% was demonstrated. The results were also verified using commercial diesel. The cavitation yield is significantly higher for vortex diode compared to orifice. The results open newer alternatives, newer engineering configurations for effective implementation of desulfurization (Suryawanshi et al., 2017).

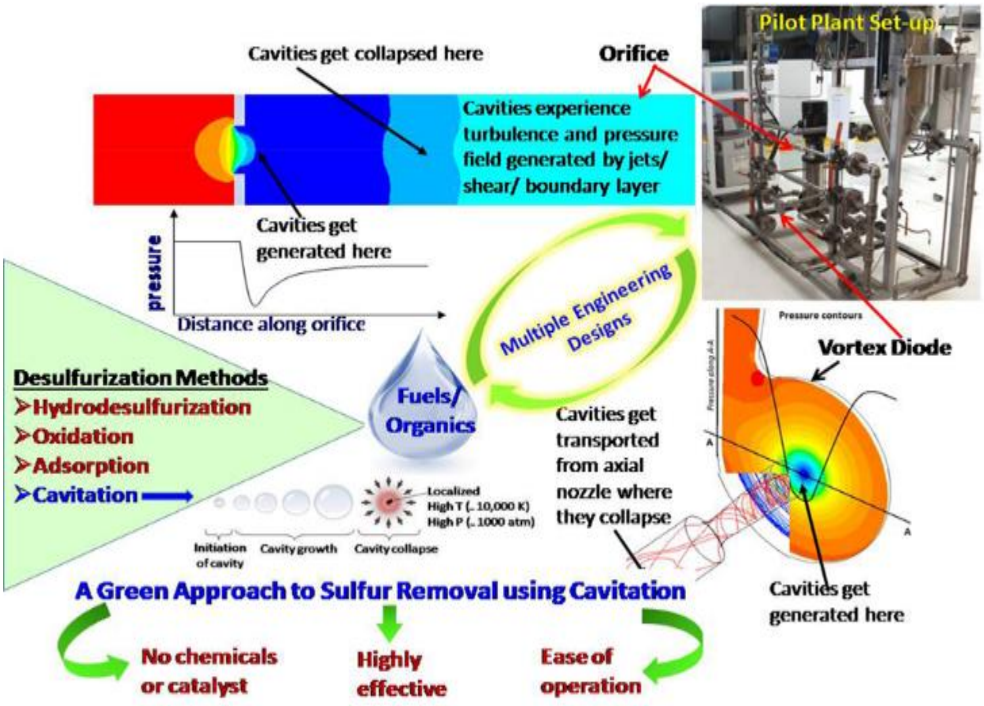

Figure 2: Schematic representation of cavitation process in orifice and vortex diode

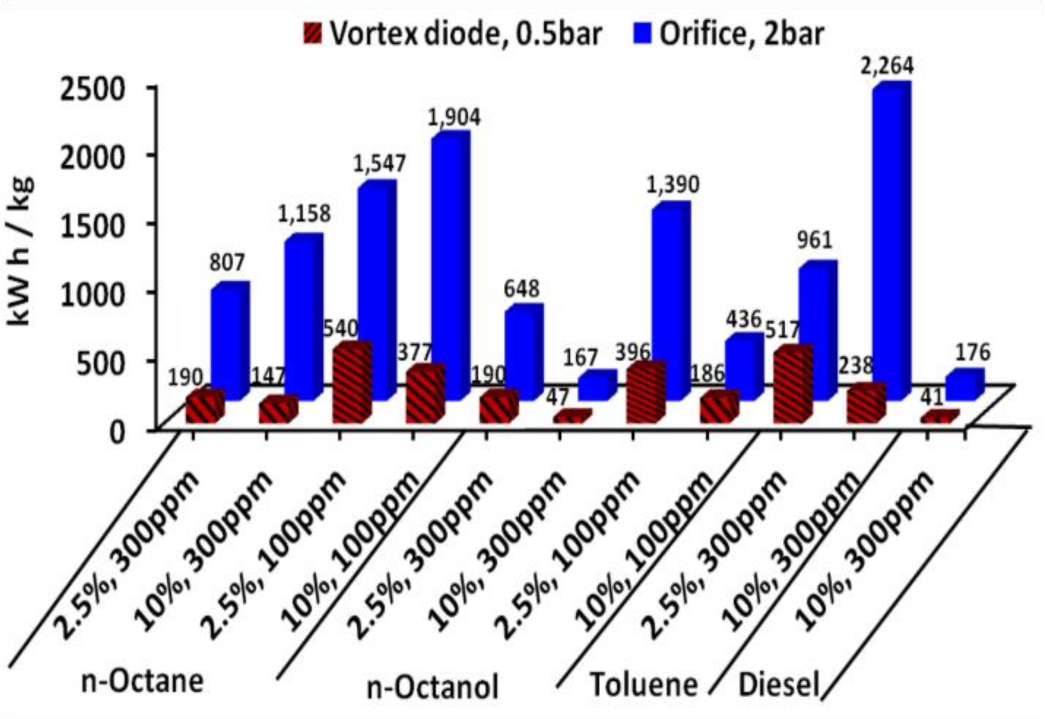

Figure 3: Cost/energy comparison for desulfurization using hydrodynamic cavitation

5. Publications/Patent

Patent

1. Bhandari V. M., Ranade V. V. and **Suryawanshi N. B**. 2015. *Novel process for desulfurization of fuels and organics*. Patent Filed-20/10/2015 (2015-INV-0092: 0230NF2015)

Publications

1. **Nalinee B. Suryawanshi**, Vinay M. Bhandari, Laxmi Gayatri Sorokhaibam, and Vivek V. Ranade. *Non-catalytic Deep Desulfurization Process using Hydrodynamic Cavitation*. Scientific Reports. 6, 33021 (2016); http://doi.org/10.1038/srep33021
2. **Nalinee B. Suryawanshi**, Vinay M. Bhandari, Gayatri Sorokhaibam and Vivek V. Ranade. *Developing techno-economically sustainable methodologies for deep desulfurization using hydrodynamic cavitation*. Fuel, 210, 482–490 (2017) http://doi.org/10.1016/j.fuel.2017.08.106
3. **Nalinee B. Suryawanshi,** Vinay M. Bhandari, Gayatri Sorokhaibam and Vivek V. Ranade. *Investigating adsorptive deep desulfurization of fuels using metal modified adsorbents and process intensification by acoustic cavitation. Ind. Eng. Chem. Res, 58,18, 7593-7606 http://doi.org/10.1021/acs.iecr.8b04043* .

Conference presentations

1. **Nalinee B. Suryawanshi**, Vinay M. Bhandari, Laxmi Gayatri Sorokhaibam and Vivek V. Ranade. Evaluating sulfur specific adsorbents, metal modifications and process intensification for enhanced sulfur removal from fuels. *American Chemical society - Asia Pacific International Chapter Conference (ACS-APICC)*, Jeju. Korea, 5-8 Nov, 2017.
2. **Nalinee B. Suryawanshi**, Vinay M. Bhandari, Laxmi Gayatri Sorokhaibam and Vivek V. Ranade.Developing sustainable methodologies for desulfurization of fuels. *Sustainable catalytic technologies*, CSIR-NCL,Pune, 8-9 June, 2017
3. **Nalinee B. Suryawanshi**, Vinay M. Bhandari, Laxmi Gayatri Sorokhaibam and Vivek V. Ranade. Newer developments in desulfurization of transportation fuels.

Recent advancements in chemical, environmental & energy engineering (RACEEE), Chennai, 23-24 Feb, 2017

4. **Nalinee B. Suryawanshi**, Vinay M. Bhandari, Laxmi Gayatri Sorokhaibam and Vivek V. Ranade. Air pollution control through deep desulfurization of transportation fuels. *International conference on sustainable development for energy and environment (ICSDEE)*, CSIR-NCL, Pune, 16-17 Jan, 2017
5. **Nalinee B. Suryawanshi**, Laxmi Gayatri Sorokhaibam, Monal S. Salvi, Vinay M. Bhandari and Vivek V. Ranade. Newer adsorbents, adsorbent modifications and process intensification for production of ultra-low sulfur diesel. *7th DAE-BRNS symposium on emerging trends in separation science and technology (SESTEC)*, Guwahati, 17-20 May 2016
6. **Nalinee B. Suryawanshi**, Vinay M. Bhandari, Vivek V. Ranade. Newer carbon adsorbents and process intensification methodologies for deep desulfurization of fuels. *National conference on carbon materials (NCCM)*, Delhi, 26-28 Nov. 2015.

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5. Suryawanshi N. B. et al. Non-catalytic Deep Desulfurization Process using Hydrodynamic Cavitation. *Scientific Reports*. 6, 33021 (2016)
6. Suryawanshi N. B. et al. Developing techno-economically sustainable methodologies for deep desulfurization using hydrodynamic cavitation. *Fuel*, 210, 482–490 (2017)

List of Abbreviations

AC	Activated carbon
ACB	Activated carbon beads
ACF	Activated carbon fiber
ASA	Amorphous silica-alumina
ASL	Aluminized SBA-15 with large pores
BDS	Biodesulfurization
BET	Brunauer - Emmett - Teller
BT	Benzothiophene
CNF	Carbon nanofiber
COD	Chemical Oxygen Demand
DBT	Dibenzothiophene
DMT	Dimethyl thiophene
DMDBT	Dimethyl dibenzothiophene
ECOD	Simultaneous extractive - catalytic oxidative desulfurization
EDTA	Ethylene diamine tetra acetic acid
EDX	Energy Dispersive X-ray Spectroscopy
FCC	Fluid catalytic cracking
FTIR	Fourier Transform Infrared Spectroscopy
HC	Hydrodynamic cavitation
HDS	Hydrodesulfurization
HKUST	University name
HRP	Horseradish peroxidase
IWI	Incipient wetness impregnation
ICP-OES	Inductive coupled plasma-optical emission spectroscopy
Ktoe	Kilotonne of oil equivalent
LPG	Liquified petroleum gas
MCP	Microporous coordination polymer
MCM	Mobile composition of matter
MT	Methyl thiophene
MOF	Metal organic framework
MP-AES	Microwave plasma- atomic emission spectroscopy
Mtoe	Million ton of oil equivalent
ODS	Oxidative desulfurization

POM	Poly oxometallate
PPM	Parts per million
PTA	Phase transfer agent
RCS	Resin derived carbon spheres
S	Sulfur
SDBS	Sodium dodecyl benzene sulfonate
SEM	Scanning Electron Microscope
SWCNT	Single wall carbon nanotubes
T	Thiophene
TBAB	Tetra butyl ammonium bromide
TBHP	Tertiary-butyl hydroperoxide
TMC	Transition metal catalyst
TOC	Total Organic Carbon
TS-1	Titanium silicate
UAOD	Ultrasound assisted oxidative desulfurization
UMCM	University of Michigan crystalline material
WHO	World health organization
XRD	X-ray diffraction

Nomenclatures

k_L	Langmuir adsorption constant
c_e	Equilibrium concentration
q_e	Equilibrium adsorption capacity
q_{max}	Maximum adsorption capacity
c_0	Initial concentration
k_F	Freundlich constant
n	Heterogeneity factor
q_e	Equilibrium adsorption capacity
A	Temkin constants
B	Temkin constants
A_T	Equilibrium binding constant
R	Molar gas constant
T	Adsorption temperature in K
b	Constant associated with heat and adsorption
C	Cost of operation (kWh/kg)
P	Pressure (bar; N/m^2)
R	Amount of sulfur removed (mg)
Rs	Indian rupees
Q	Flow rate (LPH; m^3/s)
T	Temperature (K)
t	Time (s)
v	Volume (m^3)
V	Total volume (m^3)
Y	Cavitational yield (mg/J)
ΔP	Pressure drop (bar; N/m^2)
σ	Efficiency of pump
a	Square law constant

Chapter 1

Chapter 1
Introduction

Removal of sulfur has emerged as a grand challenge in recent years in numerous applications such as fuel processing (desulfurization of transportation fuels for reducing air pollution due to SOx), number of catalytic processes, fuel cell (to avoid poisoning of the catalyst) and in waste gas desulfurization (air pollution control). The complexity in each case is different due to nature of various sulfur compounds and also due to the different norms associated with the applications - e.g. sulfur content is required to be less than 10 ppm for the use of transportation fuels whereas for fuel cell application, the sulfur content is required to be lower than 1 ppm. The research in the area of desulfurization has become imperative due to increasingly stricter norms of sulfur content in fuels over recent years for environmental pollution control apart from persistent demands to meet challenges of desulfurization by developing newer materials, material modifications and for developing newer technologies.

1.1 History and general outline

The term “Sulfur” is derived from sanskrit word “sulvere” and from the latin word “sulfurium” [1]. Sulfur is a one of the most abundant element in the universe. It is present in the form of minerals, such as galena(Pbs), gypsum ($CaSO_4 \cdot 2(H_2O)$), pyrite (FeS_2), sphalerite (ZnS or FeS), cinnabar (HgS), stibnite (Sb_2S_3), epsomite ($MgSO_4 \cdot 7(H_2O)$), celestite ($SrSO_4$) and barite ($BaSO_4$). Petroleum refineries use sulfur containing crude oil as raw material for obtaining transportation fuels such as diesel, gasoline and jet fuel. The sulfur content in the crude varies from place to place and as the oil well go deeper in obtaining the crude, the difficulty in removal of sulfur increases due to high sulfur content and increased refractory nature of sulfur compounds. According to level of sulfur concentration, crude oil can be classified as sweet or sour crude oil and sulfur concentration more than 0.5% or 1% is considered as “sour” crude. [2–5]. Table 1.1 provides typical data for the variation of sulfur concentration in crude depending upon the source.

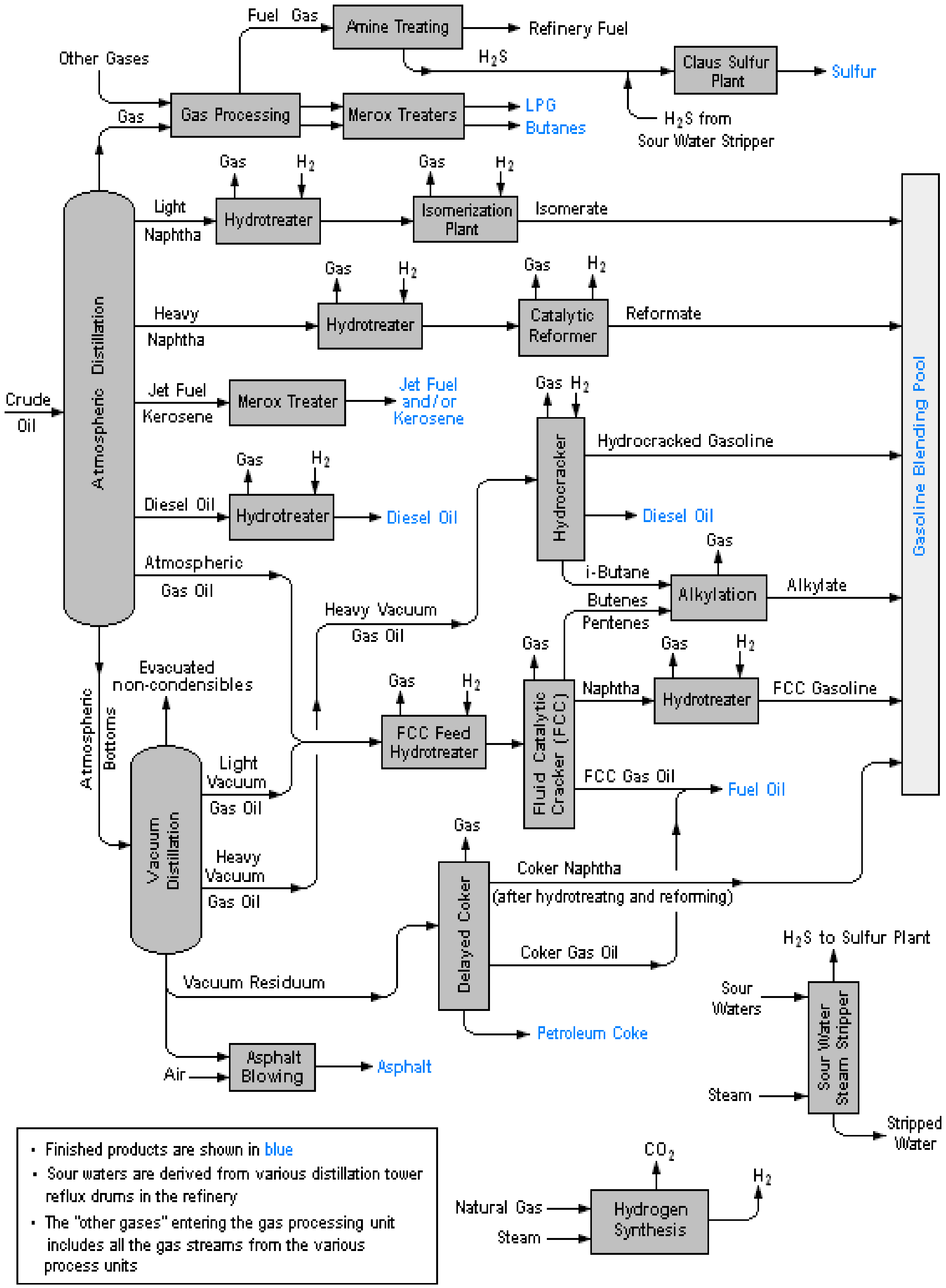
Table 1.1: Worldwide data of crude oil sulfur concentration

Location	**Crude oil, Sulfur weight %**	**Location**	**Crude oil, Sulfur weight %**
Bombay High[4,5] (India)	0.142-0.17	Arabian crude[2,3]	1.3
Rajasthan crude[4] (India)	0.34	Iranian crudes[2,3]	1.3
Indonesia[6]	0-0.5	Kuwait[2,3]	2.5
Heavy Merey (Venezuelan crude oils)[7]	2.74	Mexiacan and venezuelan[2,3]	2.5-4
Leona (Venezuelan crude oil)[7]	1.5	Tapis crude (Malaysian)[6]	0.03
Heavy Merey Venezuelan crude oils (14 years ago)[7]	2.2	Clov, Angola (west Africa)[6]	0.26

1.2 Overview of typical petroleum refinery

Petroleum refinery produces wide variety of products close to 2500. Composition of crude oil is important in deciding sequencing of different processes in refinery. Crude oil contains paraffins, naphthene, cycloparaffins, aromatics, olefins and impurities like sulfur, nitrogen, and oxygen[8].

Fractionation of crude oil gives LPG, light naphtha, heavy naphtha, jet fuel/kerosene, diesel oil, gas oil, light vacuum gas oil, heavy vacuum gas oil, vacuum residue and asphalt. Further processing of different streams is carried out using processes such as hydrodesulfurization, merox treater, catalytic reforming, isomerization, alkylation, catalytic cracking etc. Hydrotreating/ hydrodesulfurization, merox processes are required for desulfurization of liquid fuels; light nahtha, heavy naphtha, jet fuel and diesel oil and amine treatment, claus/super claus processes are required for sulfur recovery[8,9].



- Finished products are shown in blue
- Sour waters are derived from various distillation tower reflux drums in the refinery
- The "other gases" entering the gas processing unit includes all the gas streams from the various process units

Figure 1.1: Schematic diagram of typical petroleum refinery[10]

1.3 Sulfur removal processes in petroleum refinery

Petroleum refineries typically have hydrodesulfurization and merox process for sulfur removal from liquid/gaseous fractions.

1.3.1 Hydrodesulfurization

Hydrodesulfurization is one of the well-established refinery process for sulfur removal. It is effectively run for all liquid fractionation streams from light range naphtha, jet fuel to high range diesel, fuel oil and high boiling fractions. The process parameters such as temperature, pressure, catalyst etc. and reactor configurations vary depending upon the properties of the feedstock. The process involves reaction with hydrogen in presence of catalyst at high pressure (20-40atm) and temperature (300-450°C) and release the sulfur moiety in the form of H_2S. [9,11].

Advantages of HDS process

1) Effective in removal of thiophenes, sulfides and disulfides
2) Effectively removes sulfur generally up to 300ppm

Limitations of HDS process

1) Difficulty in removal of refractory sulfur compounds
2) Intensive process conditions
3) High energy consumption
4) Regeneration of catalyst

1.3.2 Adsorption processes

A wide variety of materials starting from activated carbon (AC), silica-based sorbents, zeolites and metal exchanged/ impregnated activated carbon/ zeolites/ mesoporous materials have been reported in the past for adsorption. Detailed literature review on different adsorbents is provided in chapter 2. The literature studies reveal rather a conflicting picture with many studies showing substantially lower capacities for sulfur removal except Yang and co-workers[12], success with transportation fuels such as commercial diesel is far from being achieved. Adsorption based commercial processes for desulfurization of liquid fuels are explained in following discussion.

1.3.2.1 S-Zorb process[13,14]

In the S-Zorb process of Phillips Petroleum, USA (2001, 2003), a propriety solid sorbent is employed in temperature range of 377-502^{o}C and pressure range of 7-21 kg/cm^{2} in presence of hydrogen and the sulfur is retained on the surface of the adsorbent and hydrocarbon portion is released back into the process stream. Thus, this is essentially reactive adsorption process.

1.3.2.2 Selective adsorption for removing sulfur (PSU-SARS Process)[13,14]

PSU-SARS process, developed by Pennsylvania State University, removes sulfur compound from fuels such as gasoline, diesel, jet fuel and works at low temperature and ambient pressure in absence of hydrogen. This process uses a transition metal-based adsorbent for desulfurization.

1.3.2.3 IRVAD process[13,14]

IRVAD process was developed by Black and Veatch Irritchard Inc. and Alcoa Industrial Chemicals. The process uses alumina-based selective adsorbent in a countercurrent multistage absorber. The process operates at lower pressure and works in absence of hydrogen.

1.3.2.4 Transport reactor for naphtha desulfurization (TReND) process[13,14]

TReND process was developed by Research Triangle Institute. This process uses regenerable metal oxide sorbent to retain sulfur compound on its surface. It is reactive adsorption process. Temperature range for TReND process is 426-535^{o}C with or without the presence of H_2 gas feed.

1.3.3 Extraction followed by oxidation processes

Sulfur compounds are comparatively more polar compounds than other organics present in gasoline and diesel. It is possible to extract them into the ionic liquids and other extractant. However, only extraction is not enough for achieving desired sulfur removal and process combination is generally used. Merox is one such commercial process in petroleum refineries for desulfurization of gases and liquids, however, is suitable mainly for removal of mercaptans. Merox uses NaOH as a solvent for extraction and can efficiently remove mercaptans from LPG, naphtha, kerosene and diesel. Extracted mercaptans can be converted to disulfide using air and catalyst. In another advancement of Merox process, “Merox sweetening process” heavy mercaptans are oxidized to disulfides using organometallic catalyst and air[15,16]. The Merox process has been widely accepted by the petroleum industry; and a number of units are believed to be in operation. However, the process has limitations in deep desulfurization.

1.3.4 Oxidation followed by extraction/adsorption processes

Organic sulfur compounds are more polar hydrocarbons so it is relatively easy to oxidize them[17]. Oxidative desulfurization (ODS) is usually carried out in two steps, oxidation followed by extraction or adsorption. Oxidative desulfurization requires oxidizing agent (convert sulfur containing compounds to polar oxidized species), catalyst, phase transfer agent and extractant. ODS have several advantages compared to HDS, refractory sulfur compounds such as dibenzothiophenes and alkyl derivative of dibenzothiophene can be oxidized at ambient conditions[17]. Moreover, hydrogen is not required so oxidative desulfurization is considered to be more viable option for desulfurization. Ultrasound assisted[18], photo assisted[19] and electrochemically assisted are new upcoming advancements in oxidative desulfurization. ODS based commercial processes for liquid fuels are explained in following discussion.

1.3.4.1 Petrostar process[13,14]

Petrostar process removes sulfur from diesel fuel using chemical oxidation. In this process, first water emulsion with diesel fuel is obtained, and subsequently the sulfur atom is oxidized to a sulphone using catalyst such as peroxyacetic acid. Polar oxidized sulfur compound is extracted into aqueous phase.

1.3.4.2 SulphCo's Systems[20]

This process works at relatively low temperature, low pressure and without phase transfer catalyst. Estimated capital cost of SulphCo unit for \$1000bbl^{-1}of installed capacity is less than half the cost of new high pressure hydrotreater.

Limitations of oxidative processes

1. Employ toxic and expensive chemicals such as oxidizing agent, catalyst, phase transfer agent and extractant/adsorbent
2. Energy intensive operation
3. Regeneration of extractant is a major challenge in oxidative desulfurization

1.3.5 Biological Processes

Biological route for desulfurization is being extensively investigated since last few decades. Both aerobic and anaerobic processes are reported. Anaerobic biodesulfurization is a basically a reductive process in which H_2S is liberated as an end product. This occurs through C-S bond cleavage. Main advantage of this pathway is that it maintains the calorific value of the fuel and also avoids gum formation of products. The limiting factor for anaerobic desulfurization is that, it has slow growth, difficulty in maintaining anaerobic operating conditions and specific activities of most isolated strains is insignificant for DBT[21]. Aerobic biodesulfurization is a destructive way of desulfurization of the hydrocarbon chain. It consists three main steps including hydroxylation, ring cleavage, and hydrolysis. Aerobic biodesulfurization follows oxidation pathways. Biodesulfurization is slow, has difficulty in maintaining optimum conditions for growth of microorganisms and in separation. Thus, biodesulfurization is not considered as a promising technology as of now (Soleimani[22] and Srivastava[23]).

1.4 Deep desulfurization of transportation fuels

Diesel, petrol and jet fuel are the most widely used liquid transportation fuels as compared to other fuels, and diesel and gasoline are increasingly blamed for pollution in cities due to vehicular traffic[24]. Petroleum based fuels contain significantly high amount of sulfur due to the inherent presence of sulfur in crude oil. Combustion of sulfur containing fuel in vehicles is the main source of SO_X in the atmosphere. It has potential impact on human health and environment.

Health[25]

1) SO_2 is harmful to the animals and all living beings.
2) SO_2 is also harmful to the eyes and respiratory system. SO_2 inhalation increases respiratory diseases e. g. difficulty in breathing and premature death.

Environment[25]

1) Damage to plants and reduce crop yields
2) At high SO_2 concentrations, SO_2 combines with water vapor in the air to produce sulfuric acid that causes acid rain. Acid rain can pollute water bodies and wildlife.

1.4.1 Worldwide norms/regulations for sulfur concentration in transportation fuels

US-EPA (Environmental Protection Agency) has directed sulfur level below 10ppm(w/w) in the United States of America[26–28]**.** Similarly, European countries and other developed countries have been following use of ultra-low sulfur fuel (less than 10ppm). In 2016, Indian government proposed to implement Euro-VI emission norms by 2020 for criteria air pollutants in exhaust emissions of diesel and petrol vehicles and for pollutant concentration in transportation fuels (S<10ppm). Country wise variation for sulfur regulation in diesel and petrol is shown in Table 1.2. In addition to regulations for transportation fuels, additional stringent norms have been set for criteria pollutants in ambient air. In the Table 1.3, ambient air norms for SO_2 are shown for USA, Europe, India and world health organization (WHO).

1.5 Demand for ultralow sulfur fuels in other applications

1.5.1 Fuel cells

Sulfur in the transportation fuels has been a major concern not just from environment point of view, but also from viewpoint of application in fuel cells. Fuel cell is an electrochemical device which is used to convert chemical energy to electrical energy and heat. It is used as electricity generation source for various applications.

Table 1.2: Country wise variation for sulfur regulation in diesel and petrol

Country	**Vehicle, %**[29]	**Diesel**	**Gasoline**
China[30]	25%	≤10ppm (2017 to current)	≤10ppm (2017 to current)
USA[26–28]	19%	≤15ppm (2006 to current)	≤10ppm (2017 to current)
Europe[31]	17%	≤10ppm (2009 to current)	≤10ppm (2009 to current)
Japan[32]	6%	≤10ppm (2005 to current)	≤10ppm (2005 to current)
India[33]	4%	≤50ppm (2017 to current, ≤10ppm from 2020)	≤50ppm (2017 to current, ≤10ppm from 2020)
Russia[34]	3%	≤10ppm (2016 to current)	≤10ppm (2016 to current)
Canada[35]	2%	≤15ppm (2006 to current)	≤10ppm (2017 to current)
South Korea[36]	2%	≤10ppm (2009 to current)	≤10ppm (2009 to current)
Australia[37], [38]	1%	≤10ppm (2009 to current)	≤50ppm (2008 to current)
Middle East [39,40]	-	7000-8000ppm	100-1500ppm(Current)

Hydrocarbon containing fuel is catalytically reformed for generation of hydrogen. Different fuel sources such as natural gas, liquefied petroleum gas, light distillates, methanol, ethanol, dimethyl ether, naphtha, gasoline, kerosene, jet fuels, diesel, and biodiesel are considered. In catalytic reforming, noble metals and transition metals are used as a reforming catalyst for generation of hydrogen. Even small traces of sulfur cause poising of the catalyst thereby loss of reforming activity and reduction in catalyst life. As a rule of thumb, sulfur concentration in fuels should be sub-ppm level[47]. These aspects make desulfurization a crucial research subject for the mankind and attach a high priority to it.

1.5.2 Biofuels

From sustainability point of view, biofuels can be an attractive option and is increasingly being considered in recent years. Biodiesel and biofuels such as ethanol have high potential in

Table 1.3: Ambient air quality standards for SO_2

US-EPA[41,42]	**Primary** 1-hour standard at a level of 75ppb **Secondary** 500 ppb averaged over three hours, not to be exceeded more than once per year
Europe[43]	**24 hours** 125µg/m^3 **1 hour** 350 µg/m^3
India[44,45]	**Industrial, Residential, Rural and Other Areas** **Annual:**50 µg/m^3 **24hours:**80 µg/m^3 **Ecologically Sensitive Area (notified by Central Government)** **Annual:**20 µg/m^3 **24hours:**80 µg/m^3
WHO[46]	**24 hours:** 20 µg/m^3: **10-minutes:** 500 µg/m^3

commercial use and for reduction of greenhouse gases. US-EPA has taken a decision to reduce sulfur concentration in gasoline less than 10ppm and mandatory to add 15% ethanol in gasoline from 1st Jan 2017. Thus, these biofuels are also required to meet the same stringent norms of sulfur content, in spite of the fact that the initial levels of sulfur in these are low as compared to that in petroleum fuels. Thus, deep desulfurization of biofuels is another upcoming research area.

1.6 Challenges for refinery to reach ULSD(<10ppm)

1. The existing refineries are required to install new process(es) or supplement the existing process/ upgrade the existing process. The modifications to existing HDS process involve changes in process variables, modifying/replacing catalyst and modifying reactor configuration.
2. Cost of desulfurization is a major concern. e.g. Indian "PSUs will be required to spend about Rs 28.8k crore to upgrade existing refineries for producing auto fuels with

enhanced specifications. The refiners will require a premium of Rs 0.3/liter in auto fuels price to generate adequate returns on these investments [48].

From the above discussion, it is evident that the conventional method for desulfurization in refinery is hydrodesulfurization and though it is effective in efficient removal of thiols, sulfides and disulfides, it is not effective in the removal of refractory sulfur compounds. It becomes increasingly difficult to remove sulfur compounds from fuels as the sulfur concentration is reduced and the existing methods have difficulty in removing refractory sulfur compounds which is crucial for achieving ultralow sulfur levels. The objective of the present research is to develop materials and methods for efficient removal of sulfur from transportation fuels and to evaluate techno-economic feasibility. Further, the research investigations are aimed at developing processes for the production of sulfur free fuels with high selectivity. Both adsorption and advanced oxidation processes have been studied for deep desulfurization. Newer adsorbents and adsorbent modifications were evaluated for increasing the sulfur removal capacity. Process intensification in the form of cavitation coupled adsorption was investigated in detail to find out impact on removal efficiency. A new process, a non-catalytic hydrodynamic cavitation process was developed for deep desulfurization of fuels.

1.7 Scope and organization of the thesis

From the detailed literature review, it is evident that adsorptive desulfurization holds great potential both in terms of newer materials as adsorbents and suitable modifications of existing adsorbents for improving capacity/regeneration ability. Metal modifications that provide stronger bonding with sulfur compounds appear to be more promising and multiple metal modifications have been only sparsely reported.

Further, though a large number of catalysts and catalytic processes have been explored so far, the process conditions are not very conducive especially from selectivity in desulfurization point of view. Thiophene is still difficult to remove using oxidative processes and lot of research is still required for achieving satisfactory levels of desulfurization for all refractory sulfur compounds. Further, newer developments in the form of new process, catalytic or noncatalytic, or newer technologies are essential in view of incremental benefits that are possible with conventional processes. Thus, it is imperative that newer horizons be researched that not only provide newer insights into the desulfurization processes, but also have potential from commercialization point of view in future.

In view of the above analysis, the present research specifically focuses on newer developments in the area of adsorptive deep desulfurization, including newer material development and development of newer processes that employ advanced oxidation in a completely different format using hydrodynamic cavitation. The objectives of the study include:

1. Development of newer materials as adsorbents and application studies
2. Studies on material modifications and application development - adsorbent modifications using metal impregnation, evaluating effect of different metal modifications, evaluating effect of single and multiple metal modifications
3. Characterization of materials using SEM, TEM, XRD, FTIR, BET surface area/pore size, ICP etc.
4. Process intensification in adsorption process - adsorption coupled with cavitation
5. Development of newer technologies for sulfur removal - hydrodynamic cavitation for deep desulfurization
6. Optimization of process parameters in desulfurization using hydrodynamic cavitation
7. Evaluating effect of different reactor configurations in desulfurization using hydrodynamic cavitation.

The objective of the research is to obtain insight into the above-mentioned aspects so that there is significant improvement in the existing knowledgebase which will help in deep desulfurization of transportation fuels.

The thesis is organized in 8 Chapters, including introduction, literature survey, analytical techniques and measurements, adsorptive desulfurization process, non-catalytic process for deep desulfurization of fuels using vortex diode in hydrodynamic cavitation, non-catalytic process using orifice as a cavitating device in hydrodynamic cavitation and evaluating techno-economic feasibility of the newly developed cavitation process, conclusions and scope for future work.

Chapter-1: This chapter provides background and highlights importance of the subject-desulfurization of transportation fuels. It also provides brief overview of the desulfurization processes and implications of carrying out research in this important research subject.

Chapter-2: Chapter-2 provides critical review of the literature encompassing all the major areas of research. In view of the importance of the subject and increasingly stringent government regulations worldwide, enormous research is being carried out all over the world. India has specific needs in this regard due to imports of not just crude but also of technologies for processing crude oil and in view of severe air pollution experienced in major cities which is largely attributed to vehicular emissions. Thus, Chapter-2 elaborates the state of art literature review in the area of desulfurization of transportation fuels and identifies research gaps in each area. This chapter also forms basis for the work carried out in this research study.

Chapter-3: In this chapter, characterization and analytical techniques involved in this research are discussed. Instrument details and procedures, specifically pertaining to Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDX), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Surface Area Analyzer, Micro Plasma Atomic Emission Spectroscopy (MP-AES), Inductive Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), Total Organic Carbon analyzer (TOC), Chemical Oxygen Demand analyzer (COD), Gas Chromatography-Flame Photometric Detector (GC-FPD), pH and Sulfur analyzer (TN-TS) have been elaborated.

Chapter-4: Chapter-4 discusses in detail the newer insight obtained in adsorptive desulfurization processes. It explores metal modifications of sulfur specific carbon adsorbents-both commercial (Shirasagi TAC and SRCx 4/6) and newer adsorbents derived from *Cassia fistula* biomass (CFP-450) and its impact on sulfur removal behaviour and selectivity. Single and double metal modifications were made using zinc, cobalt, nickel and copper. An attempt was made to investigate further improvements in sulfur removal using process intensification -acoustic cavitation coupled with adsorption. The removal of three refractory sulfur compounds *viz*. thiophene, benzothiophene, dibenzothiophene was studied using the newer adsorbents and the performance was compared with commercial TAC and SRCx 4/6 for both single and double metal impregnation and process intensification. The modified carbon adsorbents have high capacity for sulfur removal, up to 23mgS/g especially, for dibenzothiophene. In case of TAC, process intensification using cavitation coupled with adsorption improved sulfur removal to the extent of 100% for thiophene and for Ni-Cu modified TAC, capacity increase up to 38mgS/g for dibenzothiophene was obtained. The results indicate that combined effect of metal modification and process intensification can substantially improve the sulfur removal efficiency of carbon adsorbents.

Chapter-5: This chapter presents a novel approach developed for desulfurization of fuels or organics without use of catalyst. In this process, organic and aqueous phases are mixed in a predefined manner under ambient conditions and passed through a cavitating device. Vapor cavities formed in the cavitating device are then collapsed which generate (in-situ) oxidizing species which react with the sulfur moiety resulting in the removal of sulfur from the organic phase. In this work, vortex diode was used as a cavitating device. Three organic solvents (n-octane, toluene and n-octanol) containing known amount of a model sulfur compound (thiophene) up to initial concentrations of 500 ppm were used to verify the proposed method. A very high removal of sulfur content to the extent of 100% was demonstrated. The nature of organic phase and the ratio of aqueous to organic phase were found to be the most important process parameters. The results were also verified and substantiated using commercial diesel as a solvent. The developed process has great potential for deep desulfurization of various organics, in general, and for transportation fuels, in particular.

Chapter-6: This chapter describes the efficacy of the cavitation process and compares the cavitation yield for two types of cavitation devices-one employing linear flow for the generation of cavities and other employing vortex flow. The process involves pre-programmed mixing of the organic and aqueous phases, and can be carried out using simple mechanical cavitating devices such as orifice or vortex diode. The process essentially exploits in situ generation of oxidising agents such as hydroxyl radicals for oxidative removal of sulfur. The efficiency of the process is strongly dependent on the nature of device apart from the nature of the organic phase. The effects of process parameters and engineering designs were established for three organic solvents (n-octane, toluene, n-octanol) for model sulfur compound-thiophene. A very high removal to the extent of 95% was demonstrated. The results were also verified using commercial diesel. The cavitation yield is significantly higher for vortex diode compared to the orifice. The process has potential to provide a green approach for desulfurization of fuels or organics without the use of catalyst or external chemicals/reagents apart from newer engineering configurations for effective implementation of hydrodynamic cavitation in industrial practice and also appears to be economically sustainable.

Chapter-7: Chapter-7 summarizes important achievements and conclusions of the present study for adsorbents, adsorbent modifications, adsorptive desulfurization, new hydrodynamic cavitation process using vortex diode, new cavitation process using orifice and techno-economic analysis of the processes.

Chapter-8: Chapter-8 highlights the limitations of the desulfurization processes so far and makes important suggestions for future work.

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Chapter 2

Chapter 2
Literature Review

Origin of crude oil-based petroleum refinery dates back to 1890. The concept of flue gas desulfurization(FGD) was reported in 1850 and first major FGD unit was installed in 1932 at Battersea Power Station, owned by London Power Company[1]. Subsequently, first catalytic hydrodesulfurization unit was commercialized for naphtha reformer in 1950. Desulfurization research has been continuing since more than five decades and widely studied for all fuels. Fractionation of crude oil produces different boiling range fuel fractions such as liquified petroleum gas, naphtha, kerosene, diesel, fuel oil, heavy oil etc. and specific sulfur removal unit is recommended for different hydrocarbon feedstocks on the basis of physical characteristics. This chapter mainly reviews the desulfurization of liquid transportation fuels. Processes for desulfurization of petroleum based liquid transportation fuels have been thoroughly reviewed, critically analyzed and the research gaps have been identified. The advantages and disadvantages, especially from the point of view of techno-economic feasibility, have been highlighted.

2.1 Liquid transportation fuels

Liquid transportation fuels are the liquid form of the fuels which are used for transportation purpose. It contains the petroleum based fossil fuels (such as gasoline, kerosene, diesel), compressed natural gas, liquefied natural gas, non-petroleum fossil fuels (liquid fuels from coal and natural gas), biodiesel, alcohols, and so on[2].

The application/use of fuels correlates strongly to energy requirement of any country. Energy consumption pattern of European countries is shown in Fig 2.1. Gas/diesel oil, gasoline and kerosene - jet fuel (listed in order of significance) are by far the three most important products of last 25-year-period. Consumption of gasoline, kerosene and diesel in transportation sector is comparatively far higher than other fuels[3] as shown in Fig 2.2. Similar trend has been observed for diesel, gasoline and jet fuel consumption in other parts of the world. Higher consumption of these fuels in transportation sector causes the release of various pollutants (such as SO_X and NO_x) in the environment. SO_X is one of the criteria air pollutant, and several adverse effects due to SO_X inhalation are elaborated in Chapter-1. SO_X concentration can be controlled by implementing stringent norms for fuel quality and for exhaust emissions from vehicles. In this regard, most viable option is to desulfurize the transportation fuels at refinery level itself.

2.2 Distribution of sulfur compounds in gasoline, diesel and kerosene

Crude oil is a multi-component mixture of hydrocarbons typically having carbon range of C_1 to C_{22}-C_{70}. In fractionation process, sulfur compounds get distributed in different fractions according to their molecular weights and boiling points. Each straight run distillate has different set of sulfur compounds than other distillate. Gasoline is fractionated from fractionating column, in the temperature range of 70-120^oC (C_7-C_{11}) and consists of sulfur mainly in the form lower end sulfur compounds such as mercaptans, thiols, sulfides, disulfides, thiophene, 3-methyl thiophene, 3-nitrothiophene etc. Kerosene is another important fuel fraction obtained in temperature range of 120-170^oC and contains C_{10} to C_{16} carbon range hydrocarbons. Kerosene has sulfur mainly in the form of alkylated thiophene, benzothiophene and their alkylated derivatives. Kerosene is used to produce jet fuel of various grades. The most important stream of fuel - diesel is fractionated in the temperature range of 170-270^oC (C_{11}-C_{18}). Diesel has sulfur compounds mainly in the form of alkyl derivatives of benzothiophene, dibenzothiophene and alkyl derivatives of dibenzothiophene e.g. 4-Methyl dibenzothiophene, 4-6-dimethyl dibenzothiophene. There are about 42 alkylated benzothiophene and 29 alkylated dibenzothiophenes compounds. Compounds of type 4-6-dimethyl dibenzothiophene (DMDBT) have been considered to be most difficult for removal and usually referred as refractory sulfur compounds[4,5].

2.3 Desulfurization methods for gasoline, kerosene, jet fuel and diesel

Number of physical, chemical and physicochemical methods (adsorption, oxidation, bio-desulfurization, cavitation) have been reported for reducing sulfur level in transportation fuels. Some of them are already commercialized, and many new processes or modifications of existing alternatives are being extensively researched. The desulfurization processes can be mainly categorized in the following classes:

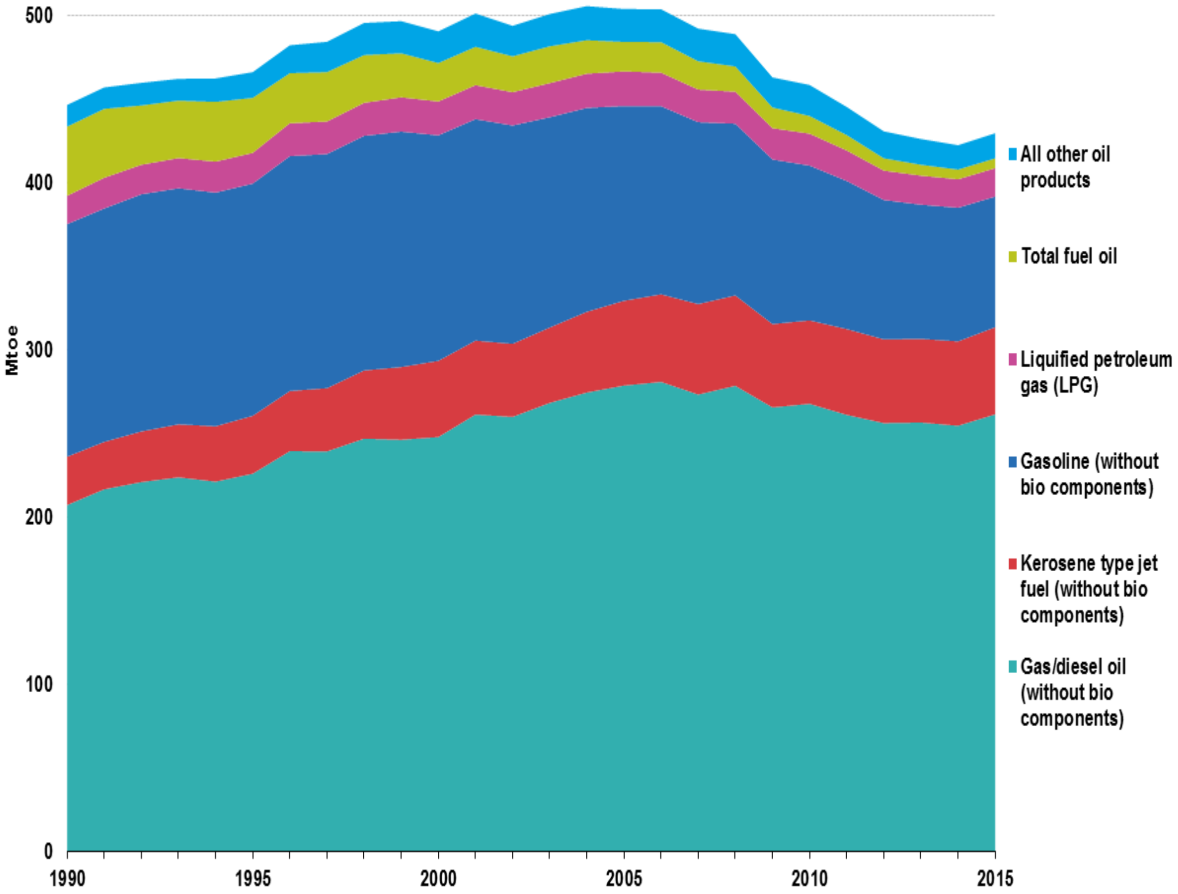

Figure 2.1 : Consumption of oil EU-28, 1990-2015, Mtoe update[3]

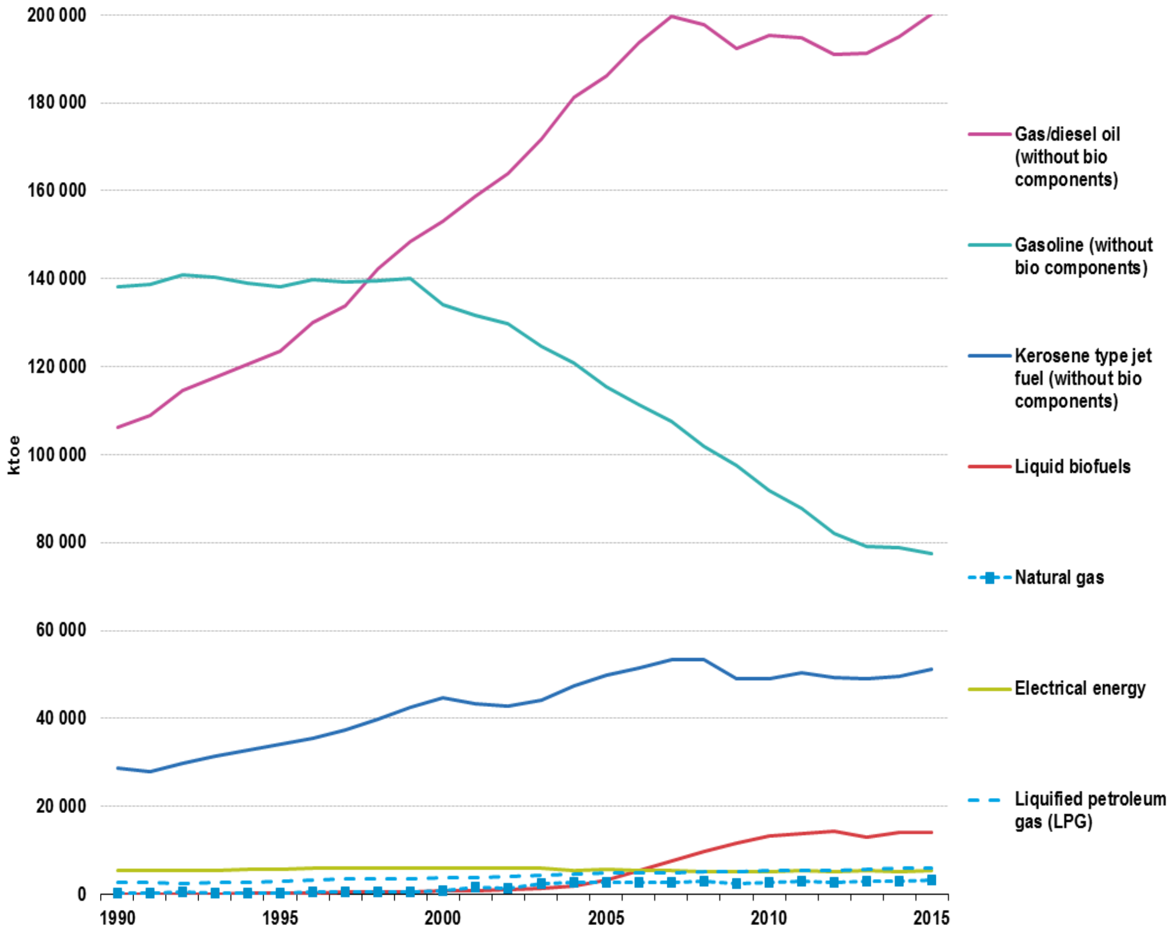

Figure 2.2 :Use of fuels in transport, EU-28, 1990-2015, ktoe update[3]

2.3.1 Hydrodesulfurization
2.3.2 Adsorption
2.3.3 Extraction
2.3.4 Oxidation
2.3.5 Biodesulfurization

2.3.1 Hydrodesulfurization (HDS)

HDS has been the subject of investigation for many years and has been reviewed by many researchers[4–7]. Brunet et al. reviewed the status of fluid catalytically cracked gasoline[8]. Reviews of hydrodesulfurization chemistry[9] and kinetics[10] also highlight the importance of this subject

In this critical review, after initial overview of HDS process, the structures and developments in HDS catalyst are discussed, followed by discussion on reactor configurations. Finally, engineering modifications in HDS process and future challenges are evaluated.

2.3.1.1 Hydrodesulfurization process

Hydrodesulfurization (HDS) process was partially discussed in chapter 1 as an introduction. HDS is a well-established commercial process for lowering sulfur content from petroleum feed stocks. It is a catalytic desulfurization process, which is usually carried out at high temperature and pressure conditions using sulphided $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$ catalysts to convert organosulfur compounds to hydrogen sulphide (H_2S) and hydrocarbons. HDS process can typically and techno-economically reduces sulfur level from a very high initial sulfur ($S >> 1000$ ppm, depending upon source of crude oil) to 300-500 ppmw[11,12].

H_2S from different refinery processes/ operations is collectively sent to the sulfur recovery unit for separating the elemental sulfur. Major contribution of H_2S is from hydrodesulfurization process and remaining from catalytic cracking process. Sulfur recovery unit consist of gas treating unit and claus process. Petroleum refineries typically have hydrodesulfurization followed by amine treatment and claus process to separate elemental sulfur from petroleum fractions.

2.3.1.2 Hydrodesulfurization catalyst:

Catalyst is critical component of HDS process and ~95% research in HDS process is dedicated to development of HDS catalyst. Effectiveness of catalyst is decided by factors such as catalyst support, promotors, method for catalyst formulation and method for catalyst post treatment. A somewhat old review on HDS catalyst was reported in 1996[13], however, in recent years many newer catalysts are being continuously explored mainly to meet the newer governmental norms worldwide on lowering the sulfur content in fuels. Catalytic activity can be improved to enhance hydro treating ability of catalyst, by incorporating acidic functional groups into the catalyst and removing inhibiting substances such as H_2S by tailoring reaction conditions for specific catalyst application.

In HDS process, a number of other side reactions occur parallel to HDS reaction in presence of H_2. Thus, it is necessary to optimize the selection of catalyst which is more favorable for HDS reaction. The catalytic activity can be improved by modifying the catalyst support such as carbon supported CoMo catalyst[14–16], binary/single metal oxide supported (such as TiO_2-Al_2O_3)[17,18], zeolite support, mesoporous molecular sieve MCM-41as a support[19], Al incorporation into the framework of MCM-41[20]. Conventional HDS catalyst consists of support of metal oxides. Co-O-Al interaction between metal oxide support and active phase metals are responsible to reduce activity of the catalyst. CoMoS have weak interaction with carbon support than metal oxides. This is the key driving force for researchers to study the effect of various forms of carbon support[21]. Advanced catalyst supports such as amorphous silica- alumina (ASA), incorporated noble metals into the ASA, Pt-Pd /ASA are used for low or medium sulfur content and low aromatic levels. At higher sulfur level ASA supported noble metals get poisoned by sulfur and NiW/ASA was suggested for deep sulfur removal[6]. Designing of noble metal catalyst has been proposed to increase resistance to sulfur poising. This type of catalyst is bifunctional and combines catalyst support with bimodal pore size distribution (e.g. zeolite) thus two types of sulfur resistance active sites are present. The active sites in large pores adsorb organic sulfur compounds while the sites in small pores are not accessible for organic sulfur compounds. Hydrogen molecule enters through small pores and reacts in larger pores[6]. Another type is monolith supports with wash coats of regular structure[22]. Sulfided CoMo or NiMo on Al_2O_3 support are extensively studied in the literature and has found place in commercial application of HDS. Study by Huang et al. provides insight into the effect of concentration of active phases (like CoMoS and MoS_2) and concentration of external acid ethylene diamine tetra acetic acid (EDTA). Increase in concentration of MoS_2 enhances the rate of olefin hydrogenation but increase in concentration of CoMOS has negligible influence on olefin hydrogenation but enhances the rate of HDS reaction. This investigation promotes selective hydrodesulfurization (HDS) of gasoline by providing a facile method to prepare highly selective HDS catalysts by finely tuning the EDTA/Co molar ratio and the Co content on the $CoMo/Al_2O_3$ catalysts[23]. In recent years, research trend for HDS catalyst is moving towards the nanoscale advancement. Nanoparticles were suggested as a catalyst or for impregnation of various nano metal precursors on the support of catalyst[24,25]. Recently, nickel and cobalt nanoparticles were reported for HDS of thiophene. Ni nanoparticles were found to be more effective than cobalt nanoparticles[25]. Carbon nanotubes were also discussed as a support for HDS catalyst and results indicated that the S content of products decreases from 1126 mg/L to below 10 mg/L[21]. Nickel supported on zinc oxide nanowires was reported as HDS catalyst by petzold et al.[26]. High activity for deep desulfurization was obtained in the initial stages but the catalyst was deactivated by coking after 16h[26].

Catalyst synthesis procedure also plays a vital role in deciding the activity of the catalyst. Conventional process for synthesis of $NiMo/Al_2O_3$ or $CoMo/Al_2O_3$ catalyst is incipient wet impregnation. The main drawback is in the form of incomplete sulfidation and lower stacking of the active phases probably due to strong interaction between support and metals sulfides. Limitations of conventional synthesis procedure can be eliminated by using other routes for catalyst synthesis such as chemical vapor deposition[27], modification of alumina support, addition of noncomplexing inorganic or organic additives, using chemical composition precursors like polyoxometalate (POM)[28]. Liang et al. reported P-Mo-Ni polyoxometalate (POM) precursor for Al_2O_3 support and found better activity than conventional adsorbent[28]. Synthesis of slurry catalyst was also reported by complete liquid phase preparation method in slurry bed reactor[29]. Arc discharge method can be used for synthesis of single wall carbon nanotubes(SWCNT) supported by bimetal (Ni and Y) HDS catalyst[21]. Results showed that bimetal catalyst have greater activity than single metal SWCNT supported catalyst and further improvement was shown by oxidizing the catalyst surface. Commercial HDS catalysts are discussed in following discussion.

Commercial Catalysts

STARS:

Akzo Nobel introduced in 1998 a highly active catalyst- Co-Mo and Ni-Mo, referred as STARS. Co-Mo STARS is reportedly preferred for high sulfur level streams (100-500ppm) at low pressure compared to Ni-Mo and Ni-Mo STARS for low sulfur level streams (below100 ppm) at high pressures[4,5,30]

NEBULA:

Commercialized by Akzo Nobel, NEBULA is considered to be an extremely active hydro treating catalyst. NEBULA is reported to be also active in sulfided form and active and carrier phases are different from conventional HDS catalysts. Hydrogen consumption is high and these catalysts are considered suitable for diesel hydrotreating both at a medium severity conditions and high pressures[4,5,30]

CENTINEL:

CENTINEL is commercialized by Criterion Catalyst and properties of CENTINEL are similar to NEBULA but slight modification in the preparation method. CENTINEL catalyst has combined effect of superior hydrogen activity and selectivity[4,5,30]

2.3.1.3 Design of new reactor configuration

Various configurations of HDS reactors are studied in literature to meet target of deep desulfurization of liquid fuels. Sie et al. reported deep HDS of gas oil using the reactor configuration of one/ two stage trickle bed. H_2S was found to inhibit the rate of deep desulfurization by strongly suppressing the catalytic activity resulting in limited desulfurization in the first reactor and thus the second reactor was recommended for deep desulfurization[22]. Babich and Moujin[6] discussed ABB Lummus technology combined with Criterion Synsat catalyst which was considered as an effective commercial technology. In this technology, newer reactor design was used with two or three catalyst beds in a single reactor. Conventional reactors are co-current in nature, hydrogen is mixed with the distillate at the entrance of the reactor and flows through the reactor. The disadvantage of the co-current reactor design is that the concentration of H_2 is the highest at the entrance and lowest at the outlet. The reverse is true for concentration of H_2S. This increases the difficulty in removing the refractory sulfur compounds. The solution to this problem can be found in the form of a counter-current reactor operation. SynAlliance has patented the counter current reactor design[4], where in a single reactor design, the initial part of the reactor follows co-current flow and last part has counter-current flow. If this has to translate in two reactors designs, the first reactor will be co-current and second reactor will be counter-current. ABB Lummus estimated that counter-current design can reduce the catalyst volume by 16% to achieve 97% desulfurization[6]. Another type of reactor configuration is an ebullated bed reactor. It was suitable for desulfurization of heavy refinery streams. This type of reactor also has good heat transfer so overheating of the catalyst was reduced and less coke formation was observed. In this unit, catalyst particles get fluidized by the feed and hydrogen thereby ensuring well mixing of the feed streams. An ebullated bed was employed in IFP, France. The main advantage of the ebullated bed reactor was that bed plugging and channeling can be avoided and the unit can be operated isothermally with a constant and low pressure drop. Another example of advanced reactor design configuration is Prime process, which consist of modified reactor design and special catalyst system[6]. This process was developed by IFP. It has mild operating conditions with relatively high space velocities that results in minimal olefin saturation of fluid catalytic cracking (FCC) gasoline, improvement in the cetane number and reduction in polyaromatic for gas oil treatment. Use of slurry bed was reported for 4-6-DMDBT removal using NiWS, NiMo and WMoNi catalyst[29]. Slurry bed is useful to avoid temperature shock to the catalyst and it helps to maintain uniform temperature throughout.

2.3.1.4 Process Conditions

The main reason for optimizing the process parameter is to achieve ultra-deep desulfurization without changing the HDS catalyst and HDS reactor. It can involve changes in established processing scheme, expansion in catalyst volume/density, H_2S scrubber from recycle gas, improved vapor-liquid distributor, change in a space velocity, change in temperature, change in pressure and so on. Haldor- Topse[5] reported effect of temperature, role of hydrogen purity, effect of improvement in vapor-liquid contact and effect of reactor volume. Isoda[30] improved the current HDS process by using nickel-supported zeolite catalyst. This scheme was divided in two steps. First, reaction is carried out at 270^{o}C for 1h at a hydrogen pressure of 250kPa and subsequently, products were further desulfurized over a CoMo/Al_2O_3 catalyst at 300°C for 2h at hydrogen pressure of 250kPa.

2.3.1.5 Complementary methods for HDS

HDS requires efficient sulfur removal from the petroleum feed under less stringent conditions. It has been an established and accepted fact that the sulfur compounds present in the petroleum fractions vary widely in their reactivity thus removal of bulky sulfur compounds is a major challenge since the reactivity decreases drastically in the order of thiophene, benzothiophenes, dibenzothiophenes and their alkylated derivatives. With the complex chemistry of sulfur removal, which is less understood even today, it becomes increasingly more difficult to remove the sulfur compounds as the sulfur content is lowered from 1000 ppm to 500 and 500 to 350 ppm and so on. There is also inhibition effect due to the presence of H_2S, nitrogen compounds and aromatics. H_2S affects HDS reaction, hydrogenation and acidity of the catalyst while nitrogen compounds probably retard reaction by competing in adsorption sites of the catalyst[31]. Generally, aromatics content is substantially high and in the range of 15-45% depending upon feedstock[32–34]. The inhibition effect due to aromatics is not very clear but is likely to be again due to preferential adsorption of aromatics and its large concentration. The sulfur compounds remaining in fuels at sulfur levels less than 500 ppm are mostly high end alkylated dibenzothiophenes which have lower reactivity in the HDS process. The lower reactivity of these refractory sulfur compounds is largely attributed to the steric hindrance. In view of the complex nature of sulfur compounds and limitation of existing HDS process, the requirement of severe process conditions and also energy and cost intensive operations, finding alternate solutions to deep desulfurization is imperative. As per the theoretical calculations to produce fuel of sulfur content of 50ppmw , it requires 3 time higher reactor volume and catalyst amount could be 4-7 times larger than present[30]. Working cost of one of the HDS unit for sulfur reduction from 19000ppm to 15ppm in diesel feedstock for 12.775 million barrels/ year capacity is $16.84/kgS and capital investment is $138million[35]. Thus, hydrodesulfurization process requires augmentation in the form of another suitable process if the goal of deep desulfurization is to be techno-economically achieved.

2.3.2 Adsorption

Solid adsorbents have been used since ancient times for various separation/purification applications. Activated carbon, zeolites, polymeric adsorbents etc. are some of the most widely used materials. Today, these solid adsorbents have applications in water treatment, food industry, pharmaceutical industry, chemical and petrochemical industry, and wastewater treatment and so on. The adsorbents often have high surface area and good adsorption capacity for the separation or partitioning of substances from gaseous or liquid phase onto its surface. This along with the simplicity of adsorption operation as compared to most of other separation processes and easy to control make it highly useful tool for industrial purifications and separations. Although a variety of adsorbents are available in the market with different matrix, porous structure and adsorbent capacity, its selection to any particular application is not straightforward. The capacity along with good sorption rates can only be realized by obtaining a material which has surface functional groups favorably affecting the interactions with specific or polar adsorbates. Sulfur compounds are known to be slightly polar than the hydrocarbons of similar nature and hence exploitation of the polarity factor appears to be most critical in successful desulfurization of transportation fuels like diesel. In view of these, the selection of the best adsorbent has been the subject of numerous investigations and a number of commercial adsorbents as well as some newly synthesized ones have been evaluated. The capacity, however has not been satisfactory for most of the adsorbents or the cost of synthesis/activation has been excessive-to the extent of being impractical in commercial application in deep desulfurization. Recently a number of new processes have been discussed as an alternative to the conventional hydrodesulfurization process. Majority of these involve adsorption as a sole mechanism or adsorption forms an integral part in the overall process. Some of the most significant work from the literature is listed in Table 2.2, 2.3, 2.4 and 2.5. Most of the reported work is still in the process of further investigation and attempting to provide feasible methodology for commercial use. Specific details pertaining to the desulfurization work reported in the literature and lacunae/limitations of the reported studies so far have been discussed in last section.

A wide variety of materials starting from activated carbon (AC), silica-based sorbents, zeolites, metal exchanged/ impregnated activated carbon/ zeolites/ mesoporous materials, clay, metal organic framework (MOF) have been reported in the past for adsorption. The literature studies reveal rather a conflicting picture with many studies showing substantially lower capacities for sulfur removal except Yang and co-workers[36], success with transportation fuels such as commercial diesel is far from being achieved. Also, there is a need to evaluate effect of various other process parameters such as aromatics, moisture content, concentration of sulfur compounds, flow rate and more importantly diffusion. The present study aims at initiating work in this regard.

A typical adsorption process is expected to offer selective removal of sulfur compounds, operate at normal temperatures and pressures with ease of operation/ ease of process control and economically achieve near total elimination of sulfur compounds from the transportation fuels. At the same time, ease of regeneration with minimum requirement of chemical and energy is also expected from commercial viability point of view.

Adsorption performance is evaluated by following parameters

1) Capacity of the adsorption
2) Equilibrium and kinetics
3) Ease of Regeneration
4) Cost of the adsorbent

Practically all the reported adsorbents have low equilibrium adsorption capacity (ratio of amount of adsorbate adsorbed (mg) per unit wt of adsorbent (gm)). For industrial operations, column operation is used and estimation of breakthrough curve is essential. A breakthrough curve is obtained by monitoring effluent concentration versus volume treated or time of treatment. Breakthrough capacity, exhaustion capacity and degree of column utilization are the important features of the breakthrough curves[37].

2.3.2.1 Carbon

Activated carbon is an inert porous carbon having high surface area, typically in the range of 500-1000 m^2/g. It has an ability to distribute chemicals on its surface and modify the internal and external surface of the carbon. Properties of typical activated carbon are shown in Table 2.1. Carbon surface modification is an important research area and a number of physical, chemical or biological modifications are possible[38]. Chemical modifications mainly involve acidic, basic surface modification or impregnation of foreign particles to incorporate newer functional groups on the carbon surface. Physical modification involves thermal treatment and biological modifications are possible by bioadsorption. Specific surface area, pore size, pore volume and surface functional groups are important factors to decide the adsorption capacity. It is necessary to understand the role of various factors in improving the adsorption capacity along with it is also primary important to know how to manipulate factors by choosing appropriate modification method to enhance the adsorption capacity of carbon[38,39].

Table 2.1 : Typical properties of activated carbon[39]

Particle density: 0.6-0.9g/ml **Porosity:0.4-0.6**	**Micropore**	**Mesopores or transitional pores**	**Macropores**
Diameter(A)	<20	20-500	>500
Pore volume(ml/g)	0.15-0.5	0.02-0.1	0.2-0.5
Surface area(m^2/g)	100-1000	10-100	0.5-2

The adsorptive desulfurization has been mainly reported for carbon adsorbents (Table 2.2) on the basis of high surface area, controllable physical texture, high mechanical strength, controllable chemical properties. Carbon derived from many sources such as coal[40–42], wood[40,42,43], polymer[43–45], rubber tires[46], biomaterials such as rice husk[47], cassia fistula[48], dates stones[49,50], bamboo[51], sucrose[52], coconut[42,53], organic waste[54] were reported for desulfurization of liquid fuels. Different forms of carbon materials such as carbon cloth[55,56], carbon aerogels[53,57], resin derived carbon spheres[58], graphite[59], nanocarbon[60] and nanofibers[61,62] were also reported as adsorbent for desulfurization of liquid fuels. Shi et al. [63] derived activated carbon from hydrothermal carbonization of sucrose followed by KOH activation and obtained a very good capacity of 41.5mgS/g with a high selectivity for the adsorption of thiophenic compounds (DMDBT > DBT > BT). Carbonized *Cassia fistula* showed low sulfur adsorption at low concentration (100ppmS) and had improved capacity at high concentration (7.5mgS/g, 500ppmw) due to the effect of capillary condensation where selectivity was in the order of (DBT > BT > T)[48]. Zhou et al.[42] reported breakthrough sulfur capacity using wood based and coconut based carbon adsorbent as 3.8mgS/g and 6.4mgS/g respectively for 10% aromatic content model diesel fuel of 400ppmw. Ania et al.[64] reported the performance of various activated carbons derived from materials such as plastic waste, coal, wood. Granular activated carbon produced from dates stone ($ZnCl_2$ chemical activation prior to carbonization) showed more than 30mgS/g adsorption capacity for DBT removal[50]. Further study on dates stone (H_3PO_4 activation) resulted in adsorption capacity upto 41.32mgS/g[49]. Activated carbon prepared from rice husk gave very low capacity of 0.07mgS/g for desulfurization of DBT from kerosene. Carbon derived from organic waste showed DBT adsorption capacity upto 68mgS/g [54]. Haji and Erkey reported carbon aerogels as adsorbents for desulfurization of a model diesel (DBT in n-hexadecane). The saturation adsorptive capacity of a carbon aerogel with pore size of 22 nm was 15mgS/g and selectively adsorbed DBT over naphthalene[53,57]. Carbon cloth having high surface area gave 22mgS/g adsorption capacity for DBT which was further improved upto 35mgS/g by HNO_3 modification[55,56]. Lan Pei et al.[58] reported desulfurization of model fuel (DBT in n-octane) using resin-derived carbon spheres (RCS) through KOH activation with various impregnation ratios (0.5 to 4). A relatively high equilibrium capacity upto 37.58mgS/g at KOH/Char=1 was obtained for resin derived carbon sphere. Wang et al.[59] reported desulfurization using 4 types of carbon sorbents such as carbon, super activated carbon (CMK-3), mesoporous carbon (Maxsorb) and graphene. A model fuel (T in n-octane) containing 200ppmw sulfur was used. A low capacity of ~1.92mg/g for graphene, 0.86mg/g for CMK-3, 0.54mg/g for AC and 0.22mg/g for Maxsorb was reported for thiophene. Higher heat of adsorption in graphene adsorbents indicated the presence of more energetic sites on graphene suggesting that the surface area may not be a critical factor for carbon adsorbent in desulfurization. Adsorption capacity followed the order: graphene > CMK-3 > Maxsorb > AC. Mikhail et al.[65] reported dimethyl disulfide removal from cyclohexane using sorbents such as charcoal, petroleum coke, cement kiln dust and clays. Capacities upto 15.8 mg/g were reported for charcoal while for others it was substantially less. Nath et al. reported nickel doped activated carbon beads (Ni-ACB) along with chemical vapor deposition of carbon nanofibers on the surface Ni-ACB (Ni-CNF/ACB) for DBT and T removal from n-octane and diesel. A high capacity for thiophene removal was reported, 85 and 88.2mgS/g, while for dibenzothiophene the values were 27.3 and 8.2mgS/g using Ni/ACB and Ni-CNF/ACB respectively. Thus, there is drastic reduction in DBT adsorption capacity by ACF incorporation onto Ni-ACB surface though thiophene adsorption capacity was good. Similar observations are observed for diesel desulfurization. Small BET surface area and pore volume of Ni-CNF/ACB were responsible for reduction in adsorption capacity for large molecular size DBT[66].

Modification of carbon surface is crucial for incorporation of specific functional groups on the surface of carbon. Desulfurization studies have been carried out using unmodified carbon[67], oxidation of carbon surface[43,64,75,78], metal modified carbon[73,75,79–84] and other foreign particle impregnation on carbon surfaces. A small number of research papers have been published on carbon adsorption in conjunction with oxygen[45], nitrogen[80] flow and some reports evaluated the effect of incorporation of phosphorous[45], oxygen[77], nitrogen[80], sulfur[77,85], boron on the surface of carbon pores. It enhances adsorptive uptake of carbon adsorbent and the different modification processes have been reviewed by yin et al.[38]. Acidic modification adds carboxyl, quinone, hydroxyl, carbonyl, carboxylic anhydride and lactone functional groups on surface of carbon. Acidic modification is possible by dry and wet operation; dry modification of carbonized material is carried out using CO_2, steam, air, O_2 streams at high temperature and wet process involves use of HNO_3, H_2SO_4, acetic acid, H_2O_2, H_3PO_4, $(NH_4)_2S_2O_8$ etc under mild reaction conditions[54].

Deliyanni et al. reported oxidation of commercial wood based carbon and polymer based carbon (polysodium salt was used as an organic precursor of carbon) by nitric acid (50% and 70%) to study the interactions of 4,6 DMDBT (10-150ppm in hexadecane) on the surface of activated carbons[43]. Zhou et al. reported oxidation of two carbon adsorbents and observed that selectivity increases in the order of BT < Nap < 2-MNap < DBT < 4-MDBT < 4,6-DMDBT, however this trend of selectivity was not same after oxidative modification of carbon material and author reported HNO_3 oxidation was more effective (66mgS/g) than O_2 oxidation[42]. Selvavathi et al. evaluated two commercially available activated carbons A and B and their modifications such as HNO_3 modified forms of A and B, nickel loaded on modified activated carbons, nickel loaded on alumina/ Silica/ Y-Zeolite, without loading of Ni on alumina /silica / y-zeolite. The order in terms of capacity of desulfurization was carbon A (acid modified) > carbon B (acid modified) > Ni/Carbon A > Ni/ Carbon B > Ni/Silica > Ni/alumina > Ni/HY-zeolite. It was observed that nitric acid modified carbon has higher breakthrough capacity (2.83 mgS/g for model fuel and 0.83mgS/g for diesel feedstock) than other adsorbents[74]. Ania et al. have reported modification of the carbon surface by oxidation with ammonium persulphate and their results revealed importance of pore size and surface chemistry. Micropore volume controls the amount of physical adsorption and mesopores control the kinetics of the process[64]. Jiang et al. have reported treatment of the carbon with concentrated sulfuric acid for obtaining high volume of mesopores that improves the surface chemistry and adds acidic groups for increased adsorption of DBT[78]. Moreover acidic group can be incorporated in carbon matrix through phosphorous[45], oxygen[77], nitrogen[80] and sulfur[77,85] and results indicated that surface modification of carbon enhances the selectivity for DBT adsorption.

Table 2.2: Desulfurization using carbon-based adsorbents

Adsorbent	**System**	**Capacity, mg/g**	**Ref**
Carbon from coconut ACC	Model diesel with 10 wt% of tert-butylbenzene (400ppmw)	Breakthrough, 6.4 mgS/g	[42]
Carbon with HNO_3 modification	Model diesel with 10 wt% of tert-butylbenzene (400ppmw)	Breakthrough, 11.3 mgS/g	[42]
Carbon with O_2	Model diesel with 10 wt% of tert-butylbenzene (400ppmw)	Breakthrough,4.9 mgS/g	[42]
Carbon from wood -ACNU	Model diesel with 10 wt% of tert-butylbenzene(400ppmw)	Breakthrough,3.8 mgS/g	[42]
Carbon with HNO_3-ACNU modification	Model diesel with 10 wt% of tert-butylbenzene (400ppmw)	Breakthrough,11.6 mgS/g	[42]
Carbon with O_2 -ACNU	Model diesel with 10 wt% of tert-butylbenzene (400ppmw)	Breakthrough,5.1 mgS/g	[42]
Activated carbon	Model diesel with 10% aromatics(687ppmw)	Breakthrough,7.15 mgS/g, Saturation, 16.29 mgS/g	[67]
Activated Carbon	Model fuel Octane-T Octane-BT Octane-DBT	 Breakthrough,1.28mg/g Breakthrough,7.37mg/g Breakthrough,11.54mg/g	[68]
Activated Carbon	Model fuel (Octane80%, Benzene 20%) MF-T MF-BT MF-DBT	Breakthrough,0.4809, mg/g Breakthrough,0.44, mg/g Breakthrough,0.89, mg/g	[68]
Carbon (S A=1040m^2/g, pore volume 0.57ml/g)	Model fuel (T in n-Octane, 200ppmwS)	Equilibrium capacity,1.12mg/g	[59]
Super activated carbon (maxsorb) (S A=3311m^2/g, pore volume 1.7ml/g)	Model fuel (T in n-octane, 200ppmwS)	Equilibrium capacity,1.45mg/g	[59]
Mesoporous carbon(CMK-3) (maxsorb) (SA=1273m^2/g, pore volume 1.2ml/g)	Model fuel (T in n-octane, 200ppmwS)	Equilibrium capacity,2.18mg/g	[59]
Graphene (S A=708m^2/g, pore volume 1.2ml/g)	Model fuel (T in n-octane, 200ppmwS)	Equilibrium capacity,2.72mg/g	[59]
Charcoal	Dimethyl disulfide in a cyclohexane	15.8mg/g	[65]

AC	Naphtha (mercaptan, disulfide, sulfide and thiophene)	0.534mg/g	[69]
AC	Diesel(297ppmwS)	<0.5mg/g	[70]
AC	Methanol(30ppmwS)	Not available	[71]
AC	Mid distillate(1200ppmwS)	~3.65mg//g	[72]
Carbon	Model fuel (DBT in Iso-Octane, 1001.87mg/L)	Equilibrium capacity, 8mg/g	[73]
Carbon-Zinc (2% loading)	Model fuel (DBT in Iso-Octane, 1001.87mg/L)	Equilibrium capacity, 17mg/g	[73]
Powder forms carbon (modified by HNO_3) at 0.4/h	model diesel (50ppm DBT, 125ppm 4-MDBT and 125 ppm 4-6 DMDBT) [300ppm]	Breakthrough, 2.83mg/g	[74]
Powder forms carbon (modified by HNO_3) at 0.4/h	Real diesel,290ppm	Breakthrough, 0.83mg/g	[74]
Resin-derived carbon spheres(RCS) through KOH activation with various impregnation ratios (0.5 to 4) [RCS-1]	Model fuel (DBT in n-Octane) range (43.38 to 347.98 mgS/L)	Equilibrium capacity,37.58mgs/g	[58]
Activated carbon [F-400]	Model fuel (DBT in n-Octane) range (43.38 to 347.98 mgS/L)	Equilibrium capacity,24.53mgS/g	[58]
[RCS-1]	Model fuel (DBT in n-Octane) range (43.38 to 347.98 mgS/L) with 5%(wt) toluene, 10%(wt) toluene, 15%(wt) toluene, 20%(wt) toluene	Equilibrium capacity, 33.58 mgS/g 31.66 mgS/g 29.57 mgS/g 29.06 mgS/g	[58]
[RCS-1]	Model fuel (DBT in n-Octane) range (43.38 to 347.98 mgS/L) with 5%(wt) cyclohexene, 10%(wt) cyclohexene, 15%(wt) cyclohexene, 20%(wt) cyclohexene	Equilibrium capacity, 35.49 mgS/g 34.10 mgS/g 32.53 mgS/g 32.36mgS/g	[58]
Carbon aerogel (pore size 22 nm)	(DBT in n-hexadecane)	15 mg/g	[53]
Activated carbon [F-400]	Model fuel (DBT in n-Octane) range (43.38 to 347.98 mgS/L) with	Equilibrium capacity,	[58]

	5%(wt) toluene, 10%(wt) toluene, 15%(wt) toluene, 20%(wt) toluene	19.66 mgS/g 16.52 mgS/g 13.91 mgS/g 12.87mgs/g	
Activated carbon [F-400]	Model fuel (DBT in n-Octane) range (43.38 to 347.98 mgS/L) with 5%(wt) cyclohexene, 10%(wt) cyclohexene, 15%(wt) cyclohexene, 20%(wt) cyclohexene	Equilibrium capacity, 21.22 mgS/g, 18.96 mgS/g, 17.05 mgS/g 16.18 mgs/g	[58]
AC (hydrothermal carbonization of sucrose followed by KOH activation	300ppmwS	41.5mgS/g (DNDBT>DBT>BT)	[63]
Biomass such as *Cassia fistula* and its carbonized and activated (physically and chemically)	500ppmw, (T, BT, DBT in n-Octane)	(7.5mgS/g, DBT>BT>T	[48]
Carbon Co (oxidized with 70%HNO$_3$ for 5h at ambient, 1gcarbon/10mlacid) CN1(heated at 350^{o}Cfor 3h in nitrogen) CN2 (heated at 650^{0}C for 3h in nitrogen, 10^{0}c/min) CS (heated at 650^{0}C for 3h in H$_2$S, 1000ppm, flow-150ml/min,10^{0}c/min)	Initial concentration 20ppmw(DBT,4-6DMDBT) with nap and MNap in a mixture of decane and hexadecane	4.68mgs/g 7.8 mg-s/g 8.03 mg-s/g 10.95 mg-s/g 9.94 mg-s/g	[75]
Carbon molecular sieve Calgaon carbon	138ppmw	1.91mg/g 1.88mg/g	[76]
Commercial wood - based carbon	Initial concentration 20ppmw [DBT,4-6DMDBT] with nap and MNap in a mixture of decane and hexadecane	4.37mgs/g	[77]

Song and coworkers[86] reported studies using Fe(III) impregnated carbon surface for model jet fuel. The oxidation reactivity of the sulfur compounds over the Fe (III) salts increases in the order of DBT < BT < 5-MBT < 2-MBT. Activated carbon was shown to have higher adsorption affinity for the sulfones and sulfoxides than thiophenic compounds due to the higher polarity of the former than the latter. Fallah et al. evaluated the effect of various modifying agents (HNO_3, $(NH_4)_2S_2O_8$, H_2SO_4, HCl and NaOH) for modifying surface of carbon cloth and it is found that modification using HNO_3 gives best results compared to other modifications[56]. Ghouti et al. evaluated effect of organic acid addition in a model fuel for desulfurization in presence of activated carbon that resulted in improved selectivity (model fuel consists of aromatics along with sulfur compound) and capacity along with fast rate of removal of sulfur compound. However, it is necessary to check the physical and chemical properties of fuel after desulfurization. As far as adsorption of sulfur compound is concerned, the major limitation in the application of carbon is their low selectivity as the hydrophobic carbon surface also attracts aromatics on the surface[87].

The introduction of metals to the surface of carbonaceous support (Table 2.3) can effectively increase the performance of desulfurization[5] and number of metals can be used in these modifications such as Fe[80,81,88], Zn[73,89], Co[46,79,81], Ni[66,74,75,82,89], Cu[66,79–82], Ag[75,79,90], Na[79], Al[84,91], Si[91], Mn[83], Mo[46], Pd[92,93], Ce[94]. In various chemical modifications of surface, metals take part in oxidation and reduction reactions. The main objective behind metal impregnation is to enhance the adsorption forces and selectivity by inducing reactive/strong physico-chemical adsorption. Research study by Ania et al. on carbonization of transition metal based polymeric salts of polystyrene sulfonic acid/co-maleic acid indicated that highly porous material can be obtained and the content of metals can be controlled by selective washing[64]. Selectivity was improved due to highly dispersed metals in adsorbents. Besides micro porosity, the presence of metals and their speciation were proven to be important for DBT adsorption on the surface. Seredych et al. discussed template derived carbons with highly dispersed metals and their specific properties along with high volume of mesopores that enhance the physical adsorption/ reactive adsorption on surface of active centers[81]. Ania et al. [79] showed that incorporation of sodium, cobalt, copper and silver metals not only provides active sites, but also act as structural stabilizers of the carbon materials, and work as a catalyst initiator in reactive adsorption. Copper and cobalt loaded carbons showed the highest adsorption capacity due to the increased sulfur-sulfur interaction that enhances the adsorption capacity. Prajapati et al. evaluated effect of nickel on surface of

Table 2.3: Impact of metal modified carbon in desulfurization

Adsorbent	System	Capacity, mg/g	Ref
Source-Rubber Co-Cu/AC	85% hexane and 15% toluene thiophene (T), benzothiophene (BT), dibenzothiophene (DBT), 5- (MBT), 4- (MDBT) and 4,6- (DMDBT) (50ppm each)	Compound(mg/g) 1.84 2.12 3.52 2.48 3.44 3.4	[46]
C-Si C-Si-Cu C-Si-Co C-Si-Fe C-Al C-Al-Cu C-Al-Co C-Al-Fe C-Z(zeolite) C-Z-Cu C-Z-Co C-Z-Fe	DBT(178ppmwS) in hexane Carbon containing polymer was ion exchanged with nitrates of Cu(II), Co or Fe, As template alumina, amorphous silica, zeolite were used.	138.6(mgS/g) 114.3 120.2 103.1 81 99.7 89.4 66.5 51.4 69.8 75.5 68	[81]
Ni-Carbon A	Liquid paraffin oil doped with 50ppm of DBT, 125ppm of 4-MDBT and 125ppm of 4,6-DMDBT	0.81mgS/g	[74]
Ni-Carbon B	Liquid paraffin oil doped with 50ppm of DBT, 125ppm of 4-MDBT and 125ppm of 4,6-DMDBT	0.58mgS/g	[74]
Carbon-Fe	Model fuel contained same molar concentrations of dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (DMDBT), naphthalene (Nap) and 1-methylnaphthalene (1-MNap) in mixture of decane and hexadecane 1:1 each (Total S conc = 20ppmw) Carbon containing polymer was ion exchanged with nitrates of Fe and Cu	6.53mgS/g (without arenes) 4.22mgS/g (with arenes)	[80]
Carbon-Cu	Model fuel contained same molar concentrations of dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (DMDBT), naphthalene (Nap) and 1-methylnaphthalene (1-MNap) in mixture of decane and hexadecane 1:1 each	6.43mgS/g (without arenes) 4.28mgS/g (with arenes)	[80]

	(Total S conc = 20ppmw)		
Carbon-CuA	Model fuel contained same molar concentrations of dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (DMDBT), naphthalene (Nap) and 1-methylnaphthalene (1-MNap) in mixture of decane and hexadecane 1:1 each (Total S conc = 20ppmw)	4.75 (without arenes) 4.5 (with arenes)	[80]
Mn-AC2, Mn-AC4, etc., where the numbers indicate the concentration of manganese chloride	DBT in commercial diesel 835–11,890mg/kg		[83]
Ac		18.4mg DBT/g	
Mn-Ac2		25.8	
Mn-AC4		43.2	
Mn-AC6		41	
Mn-Ac8		29.6	
Ac-Pure AC-Co AC-Mo	T, BT, MBT, DBT, MDBT, DMDBT 50ppm each in hexane: toluene mixture (Thermal coprecipitation method is used for metal impregnation)	AC-Pure>AC-Co>AC-Mo>Ac-Co-Mo	[95]
AC-Co-Mo (Thermal coprecipitation method is used for metal impregnation)	T, BT, MBT, DBT, MDBT, DMDBT	T-2.2mgT/g BT-2.32 MBT-2.72 DBT-3.68 MDBT-3.64 DMDBT-3.72	[95]
AC-830 Norit	BT and DBT in hexane, (500ppm)	BT=0.08mmolS/g DBT=0.15mmolS/g	[92]
$PdCl_2$-AC830 Norit	BT and DBT in hexane, (500ppm) (wet impregnation of $PdCl_2$ in acidic media followed by drying at 130ºC under He flow)	BT=0.15mmolS/g DBT=0.17	[92]
AC1240 Norit	BT and DBT in hexane, (500ppm)	BT=0.10 DBT= 0.13	[92]
$PdCl_2$/ AC1240 Norit	BT and DBT in hexane, (500ppm) (wet impregnation of $PdCl_2$ in acidic media followed by drying at 130ºC under He flow)	BT=0.08mmolS/g DBT=0.14mmolS/g	[92]

AC ACO(oxidized) AC-Ce	DBT in petroleum ether(500ppmS) adsorption from model fuels (Classical soaking impregnation method)	(10.2) mgS/g 7.62(12.2) mgS/g 8.15(14.2) mgS/g	[94]
Cu/Ni-CNF Carbon nano fiber(CNF) Prepared using chemical vapor deposition with acetylene as the carbon source	T in n-Octane (<70ppmw	Breakthrough 0.25mgS/g	[61]
NI/ACB CNF-Carbon nanofiber) ACB (Activated carbon beads)	Two model fuels are used (n-octane containing TH/DBT or a commercial diesel blended with TH/DBT) DBT in n-Octane(800ppmS) T in n-Octane(800ppmS) DBT in diesel(800ppmS) TH in diesel(800ppmS)	27.3mgS/g 85mgS/g 7.1mgS/g 41.1mgS/g	[62]
Ni-CNF/ACB (CNF-Carbon nanofiber) ACB (Activated carbon beads)	DBT in n-Octane(800ppmS) T in n-Octane(800ppmS) DBT in diesel(800ppmS) TH in diesel(800ppmS)	8.2mgS/g 88.2mgS/g 8.1mgS/g 62.3mgS/g	[62]
Carbon Carbon-Zinc	Model fuel (DBT in Iso-Octane, 1001.87mg/L)	Equilibrium capacity, 8mg/g 17mg/g	[73]

activated carbon bead (ACB) and ACB substrate (without Ni) and found capacity of nickel loaded ACF was comparatively higher than that without nickel. It is believed that direct Ni-S interaction was dominant in adsorption of DBT rather than π-complexation or π-H interactions[66]. Bimetallic doping of Ni/Cu on carbon nanofiber (CNF) was recently evaluated by Prajapati[61]. However, the breakthrough and saturation capacities were low: 0.25 and 0.60mgS/g adsorbent, respectively at 30°C and using 35ppm(w/w) sulfur concentration. The desulfurization by Ni/Cu-CNF was attributed to the high BET surface area, large loading of Ni nanoparticles and graphitic characteristics of the material. Co/Cu bimetallic incorporation on carbon surface showed enhanced simultaneous adsorptive desulfurization of the sulfur compounds in the order of DBT > MDBT > DMDBT > MBT > BT > T[46]. Bimetallic loading of Co-Mo was reported to provide good sulfur removal capacity for AC/CoMo adsorbent where the order for different sulfur compounds was found to be T < BT < DBT < MBT <MDBT < DMDBT[95].

2.3.2.2 Zeolite

Zeolite are porous crystalline aluminosilicates. Zeolite framework is an assembly of SiO_4 and AlO_4 tetrahedra joined in various regular arrangements through shared oxygen atom to form an open crystal lattice containing pores of molecular dimensions. Zeolite structure is determined by crystal lattice and having the uniform pore sizes[39]. Each aluminum unit introduces one negative charge on the framework that must be balanced by exchangeable cations. Exchangeable cations are located at preferred sites within the framework and play a very important role in determining the adsorptive properties. Si/Al ratio decides the hydrophobic and hydrophilic properties of the adsorbent. Transition from hydrophilic to hydrophobic normally occurs at Si/Al ratio between 8 and 10. Al rich sieves have high affinity for water and other polar molecules. Si rich sieves are essentially hydrophobic and adsorb n-paraffins over water. Choice of framework, Si/Al ratio and cationic form have major influence in adsorption properties[39]. Zeolite has been reported as a catalyst and catalyst support for many reactions specifically in petroleum refineries and waste water treatment.

The application of zeolite for adsorptive desulfurization of liquid fraction was reported more than 30 years back by Yonus et al.[96] for the desulfurization of a fuel fraction of 180-350^{o}C using Na-Y zeolite and natural mordenite. Table 2.4 highlights the literature on sulfur removal application of zeolite based adsorbents. Zeolites have been reported as an adsorbent in natural form and in synthetically prepared form for desulfurization of various liquid fuels. Among synthetically prepared zeolites, Y zeolite is extensively studied due to properties such as high surface area, high ion exchange capability and high thermal stability. Major part of zeolite study for adsorptive desulfurization is reported for cation exchange and metal impregnated zeolites. Cation exchange with zeolite can be possible by solid phase exchange, liquid phase exchange and vapor phase exchange. In adsorptive desulfurization, majority of work pertains to liquid phase metal exchange methodology for cation exchange with zeolites. Mechanism for adsorptive desulfurization varies on the basis of cation/ metal (Ni, Cu, Zn, Co, Ag, Fe, Pd, Ce, La) exchanged / impregnated on the zeolites. Three different mechanisms for sulfur adsorption on the surface of zeolite were reported namely, π complexation, direct sulfur-metal interaction and reactive adsorption. Yang and coworkers[36] proposed the π complexation mechanism for adsorptive desulfurization on zeolite, while Song and coworkers[97] have suggested direct sulfur-metal interactions. Direct metal-sulfur interaction hypothesis suggests no competitive reaction between aromatics, nitro compounds and cyclic sulfur compounds and therefore, performance of adsorptive desulfurization does not get affected in the presence of other similar nature organic compounds. In contrast, π complexation mechanism can explain the deteriorating performance of adsorptive desulfurization in presence of competitive organic compounds like toluene and xylene. Yang and coworkers used Cu-Y and Ag-Y zeolites[36] (2003) and obtained good capacity for thiophene sulfur removal from benzene and n-octane mixtures. Further carbon was used as a guard bed for zeolites for sulfur removal from gasoline and commercial diesel[36,98] and showed significant improvement in capacity (34 cc/g for commercial diesel) for sulfur compounds, such as 4,6-DMDBT. Yang and coworkers have shown ambiguity about initial concentration throughout their successive work. In few publications mentioned initial sulfur content 430ppmw for the apparent value of 297ppmw [70,99,100]. Different commercial adsorbents and configurations like Activated carbon + Selexsorb CDX + ion exchanged zeolite are compared with Cu-Y by Yang and coworkers [70]. Velu et al.[101] reported the sorbents with metals such as Ni, Cu, Zn, Pd and Ce on Y-zeolite. Song and coworkers[97] reported Cu-exchanged Y-zeolite at ambient conditions and at 200°C and the results of synthetic gasoline (thiophene in iso-octane, 190ppm) for Cu-Y zeolite were in agreement with those reported by Yang and co-workers. However, the results were different with real gasoline which was attributed to an analytical error. Breakthrough capacities of Cu-Y zeolite adsorbent were reported as 0.22mg/g at ambient condition and 0.49mg/g at 200°C for real gasoline (305ppmw).

Table 2.4: Desulfurization using zeolite-based adsorbents

Adsorbent	**System**	**Capacity**	**Ref.**
Ac/Cu-y Zeolite	Synthetic gasoline (T in n-Octane)	Breakthrough ,16.6 mg S/g	[110]
Ac/Cu-y Zeolite	Real gasoline(335ppmw)	0ppmw at 14.7ml/g Breakthrough, 4.9 mg S/g, saturated,12.592g/g	[36,98]
Ac/Cu-y-Zeolite	Real diesel (430ppmw	0.11ppmw at 15ml/g, breakthrough~6.45mg/g	[36,98]
Cu(I)-Y Zeolite	Model fuel Octane-T, 300ppmw S Octane-BT, 300ppmw S Octane-DBT, 300ppmw S	Breakthrough,13.78 mg/g Breakthrough,23.40 mg/g Breakthrough,29.17 mg/g	[68]
Cu(I)-Y (LPIE-RT)	Diesel(430ppmws)	Breakthrough 5.33mg/g, saturated 11.97mg/g	[98]
Cu(I)-Y (LPIE-RT)	Gasoline (335ppmws)	Breakthrough 4.57, saturated 12.61	[98]
AC/Cu(I)-Y (LPIE-RT)	Diesel 430ppm	Breakthrough 7.57, saturated13	[98]
AC/Cu(I)-Y (LPIE-RT)	Gasoline 335 ppm	Breakthrough,5.90, saturated 15.87	[98]
Cu(I)-Y Zeolite (regeneration study has been reported for MF-DBT)	Model fuel (Octane80%, Benzene20%) MF-T, 300ppmw S MF-BT, 300ppmw S MF-DBT, 300ppmw S	Breakthrough,2.21mg/g Breakthrough,3.2 mg/g Breakthrough,4.809mg/g	[68]
Cu-y Zeolite	Model Fuel Iso Octane-T, 190ppmw	Breakthrough ,17.8 mg S/g	[97]
zeolite	Model diesel(300ppmw) 4-6-DMDBT	Breakthrough,1ml/g	
Cu-y Zeolite	Real gasoline(305ppmw)	Breakthrough 0.22 mg/g for<1ppmw,0.37 mg/g to 1ppmw	[97]
Cu-y Zeolite at 200^{0}C	Real gasoline (305ppmw)	Breakthrough 0.49 mg/g	[97]
Ni(II)-Y (LPIE-RT)	Diesel 297 ppm	Breakthrough,2.70mg/g, saturated 6.53mg/g	[99]

Ni(II)-Y (LPIE-135)	Diesel 297 ppm	Breakthrough,3.82mg/g, saturated 6.82mg/g	[99]
Ni(II)-X (LPIE-RT)	Diesel 297 ppm	Breakthrough,4.58mg/g, saturated 8.03mg/g	[99]
Ni(II)-Y (SSIE)	Diesel 297 ppm	Breakthrough,5.06mg/g, saturated 9.25mg/g	[99]
DX/Ni(II)-Y (SSIE)	Diesel 297 ppm	Breakthrough,6.11, saturated 10.59	[99]
Ce(IV)-Y (LPIE-80)	Model jet fuel(507ppmws)	2.30mg/g	[101]
Ce(IV)-Y (LPIE-80)	Diesel(297ppmws)	1.04mg/g	[101]
CDX/Cu(I)-Y (LPIE-RT)	Diesel 297 ppm	Breakthrough,7.11, saturated 10.97	[70]
AC/CDX/Cu(I)-Y (LPIE-RT	Diesel 297 ppm	Breakthrough,9.33, saturated 13.63	[70]
Cu(I)-Y (VPIE)	Diesel 297 ppm	Breakthrough,8.89, saturated 13.12	[100,111]
CDX/Cu(I)-Y (VPIE)	Diesel 297 ppm	Breakthrough,10.44, saturated 14.02	[100,111]
Zeolite 5A	Naphtha (mercaptan, disulfide, sulfide and thiophene)	0.123mg/g	[69]
Zeolite 13X	Naphtha (mercaptan, disulfide, sulfide and thiophene)	0.77mg/g	[69]
Ni-Y (350◦C;>10 h in He)	Commercial Diesel(200ppmw)	Breakthrough, 3ml/g	[102]
Cu-Y (450◦C;>10 h in He)	Commercial Diesel(200ppmw)	Breakthrough, 2ml/g	[102]
Fe-Y (350◦C;>10 h in He)	Commercial Diesel(200ppmw)	Breakthrough, 2ml/g	[102]
Zn-Y (350◦C;>10 h in He)	Commercial Diesel(200ppmw)	Breakthrough, 1.5ml/g	[102]
Co-Y (350◦C;>10 h in He)	Commercial Diesel(200ppmw)	Breakthrough, 1.5ml/g	[102]
Ni-Y (350◦C;>10 h in He)	Model diesel fuel (BT-50, DBT-50,4-6-DMDBT-50) Total S=150ppmw	Breakthrough, 42mg/g	[102]
Ni-Y (350◦C;>10 h in He)	Model diesel fuel (BT-100, DBT-100,4-6-DMDBT-100) Total S=300ppmw	Breakthrough, 34.78mg/g	[102]
Ni-Y (350◦C;>10 h in He) prepared from Ni-chloride	Model diesel fuel (BT-100, DBT-100,4-6-DMDBT-100) Total S=300ppmw	Breakthrough, 30.57mg/g	[102]
Cu-Y (450◦C;>10 h in He)	Model diesel fuel (BT-50, DBT-50,4-6-DMDBT-50)	Breakthrough, 31 mg/g	[102]

	Total S=150ppmw		
Ni-Y (350◦C;>10 h in He)	Model diesel fuel (BT-50, DBT-50,4-6-DMDBT-50) TotalS=150ppmw and0.5%Benzene(v/v)	Breakthrough, 11.80mg/g or 112ml/g	[102]
Ni-Y (350◦C;>10 h in He)	Model diesel fuel (BT-50, DBT-50,4-6-DMDBT-50) TotalS=150ppmw and5%Benzene(v/v)	Breakthrough, 0.84mg/g or 8ml/g	[102]
Ni-Y (350◦C;>10 h in He)	Model diesel fuel (BT-50, DBT-50,4-6-DMDBT-50) TotalS=150ppmwand25%Benzene(v/v)	0 mg/g or 0ml/g	[102]
Ni-Y (350◦C;>10 h in He)	Model diesel fuel (BT-50, DBT-50,4-6-DMDBT-50) Total S=150ppmwandmoisture-5000ppm	Breakthrough, 30.57mg/g (for 300ppmw) Breakthrough, 14.23mg/g (for 150ppmw)	[102]

Salem et al.[69] reported studies on desulfurization of naphtha using zeolite 5A and zeolite 13X. Zeolite 13X was found to have higher capacity for sulfur at low concentrations while at higher concentration, the capacity of activated carbon was 3 times greater than 13X zeolite at 20°C. Zeolite 5A was not suitable for sulfur removal from naphtha. Wang et al.[68] reported breakthrough capacity using Cu (I)Y zeolite for three sulfur compounds - T, BT, DBT as 2.21, 3.2 and 4.809 mg/g, respectively in a synthetic fuel of n-octane (80%) and benzene (20%). Regeneration was carried out by *in situ* calcinations in air at 350^{o}C for 10h followed by activation/auto reduction in flowing helium at 450^{o}C for 18h. The higher adsorption amount on Cu(Y) and $AgNO_3$/MCM-41 than AC was believed to be due to the formation of π-complexation bond between the thiophenic compounds and anionic metal. The π-complexation sorbents were prepared by introducing d-block metal cations (Ag^+, Cu^+, Pd^{2+}, Ni^{2+}, Zn^{2+}) into various support (zeolite, silica, carbon). Bhandari et al.[102] reported desulfurization application of ion exchanged zeolites such as Cu-Y, Ni-Y, Fe-Y, Zn-Y for model diesel (300ppmw, BT-100, DBT-100, 4-6-DMDBT-100; 150ppmw: BT-50, DBT-50,4,6 DMDBT-50). A detailed analysis on the effect of various parameters such as effect of initial concentration, preparation methodology, moisture content in a model fuel and effect of aromatics in a model fuel (0.5%, 5%, 25% benzene in n-octane) was presented. A very good breakthrough capacity, 31mg/g and 42mg/g was reported for Cu-Y and Ni-Y adsorbent respectively. However, capacity for commercial diesel was substantially lower: Ni-Y (3ml/g) > Cu-Y (2ml/g) > Fe-Y (2ml/g) > Zn-Y(1.5ml/g) as compared to synthetic diesel fuel. From the literature, Ce, Cu, Ag and Ni modified zeolites are found to be suitable metals for improving the adsorptive desulfurization on Y zeolite. Thus, in the last five years, the emphasis is on bimetallic cation exchange or other chemical modifications for Ce, Cu, Ag and Ni exchanged Y zeolite. Li et al. proposed the mechanism of competitive adsorption over K doped NiY zeolite using *insitu* FTIR spectroscopy[103]. Similarly, Zu et al. estimated the correlation between the active sites of three Y zeolite adsorbents and associated possible reactions on the surface in the presence of methyl thiophenes[104]. Song et al.[105] have reported elaborate studies on the effect of bimetal exchanged Cu^1-Ce^4Y zeolite for model gasoline (thiophene, benzothiophene) and also on the effect of toluene, pyridine and cyclohexene in adsorptive desulfurization. High selectivity of Cu^1-Ce^4Y for sulfur removal was attributed to synergistic interaction between Cu and Ce^{4+}. Adsorbents can bind organic sulfur compound through π complexation and direct metal-sulfur interaction for Cu and Ce respectively. Zhang et al. [106] have investigated the single ion exchange of Cu^{2+}, Zn^{2+}, Ag^+ and double metal ion exchange of Cu^{2+}- Zn^{2+}, Zn^{2+}- Nd^{3+}, Ni^{2+}- Nd^{3+} on Na-Y zeolite. Ag-Y zeolite and have found effective for desulfurization of DBT and 4-6-DMDBT with adsorption capacity increase up to 42mgS/g. Complete regeneration for Ag-Y was carried out using air calcination at 450^{o}C. Tian and coworkers reported adsorptive desulfurization using La-Y, Na-Y, La-Na-Y and Ce-Y zeolites[107,108] and effect of mesopore on hierarchically beta zeolite, Ce-beta zeolite[109], Y zeolite and Ce-Y-Zeolite was also evaluated[104]. Mesoporous materials showed better performance for sulfur removal (36% for Ce-Y zeolite for FCC gasoline) than microporous materials and it was found that the mesoporous material significantly increases the sulfur adsorption performance in presence of toluene and cyclohexene.

2.3.2.3 Mesoporous materials for desulfurization

Mesoporous materials have pores with diameters between 2 to 50 nm. Typical mesoporous materials include silica and alumina having homogenous distribution of mesopores. MCM-41 and SBA-15 are two well-known commercial mesoporous materials. SBA-15 and MCM-41 surfaces can be modified by metal exchange/ impregnation for effective deep desulfurization. Table 2.5 shows the literature on mesoporous materials. McKinley and Angelici[112] reported sulfur removal using silver loaded mesoporous materials for model fuel comprising DBT and 4,6-DMDBT. However, the sorption capacity was very low. Ko et al.[113] and Park et al.[114] used SBA-15-supported nickel sorbent and evaluated effect of different nickel loadings for desulfurization of commercial diesel having 240ppmw of initial sulfur concentration. SBA-15-supported nickel sorbent with 30wt% of Ni loading gave the breakthrough capacity of 1.7mgS/g at a breakthrough sulfur level of 10ppmw. However, when using the same SBA-15-supported nickel sorbent for desulfurization of a commercial ULSD with 11.7ppmw of sulfur, it was found that the breakthrough capacity was only 0.47mgS/g. Song and coworkers[115] also reported mesoporous silica based materials SBA-15 and MCM-48 and evaluated effect of Ni loading along with ultrasonication for better Ni dispersion on SBA-15 and MCM-48. Desulfurization was carried out for 20wt% nickel loading (Ni20/MCM-48) in a fixed-bed flow sorption system at 220^{o}C for initial sulfur concentration 14.5ppmw (4,6 DMDBT). A breakthrough capacity of 2.1mgS/g at sulfur level of 1ppmw was reported. Effect of ultrasonication indicates that alkyl DBTs are adsorbed on the sorbent surface of SBA-15 and MCM-48 with Ni impregnation possibly through an interaction between the sulfur atom in the sulfur compounds and the exposed nickel atoms on the surface, and a part of the adsorbed alkyl DBTs (~6%) reacts further with the metallic nickel. The breakthrough capacity of the Ni20/SBA-15 prepared by the incipient wetness impregnation (IWI) method without ultrasonic

Table 2.5: Mesoporous materials in desulfurization

Adsorbent	**System**	**Adsorption Capacity**	**Ref.**
SBA-15	ULSD, model diesel	0.01mgS/g	[115]
SBA-15-Ni (20) at 200ºC	ULSD 14.5ppmw	0.43 mgS/g at a breakthrough sulfur level of 1ppmw	[115]
SBA-15-Ni20 Ultrasonication used at 200ºC Ni7/SBA-15 Ni13/SBA-15 Ni20/SBA-15 Ni31/SBA-15 Raney Nickel Ni55/SiO_2–Al_2O_3	ULSD 14.5ppmw	0.98mgS/g 0.47mgS/g 1.00mgS/g 0.98mgS/g 0.6mgS/g 0.02mgS/g 0.32mgS/g	[115]
$AgNO_3$/MCM-41	Model fuel (Octane80%, Benzene20%) MF-T MF-BT MF-DBT	 Breakthrough,0.89mg/g Breakthrough, 1.28mg/g Breakthrough, 3.206mg/g	[68]
$AgNO_3$/MCM-41	Model fuel Octane-T Octane-BT Octane-DBT	 Breakthrough, 5.77mg/g Breakthrough, 12.18mg/g Breakthrough, 17.63mg/g	[68]
MCM-48	ULSD 14.5ppmw	0.02mgS/g	[115]
at 200ºC after ultrasonication Ni7/MCM-48 Ni13/MCM-48 Ni20/MCM-48 Ni31/MCM-48 Raney Nickel Ni55/SiO_2–Al_2O_3	ULSD 14.5ppmw	 0.32mgS/g 0.82mgS/g 2.10mgS/g 0.55mgS/g 0.19mgS/g 0.41mgS/g	[115]
Ni20/MCM-48	Model diesel (4-6DMDBT in n-decane (400ppmw)	2.11mgS/g	[115]
Ni/ASL60-4 (Ni/Al-SBA-15)	Diesel,187.2ppm	Breakthrough, 0.92mg/g (100% regeneration)	[117]
4 wt.% Ag/ TiOx - Al_2O_3	JP-5, 1172ppm	Breakthrough, 0.91mg/g (~100% regeneration)	[112]

aid was only 0.43mgS/g at a breakthrough sulfur level of 1ppmw. This measured capacity was similar to that (0.47mgS/g sorb) of Ni/SBA-15 sorbent reported by Park et al. for desulfurization of a ULSD with 11.7ppmw sulfur[114]. Breakthrough capacity on Ni20/SBA-15 prepared by the IWI method with the ultrasonic aid was increased to 0.98mgS/g, ~ two times higher than Ni20/SBA-15 without the ultrasonic aid. The method of preparation of metal doped SBA-15 also has impact on desulfurization and Tian et al.[116] reported incorporating copper species on SBA-15 using solid state grinding and by calcination of metal precursors with SAB-15. Solid state grinding was found most effective for formation of homogenous uniform layer of Cu on the surface of SBA-15 without any blocking the pores, consequently comparatively high adsorption capacity was obtained for solid state ground Cu doped SBA-15. Zhang et al.[117] reported the bimetal exchange of Ag/Al, Ni/Al, Ce/Al on SBA-15 for desulfurization of model diesel and commercial diesel. Ni/Al doped SBA-15 showed maximum sulfur adsorption capacity than other bimetal exchanged SBA-15. It was also observed that Ni was present in the form of Ni ions after the desulfurization and for regeneration. The reason may be that the Ni ions can be firmly anchored on the aluminized SBA-15 by ion-exchanging. Mesoporous materials were also reported as a support material for ionic liquids for easy separation of catalyst in oxidative desulfurization process[118]. These reports are discussed in oxidative desulfurization section.

2.3.2.4 Desulfurization using metal adsorbents

Ma et al.[119] reported studies on model gasoline and real gasoline, using Ni based adsorbent (88wt% of nickel in metallic state with the remaining made up of aluminum metal) and obtained selectivity order of 2,5-DMT < 2-MT ≈ 3-MT < T < BT < 1-octene. It was suggested that adsorption of sulfur compound on the nickel surface involves C-S bond cleavage as evidenced by the formation ethyl benzene from benzothiophene. Olefins have strong effect on desulfurization performance probably by competitive adsorption via π electron/ competitive scramble for the activated hydrogen on the surface. Increase in temperature increased the rate of adsorption, probably through hydrogenation of olefin accelerating the rate of reaction. The study also showed that activity can be improved with increase in the Ni surface area and introducing active hydrogen into the Ni surface. Song and coworker[119] reported desulfurization using Ni/alumina (Ni-58%) at ambient condition and at 200°C. Breakthrough capacity up to 7.3mgS/g was reported for real gasoline (S:305ppmw). Song and coworkers[120] also reported Ni/SiO_2-Al_2O_3 (55 wt% Ni in metallic state) as adsorbent for the desulfurization of real jet fuel and obtained breakthrough capacity of 6mg/g and 16mg/g for parent (736ppmw) and light JP-8 fuel (380ppmw) respectively. It was believed that direct interaction between the heteroatom in the adsorbate and surface nickel plays an important role to provide resistance to adsorption due to steric hindrance. Kong et al.[121] reported breakthrough studies using Ni/ZnO adsorbent that was prepared by homogenous precipitation using urea hydrolysis. A high capacity of 360mgS/g was reported for the synthetic fuels - model gasoline fuel consists thiophene in hexane along with isopentene-35%, toluene-15%, and cyclohexane-10% (100ppmw). In this reactive adsorption mechanism, Ni reacts with sulfur to form Ni-S, which subsequently reacts with hydrogen to form H_2S. The H_2S reacts with ZnO and sulfur moiety gets stuck in the form of ZnS in the adsorbent. Kim et al. compared activated carbon, activated alumina and nickel-based adsorbent and selectivity and mechanism were discussed on the basis of quantum chemical calculations for a complex model fuel. The adsorption capacity was obtained in the order of alumina < Ni/SiO_2 - Al_2O_3 < activated carbon.

2.3.2.5 Metal organic framework (MOF)

MOF is a three-dimensional porous structure and consists of metal sites/cluster connected through organic ligand. It is a hybrid combination of inorganic and organic materials. MOFs have high surface area (upto 2500m^2/g) than ordinary adsorbents (carbon, zeolite, mesoporous silca) and can be functionalized by metals, acids and bases. MOF has been extensively studied since last 10 years for desulfurization. Matzger and coworkers[122,123] reported the microporous coordination polymers (MCPs) as efficient adsorbents for the removal of BT, DBT and 4-6- DMDBT from model diesel and commercial diesel. MCM such as HKUST-1, UMCM-150, MOF-505 were used in their study. UMCM-150 gave capacity of 25.1 and 24.3 mgS/Kg for DBT and 4-6-DMDBT which is significantly lower compared to many adsorbents. Though, complete regeneration using toluene has been reported for UMCM-150, due to low capacity, these materials can have little commercial value. Brieva et al. investigated several commercial MOF systems for removal of T, BT, DBT and 4-6-DMDBT under different experimental conditions and compared with Y-Zeolite [124]. Although author claimed about first use of MOF for desulfurization of transportation fuels, literature on microporous coordination polymers for desulfurization of transportation fuels has been reported since 2008. Li et al.[125] reported the removal of thiophene, benzothiophene and 4-6- Dimethyl dibenzothiophene using five metal organic frameworks (MOF-5, HKUST-1, MIL-53(Fe), MIL-53(Cr) and MIL-101(Cr)). The effect of adsorbate-adsorbent interaction was evaluated using infrared spectra and temperature programmed desorption. Metal sites and structure of MOF are considered to be most significant factors for adsorptive desulfurization. Hasan et al.[126] reported a composite material of nonporous and porous MOF. Nonporous/nonsoluble MOF (particle size much larger than cavity size of porous MOF) Cu(I) composed with porous MOF, MIL100-Fe and Cu. Experimental results showed that although porosity gets reduced by increasing Cu(I) in the composite, it enhances the adsorptive desulfurization due to homogenous dispersion of Cu (I). Chen et al.[127] evaluated the contribution of each fragment of MOF for adsorptive desulfurization using density functional theory. Results revealed that MOF with coordinatively unsaturated sites have strongest binding strength with sulfur compounds. Moreover, it was observed that MOF with unsaturated Fe has strongest adsorption strength than Zn and Cu. Jhung and coworkers[126,128–130] reported various applications of MOF in the area of environmental pollution control in general and desulfurization in particular. Khan et al. investigated the effect of oxidizing agent in removal of sulfur compounds using MOF and found significant improvement after addition of the oxidizing agents like diethyl ether and water[128]. In the review, Khan et al. discussed use of MOF in desulfurization and denitrogenation of liquid and gaseous feedstock and possible interactions between MOF and sulfur/nitrogen containing organic molecules[131]. Haung et al. immobilized (Cr)-MIL-101-SO_3H by Ag and obtained 10 times improvement (27mg/g) in the adsorption capacity[132]. Tang et al. reported desulfurization studies using PCN-10 and compared hydrated and dehydrated forms where the capacity was high at 75mgS/g for dehydrated PCN-10 [133]. Although MOF have potential to provide good sulfur removal capacity, it has some limitation such as stability and in terms of operating temperatures. Further, the structure of MOF may collapse or get blocked after adsorption of sulfur compounds which poses problem in regeneration of MOF. For adsorption at ambient conditions, stability may not be serious issue and morphological changes can be avoided by material modifications.

2.3.2.6 Challenges in adsorptive desulfurization

2.3.2.6.1 Effect of aromatics

Gasoline and diesel contain aromatics up to 15-45%[32–34]. Similar to sulfur, that is slightly polar, aromatics also compete in adsorption on the basis of affinity and as a consequence, there is huge reduction in sulfur removal capacity in presence of aromatics. Typically, the research on desulfurization is carried out with synthetic fuels that do not contain aromatics and hence the reported capacity has little relevance in real life desulfurization of fuels. Lan Pei et al.[58] reported desulfurization of model fuel (DBT in n-octane) using resin-derived carbon spheres (RCS) where effect of aromatics was discussed using toluene and cyclohexane and only marginal reduction in sulfur removal capacity was indicated with increase in aromatics. Contradicting such studies, Fallah et al.[55] and Wang et al.[68] found adverse effect of aromatics and observed significant reduction in adsorption capacity. Kim et al.[67] reported studies on activated carbon, with sulfur concentration of 687ppmw in the model fuel containing 10wt% of butyl benzene where breakthrough capacity of 7.15mgS/g was obtained. Introduction of K cation improved the desulfurization capability of Ni-Y zeolite in presence of aromatics[103]. Yang and coworkers have tried to explain competitive adsorption of sulfur compounds and aromatics on the basis of bond energy difference between thiophene and benzene[36]. However, to date, there is no direct correlation for the effect of aromatics on desulfurization. Thus, it is necessary to systematically evaluate effect of aromatics in adsorptive desulfurization for successful translation of the results in desulfurization of commercial fuels.

2.3.2.6.2 Regeneration of saturated adsorbents

Adsorption is a cyclic operation and commercialization of any adsorption process depends on the ease of regeneration. In case of desulfurization, major emphasis is still on development or finding suitable materials having good adsorption capacity and selectivity for high end refractory sulfur compounds and due to limited success in this aspect, the number of studies on regeneration are few and sparse. Conventionally, regeneration of sulfur selective adsorbents can be carried out by solvent elution or using thermal treatment. Recently, ultrasound assisted adsorbent regeneration was reported[134]. Regeneration of layer bed adsorbents (activated carbon/Cu(I)-Y and Selexsorb CDX/Cu(I)-Y) was reported using solvent elution and air calcination[70]. In solvent elution, four solvents (CCl_4, DMF, methanol, toluene) were used for regeneration at ambient conditions. In second approach, air calcination was carried out at 450^{o}C followed by auto reduction of Cu species and it was concluded that air calcination was more effective than solvent elution. Selexsorb CDX/Cu(I)-Y could be fully regenerated while regeneration of the activated carbon/Cu(I)-Y bed was to the extent of 85% of the original adsorption capacity[70]. Similarly a complete regeneration of Ag-Y was reported by air calcination at 450^{o}C[106]. Regeneration of saturated Ni/ASL60-4 (prepared by exchanging Ni ions onto the aluminized SBA-15(Pore size~11.55nm) at 60^{o}C) was successfully reported up to 3 cycles using dry air at 350°C[117]. Fallah et al. showed ultrasonic assisted regeneration at high temperatures to be more efficient in the case of desulfurization of carbon cloth[56]. Activated carbon fiber (ACF) saturated with sulfur compounds could be regenerated by toluene, 1-methyl naphthalene and tetralin and 1-methyl naphthalene was found to be most effective solvent[134]. Oxidative regeneration of Ni exchanged zeolite Y was reported to be effective for multiple cycle adsorption - regeneration, only when feed was pretreated using an alumina bed[135]; absence of pre-treatment resulted in gradual deterioration of adsorption performance due to additive buildup of impurities from fuel[135]. Regeneration of PCN-10 MOF was carried out by washing with methanol and dichloromethane and then drying in vacuum at 393K for 6h for 5 cycles[133]. Rigorous regeneration of spent bamboo - derived biochar was reported by solvent washing followed by thermal treatment with N_2 flow[51]. Thus, complete regeneration of adsorbents as reported in many reports, appears to be viable thereby strengthening applicability of adsorptive desulfurization in industrial operations.

2.3.3 Extractive desulfurization

Extraction process for desulfurization of transportation fuels is recommended in various configurations with other processes. It can be used as a primary process for desulfurization by extracting direct sulfur compounds from fuels. It can also be used as a supplementary process for oxidative desulfurization. In extractive desulfurization, extractant plays an important role for the removal of sulfur compounds from transportation fuels. Important properties of the suitable extractant for desulfurization process are mentioned below

1) High selectivity for sulfur compounds
2) Low retention/mixing time
3) Low mass ratio
4) Easy to regenerate
5) Low cost

2.3.3.1 Direct extraction of sulfur compounds

In this process, direct extraction of sulfur compounds is followed by regeneration of extractant. The common extractants are organic solvents such as methanol, dimethyl formamide, dimethyl sulfoxide, lactones, ethylene glycol and acetonitrile, anion based ionic liquids, cation based ionic liquids.

Ionic liquids are extensively used for extraction of sulfur compounds due to high thermal stability, low volatility and high solubility of sulfur compounds in ionic liquids. Anions used in ionic liquids are alkyl sulfate, thiocyanate, acetate, dialkyl phosphate and cations used are imidazolium, pyrrolidinium. Wasserscheid and coworkers (2001) reported use of ionic liquids, probably for the first time, for desulfurization. Recently, use of magnetic ionic liquids has been increasingly reported for extractive desulfurization. Strong magnetic properties of ionic liquids make them easy to separate and reuse. Zhu and coworker used pyridinium based magnetic ionic liquids for oxidized sulfur compounds with high efficiency and ease of recovery [136]. Yao et al. carried out extraction of thiophene and dibenzothiophene at ambient temperature using guanidinium based [TMG]Cl/1.5$FeCl_3$ strong magnetic ionic liquid with 100% desulfurization efficiency and 7 times recycling without any noticeable decrease in desulfurization efficiency[137].

Regeneration of extractant is crucial limiting factor for commercialization of extractive desulfurization. Organic solvents have difficulty in separation and issues such as flammability and volatility.

2.3.3.2 Extraction of oxidized sulfur compounds

In this process, first sulfur compounds get converted into sulfone by oxidation followed by extraction of sulfones into the extractant phase. Simultaneous oxidation and extraction (ECOD) are also possible. Organic sulfur compounds are more polar hydrocarbons and thus are relatively easy to oxidize[138]. Oxidative desulfurization (ODS) is usually carried out in two steps, oxidation followed by extraction/ adsorption/ distillation. It also includes commercial processes such as petrostar process, SulphCo's process.

Limitations of ECOD processes

1. Use of toxic and expensive chemicals/materials such as oxidizing agent, catalyst, phase transfer agent and extractant/adsorbent.
2. Energy intensive operation
3. Regeneration of extractant is a major challenge in oxidative desulfurization

2.3.4 Oxidative desulfurization

As mentioned earlier in extractive desulfurization section, organic sulfur compounds are more polar than hydrocarbons so it is relatively easy to oxidize organic sulfur compounds than organic hydrocarbon. Oxidative desulfurization requires oxidizing agents (convert sulfur containing compounds to polar oxidized species), catalyst and phase transfer agent. ODS have several advantages compared to HDS, refractory sulfur compounds such as dibenzothiophenes and alkyl derivative of dibenzothiophene are easily oxidized at ambient conditions. Moreover, hydrogen is not required so oxidative desulfurization is considered to be a viable option for desulfurization. A number of oxidative systems have been investigated such as H_2O_2/organic acids, H_2O_2/heteropolyacid, H_2O_2/Ti-containing zeolites and other non hydrogen peroxide system such as tertiary-butyl hydroperoxide (TBHP), O_2, NO_2 etc. ODS is a promising desulfurization process, has been subject of many research works due to mild operating conditions of ambient temperature and pressure, and good reactivity for refractory sulfur compounds as against hydrodesulfurization. ODS has a potential to complement HDS or integrate with adsorption, extraction, heat treatment and distillation to achieve deep desulfurization[6]. Ultrasound assisted[139], photo assisted[140] and electrochemically assisted processes are newer variants in oxidative desulfurization.

2.3.4.1 Oxidizing agent

Hydrogen peroxide (H_2O_2) is an effective oxidizing agent as compared to other oxidizing agents and it is most widely accepted oxidant for oxidative desulfurization due to low cost-inexpensive and green nature. Another advantage of H_2O_2 is that there are no other degradation products except water. Otsuki et al. reported oxidative desulfurization of methyl phenyl sulphide, thiophenol, diphenyl sulphide, 4-methyldibenzothiophene (4-MDBT), DBT, benzothiophene (BT), 2-methylthiophene (2-MT), 2,5-dimethylthiophene (2,5-DMT) and thiophene compounds using H_2O_2 as an oxidizing agent and formic acid as a catalyst for light gas oil and vacuum gas oil (VGO) and 93% sulfur removal was obtained at 50^{o}C using acetonitrile as an extraction solvent[138]. Chen et al.[141] investigated oxidative desulfurization of thiophene and 3-methyl thiophene using silica gel loaded with metal oxides (CuO and Co_2O_3) along with H_2O_2-formic acid in presence of phase transfer catalyst. Authors used 524ppm (w/v) initial sulfur concentration of each sulfur compound in n-hexane or xylene and evaluated influence of solvent nature, temperature variation, olefin concentration and nature of phase transfer catalyst. It was found that xylene inhibits the rate of desulfurization and also olefins (0-31%) reduce the desulfurization performance significantly. Polyethylene glycol octyl ether was considered as a best phase transfer catalyst (T-84.5%, 3-methyl thiophene-90.7%) followed by SDBS, TBAB, polyglycol-400. Hydrogen peroxide was found to be effective in the oxidation of organic sulfur compounds normally found in fuels and was considered as a promising oxidizing agent for the industrial desulfurization of light oils[141]. Song and coworkers studied catalytic oxidation by first mixing fuel with air in the presence of a catalyst to produce hydroperoxides *in situ* that further oxidizes the sulfur compounds to their corresponding sulfones in the second step in the presence of a catalyst. The generated sulfones were then removed by adsorption for obtaining ultra-low sulfur fuels[142]. Collins et al.[143] used H_2O_2 along with phosphotungstic acid and tetra octyl ammonium as catalyst and phase transfer agent for oxidation of DBT in a water-toluene mixture and obtained desulfurization to the extent of 65%-80%. Te et al. reported reactivity of DBT, 4-MDBT and 4,6 DMDBT in a model diesel using polyoxometalate/ H_2O_2 system and found order of reactivity as DBT > 4-MDBT > 4-6-DMDBT apart from high conversion of DBT by increasing temperature or increasing reaction time[144]. Garcia- Gutierrez et al. reported oxidative desulfurization using H_2O_2/Mo-/gama-Al_2O_3 for model fuel (320ppm) for catalysts alumina and Mo having different acidity values and found that activity for sulfur elimination depends mainly on the presence of hepta and octamolybdates species on the supported catalyst and the use of a polar solvent and phosphate incorporation increases the sulfur elimination that can be achieved up to 10ppmw at 60^oC and at atmospheric pressure[145]. Kong et al.[146] synthesized Ag/TS-1(0.06wt %) catalyst with H_2O_2/ water for oxidation of sulfur compound in gasoline. A large amount of Ag loading reduces the performance of TS-1 by steric hindrance where sulfur removal from 136.5 to 18.8ppmw was obtained after 4h. Park et al.[114] synthesized mesoporous TS-1 catalyst by nano casting route using two different carbon template sources of CMK-3 and commercial carbon black. This mesoporous TS-1 exhibited significantly higher catalytic activities than conventional TS-1 during oxidative desulfurization. Oxidative desulfurization of fuel using H_2O_2 as an oxidizing agent creates a biphasic catalytic system: Sulfur compound present in organic phase while H_2O_2 and catalyst in an aqueous phase. Oxidation reaction rates in a biphasic system are typically low due to mass transfer limitations which can be overcome by using surfactant, increasing mixing speed and ultrasound. Few fuel soluble oxidants such as TBHP have also been used as a oxidant for oxidative desulfurization[114]. Gonzalez et al. reported carbon promoted ODS using H_2O_2 with low concentration of formic acid for achieving <10ppm sulfur level in JP-8 jet fuel and wood based carbon was more effective than peat based type of carbon[147]. Oxidative desulfurization using emulsion catalysis is a promising approach to selectively oxidize sulfur compounds [148]. Amphiphilic catalyst may act as an emulsifying agent to stabilize the emulsion droplet instead of common surfactant and it assembles at the interface of the emulsion droplets. Different quaternary ammonium cations and heteropoly tungstophosphate ions were used. Amphiphilic catalyst with proper quaternary ammonium cation can form metastable emulsion droplets in diesel with aqueous H_2O_2 solution. It has high oxidative activity and can be separated after the reaction by centrifugation and demulsification. 4,6 DMDBT can be completely oxidized to sulfones at 300°C in 80 min by using stoichiometric H_2O_2 and $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$ as a amphiphilic catalyst[149]. Similarly, another emulsion catalyst $[C_{18}H_{37}N\ (CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ was used to estimate the reactivity of BT, 5-MBT, DBT and 4,6-DMDBT. Results indicated the reactivity order as 4,6-DMDBT > DBT > 5-MBT > BT for oxidative desulfurization[143]. $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$ and $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ showed good performance by consuming only hydrogen peroxide ($O/S<3$) as compared to other systems[148] and emulsion catalyst decreased sulfur from 6000 to 30 ppmw after oxidation and extraction[148]. Organic peracids type oxidant can be produced from the reaction of H_2O_2 and carboxylic acid. Commonly used carboxylic acids are formic and acetic acid. Possible *in-situ* generation of organic peracids and its use as an oxidant for oxidative desulfurization has also been reported. Another oxidant, TBHP is soluble in organic fuel phase [114] thus the advantage of single phase can be exploited by using organic oxidants such as peracid and hydroperoxide for obtaining higher mass transfer rates. A commercial operation for the fuel and TBHP reaction can be performed in a fixed bed catalytic process at ambient temperature and pressure. T-butyl alcohol is produced as a co product during the oxidation which can be easily removed from the fuel during post processing. This process is believed to have capacity of reducing sulfur level to 10ppmw in diesel.

2.3.4.2 Catalyst for oxidative desulfurization

Catalyst plays an important role in oxidative desulfurization. Although homogenous catalysis is effective for complete sulfur removal, difficulty in the separation of catalyst makes process unfavorable for oxidative desulfurization. In heterogenous oxidative desulfurization, reactive functional sites on the catalyst surface are effectively used to oxidize the sulfur compounds. The commonly used homogenous catalysts include formic acid, heteropoly acid, organic acids, phosphotungstic acid, tetra octyl ammonium, polyoxometalate, Mo-/gama-Al_2O_3, Ag/TS-1

(0.06%, wt), mesoporous TS-1, emulsion catalyst, amphiphilic catalyst, quaternary ammonium cations, heteropoly tungstophosphate ions, tetraoctyl ammonium bromide. Among all the above-mentioned catalyst, polyoxometalate has shown maximum improvement in the performance of oxidative desulfurization. A combination of polyoxometalates (POM) and H_2O_2 produces super effective ODS[150]. POMS possess unique properties that make them useful for diverse applications. The stability of POMs combined with their structural flexibility to incorporate various elements in their framework would make them attractive catalyst. To date, POM have proved to be among the best catalyst for ODS processes. However, solubility of POM complicates their recovery and reuse.

The most important advantage in the use of heterogenous catalytic oxidative desulfurization (HCOD) is that separation of the catalyst is easy - facilitating reuse of the catalyst that significantly reduces overall cost of operation. The common forms of heterogeneously catalyzed desulfurization processes include:

1. Heterogenous catalytic oxidation followed by extraction
2. Extraction followed by heterogenous catalytic oxidation
3. Simultaneously extraction and catalytic oxidation (ECOD)

ECOD is possible by using various novel catalysts such as polyoxometalates (POM) on zeolite/ carbon/MOF/graphene, Ti containing zeolite, silica gel loaded with metal oxide, MoO_x/Al_2O_3 and silica catalyst, Ti based catalyst. In recent years, new strategies have been developed to immobilize POM on various supports to form new catalytically active and easily recoverable catalyst such as mesoporous silica, TiO_2 and Al_2O_3 nanocomposites and microporous materials such as zeolite and metal organic frameworks (MOFs). POM is also referred to as heteropolyacids. POMs are hydrous salts of anionic metal-oxygen cluster of transition metals. POM has acidic nature with redox properties. MOFs have a structure with large, regular, accessible cages and channels that may act as nanoreactors since they can accommodate catalytically active molecules. MOF porous MIL-101(Cr) was reported to have high porosity and high thermal and chemical stability that provides good support for POM to incorporate into MOF. Oxidative desulfurization of jet and diesel fuels were reported by catalytic air oxidation using *insitu* hydroperoxide[142]. Template method for a hybrid catalyst material POM@MOF-199 anchored on MCM-41 was discussed for oxidative desulfurization of DBT under molecular oxygen[151]. Juliao et al.[150] reported ODS by incorporation of zinc-substituted polyoxotungstate anion into MIL-101(Cr) nanocages. The catalytic performance of this heterogeneous catalyst and POM was investigated for desulfurization of model diesel fuel. The efficiency of the extraction solvent in the ODS process was also evaluated using ionic liquid (1-butyl-3-methylimidazolium hexaflurophosphate) and an organic polar solvent (acetonitrile), in which sulfur compound is extracted after oxidation of sulfur compounds. Polyoxometalate react with H_2O_2 on the surface of catalyst and generate polyoxoperoxo complexes for oxidation of sulfur compounds. Automatic regeneration of catalyst sites can be affected by continuous adsorption of H_2O_2 on the surface. Mesoporous silica immobilized by cesium salts of tungsten substituted molybdophosphoric acid for oxidative desulfurization of DBT[152]. Complete oxidation of sulfur compounds using simultaneous oxidation and extraction process is recently reported on phosphomolybdic acid modified graphene oxide catalyst, H_2O_2 as an oxidizing agent and acetonitrile solvent for extraction of sulfur compounds[152]**.** Ionic liquids are widely used as an extractant in oxidative desulfurization of liquid fuels (Details are provided in section 2.3.3). However, limitation due to difficult separation is a major drawback for its commercialization. A number of methodologies are being considered for the immobilization of ionic liquids on various supports that makes the process more techno economically viable from commercialization point of view. Graphene-analogue hexagonal supported with tungsten-based ionic liquid[153] and ionic liquids supported on metal-organic frameworks[154] were reported for oxidative desulfurization of fuels.

Some of the other types of heterogenous catalysts were also evaluated in the literature that include Cu–Fe/TiO_2 and eutectic ionic liquid[155] and functionalized-activated carbon in a biphasic diesel - acetonitrile system[156]. Recently metal free heterogenous catalytic system using reduced graphene oxide as a catalyst and oxygen as an oxidant was developed where the oxidation treatment was found to be effective for improving catalytic activity [157].

2.3.4.3 Process intensification in ODS

2.3.4.3.1 Ultrasound intensified oxidation process

Ultrasound assisted ODS is widely reported in literature and significant improvement in the performance of ODS can be obtained[158]. Use of ultrasound in appropriate manner results in acoustic cavitation which involves the formation, growth and subsequent violent collapse-implosion of cavitation bubbles. The cavitation during sonication generates a microenvironment with highly localized extreme temperatures (>5000k) and pressures (1000atm) subsequently generating oxidizing species for oxidation apart from effecting very fine emulsion that greatly improves the interfacial surface area[139,159]. Mei et al. reported ultrasound assisted oxidative desulfurization process, using phosphotungstenic acid and tetraoctyl ammonium bromide with ultrasound energy at 75^{o}C to oxidize organic sulfur compound that were subsequently extracted in acetonitrile. DBT and its derivatives were removed from diesel fuel to the extent of 99%[139]. Wan and Yen et al. have successfully optimized the UAOD process by using longer alkyl substituted quaternary ammonium salts (QAS) with small anions as phase transfer agent, transition metal catalyst and H_2O_2 and obtained high conversion of BT, DBT, and alky derivatives of BT and DBT to corresponding sulfones along with complete recovery and reuse of the solvent[160]. Chen et al. also made an attempt to optimize the UAOD reaction conditions including different reaction ratios of TMC, H_2O_2, PTA and sonication time for the removal of thiophene compounds[161]. Chen et al. however reported unsatisfactory efficiency with thiophene and its derivatives remaining even after UAOD[161]. Wu and Ondruschka studied effect of temperature, sonication frequency, sonication power on the performance of desulfurization and recommended optimum parameters as 25 to 70^{o}C, 20 KHz, <200W, temperature, sonication frequency and sonication power, respectively[159]. Continuous-flow ultrasound assisted oxidative desulfurization (UAOD) process for efficient diesel treatment by injection of the aqueous phase was also discussed in the literature[162] apart from multi-objective of sono-photochemical airlift reactor.[163] The mechanism of UAODS is however, not still very clear[160,164–167].

2.3.4.3.2 Hydrodynamic cavitation (HC)

Hydrodynamic cavitation is a physicochemical process that employs mechanical devices such as orifice, in which formation, growth and collapse of cavities result in generation of oxidizing species such as hydroxyl radicals or hydrogen peroxide to facilitate subsequent oxidation reaction. HC is also reported as a useful tool for oxidizing organic pollutants in waste water treatment. Application of HC for desulfurization of liquid fuels was first reported along with catalyst combinations in the patent of Kozyuk et al.[168]. Bhandari et al. have reported for the first time a non-catalytic process using hydrodynamic cavitation for desulfurization of organic solvents and fuels by employing novel two phase process[169]. Bhandari and coworkers used both vortex diode and orifice as hydrodynamic cavitation devices and concluded that vortex diode was more efficient and energy saving device for deep desulfurization of fuels[170,171].

2.3.4.3.3 Photooxidation

Another oxidation process variant, photooxidation, can be carried out by irradiation of ultraviolet rays, visible rays, combine-uv-visible rays, laser beams, solar light in presence of catalyst or in absence of catalyst[143,146,172,173]. Titanium-based catalyst was used in a most of these oxidations[143,172,173]. Possible mechanism of photo oxidation was also discussed in the literature[174,175].

Some studies on radiation assisted oxidation[176] and plasma oxidation[177]were also reported for desulfurization. Electrochemical desulfurization can be reductive or oxidative and one of the advantage of electro ODS over electroreduction is no H_2S generated and the sulfur oligomers can be removed by distillation. Electrochemical desulfurization has been reviewed by Lam et al.[178]. The products of electro-ODS of thiophenes are SO_2 and RSH molecule. The performance of electro-ODS can be improved by using mediators such as Fe^{3+}, Ce^{4+}, Cl, I, Br (Wang et al., 2007 a,b). Efficiency of electro ODS can be improved by adding catalyst such as Au, Pt, Pb etc[178–180].

2.3.5 Biodesulfurization

Biodesulfurization can be carried out in two ways: aerobic and anerobic. Aerobic biodesulfurization follows oxidation pathways and it can be considered as a part of oxidative desulfurization. Biodesulfurization however, is not considered as a promising technology as of now [174] due to inherent resistances involved in process itself.

Anaerobic biodesulfurization was first proposed in the 1950 by Zo Bell and is less explored compared to aerobic pathway. Anaerobic biodesulfurization involves a reductive process in which H_2S is liberated as a product through C-S bond cleavage. Main advantage of this pathway is that it maintains the calorific value of the fuel and also avoids gum formation of product. The limiting factor for anaerobic desulfurization is that, it has slow growth, difficulty in maintaining anaerobic condition and that specific activity of most isolated strains is insignificant for DBT[181]. Kim et al. investigated desulfurization by *Desulfovibrio desulfuricans M6*. This anaerobic strain could degrade 96% and 42% of BT and DBT, respectively. Metabolite analyses proved that this strain could convert DBT to biphenyl and H_2S. Some anaerobic microorganisms, such as *Desulfomicrobium scambium* and *Desulfovibrio* *longreachii* were reported to have the ability to desulfurize only about 10% of DBT dissolved in kerosene[181].

In aerobic biodesulfurization, the oxidative and carbon-destructive series of enzymatic actions that attack carbon atoms in DBT phenyl ring is known as Kodama pathway. It consists of three main steps including hydroxylation, ring cleavage, and hydrolysis. Several different genera, majority of which are *pseudomonas* cultures have been reported to carry out desulfurization through DBT carbon destructive pathway[182,183]. Enzymatic attack at a carbon atom, typical of many aromatic hydrocarbon degradation pathways, is undesirable for a process designed to selectively remove organic sulfur compounds without oxidation of other aromatics found in petroleum products. Due to the undesired breakage of carbon-carbon bonds in benzene rings, this type of desulfurization is considered to be a destructive process. The specific oxidative BDS (oxidative C–S bond cleavage) pathway is often referred to as the '4s pathway' because of the four sulfur-containing intermediates (sulfoxide–sulfone–sulfinate–sulfate). It involves consecutive biocatalytic oxidation of DBT sulfur to sulfoxide, sulfone, sulfinate and hydroxybiphenyl [184–186]. Caro et al.[184] reported BDS of DBT in oil–water emulsions by aerobic *Rhodococcus erythropolis* IGTS8 strain. Madeira et al.[187] performed a stepwise evaluation of the enzymatic oxidation of DBT by horseradish peroxidase (HRP). Reactions were carried out in monophasic organic media containing 25% (v/v) acetonitrile and best results were observed in a reaction medium at pH 8.0 presenting HRP 0.06 IU/ml, DBT 0.267 mM, DBT:H_2O_2 molar ratio of 1: 20 (stepwise hydrogen peroxide addition) and incubated at 45^oC for 60 min. Under these conditions 60% of DBT was converted into DBT sulfoxide (12%) and DBT sulfone (46%). Alves et al. tested enzymatic hydrolyzates of recycled paper sludge as suitable feedstock for BDS by *Gordonia alkanivorans strain 1B*[188]. Only the hydrolyzate obtained after enzymatic mixture dialysis (dialyzed hydrolyzate) allowed DBT desulfurization, in spite of faster bacterial growth occurring on non-dialyzed hydrolyzate. For dialyzed hydrolyzate, 250M DBT was consumed after 96 h displaying a maximum specific productivity of 2-hydroxybiphenyl. Mohebali et al.[185] investigated ability of a newly isolated bacterium, *Gordonia lkanivoransRIPI90A* (GenBank accession number DQ321498) to desulfurize both DBT and DBT containing hexadecane during both the growth and resting stages. Completely degradation by DBT desulfurizing bacterium *Mycobacterium sp.ZD-19* within 10 h or 42 h, and 100% DBT or 4,6-DMDBT was removed within 50 h or 56 h, respectively. Diphenylsulfide (DPS) possessed the lowest desulfurization efficiencies with 60% being transformed within 50 h and 80% at 90 h. The genes responsible for the '4S' metabolic pathway (oxidative C–S cleavage) have been cloned, sequenced and engineered from a variety of microorganisms, and have been transferred to several bacterial species after its initial discovery in *Rhodococcus erythropolisstrain IGTS8*. In the past few years several new *flavin reductases*, including thermo-tolerant enzymes, have been discovered. In addition, the least well understood enzyme in the pathway, HPBS desulfinase, is getting better characterized. Despite considerable progress in understanding of BDS, there are several bottlenecks that restrict commercialization of this process, such as biocatalyst's desulfurization rate and ability of destroying organic sulfur compounds. Further, little information is available on selectivity of degradation and application of single component data for mixtures.

2.4 Summary of literature review and comments

HDS is extensively researched and also established commercialized catalytic process for desulfurization. Effect of different catalysts, catalyst support such as Al_2O_3, MCM-41, carbon, zeolite, metal oxides, amorphous silica alumina have been studied. Resent trends indicate preference to nanoforms of various supports and impregnation of nanometal or polyoxometalate as a promotor for the support. Slurry bed, fluidized bed, trickle bed, fixed bed reactor designs are reported for HDS reactions. Complex chemistry of sulfur removal, which is less understood even today, suggests that it becomes increasingly more difficult to remove the sulfur compounds as the sulfur content is lowered from 1000ppm to 500 and 500 to 350ppm and so on. There is also inhibition effect of different poisons such as H_2S, nitrogen compounds and aromatics. The H_2S affects HDS reaction, hydrogenation and acidity of the catalyst while nitrogen compounds probably retard reaction by competing in adsorption sites of the catalyst. The lower reactivity of these refractory sulfur compounds is largely attributed to the steric hindrance. In view of the complex HDS process, the catalyst, the requirement of severe process conditions of high temperatures and pressures, resulting in cost intensive operation and also the difficulty in reaching deep desulfurization levels, it is imperative that alternative process be developed that can either replace HDS or supplement HDS.

Adsorptive desulfurization is one of the best possible alternative or supplementary process for HDS. Carbon, zeolite, metal oxides, metal organic frameworks, SBA-15, Al_2O_3 are more commonly used adsorbents for desulfurization and many more newer materials are being researched. Carbon and its modified forms are most widely studied among all other adsorbents.

Carbon have high surface area, good mechanical strength, high thermal stability, easy for modifications, effective regeneration and less expensive as compared to other adsorbents. Nanocarbon, aerogels, carbon cloth, graphene, nanofibers, nanotubes are recent developments in adsorptive desulfurization. Acid modification, base modification and metal impregnation are more extensively studied areas for carbon-based adsorbents. Increment in the adsorptive capacity of sulfur compound to be due to increase in concentration of acidic functional groups and not due to either increase in mesoporous surface /volume or increase in microporous surface /volume. Hydrogen bonding interaction involving surface functional groups play an important role in adsorptive desulfurization. Single metal impregnation on carbon surface for desulfurization is an adopted idea from HDS catalyst and majority of literature has been generated on this topic. Metal sulfur interactions provide stronger chemical bonding force than π complexation and therefore this aspect needs significant inputs. Further, effect of more than one metal on carbon surface has not been well investigated that can provide more benefits in terms of increased capacity for desulfurization. Process intensification such as acoustic cavitation coupled adsorption can also improve the performance of desulfurization process.

Zeolite and its ion exchanged forms, though have been discussed widely in the literature, may have little potential for growth in future as the developments in this area have resulted into only incremental benefits and no major breakthrough. Zeolite is not a promising commercial adsorbent due to poor regeneration ability and high cost involved in synthesis of zeolite. MOF is another promising advanced material for desulfurization, has high surface area, good adsorption capability but has problems due to stability and high temperature operability issues.

ODS have several advantages compared to HDS as refractory sulfur compounds such as dibenzothiophenes and alkyl derivative of dibenzothiophene can be easily oxidized at relatively mild operating conditions, moreover, hydrogen is not required. ODS process involves addition of oxidizing agent, catalyst, phase transfer agent, extractant and adsorbent. A number of variants of oxidative desulfurization process are available both in the area of homogenous catalysis and heterogenous catalysis. H_2O_2, TBHP, O_2, NO_2, air, superoxide anion, organic peracid, HNO_3, K_2FeO_4, O_3, peroxy salts, H_2SO_4 are the commonly used oxidizing agent. The ODS performance can be improved by assistance of photons, ultrasound, plasma, electrochemical reactions, hydrodynamic cavitation, radiation and so on and close to 100% sulfur removal can be obtained. The mechanism is complex and less understood apart from scale-up issues that make these processes less attractive for commercialization.

Extraction, in principle, appears to be an excellent alternative, especially when coupled with advanced oxidation process. Ionic liquids can be useful solvents in desulfurization of fuels. Commercial processes, e.g. Merox, are established operations for removal of thiols, sulfide and disulfide. The major limitation is in the form of extractant used in ODS process that should have specific properties suitable for extraction of only sulfur compounds and reusability.

Biodesulfurization, both aerobic and anaerobic, are less attractive alternatives, as of today, from commercialization point of view though huge research potential exists in this area. The limiting factor for anaerobic desulfurization is that, it has slow growth, difficulty in maintaining anaerobic condition and that specific activity of most isolated strains is insignificant for DBT**.** Biodesulfurization process can have low capital cost, no emission of greenhouse gases and high value of biodegradable products. Yet, no single biological based desulfurization process has been commercialized or close to commercialization.

The critical literature analysis as above clearly brings out research gaps in practically all the areas of desulfurization. For HDS processes, more focus is seen on the catalyst and process development, for extractive and oxidation processes, the focus is largely on the suitable extractants, optimization of process in terms of catalyst and oxidizing agent apart from coupling of the steps - reaction and separation. The biodesulfurization is clearly broad research area in terms of inputs from microbiology, biochemical engineering and application development. In the area of adsorptive desulfurization, there is vast potential not just for development of most suitable adsorbents, their characterization and application, but also with respect to the modifications (chemical or physical) of the existing known adsorbent materials for improved performance. Finally, there appears to be huge scope for newer process development, especially non-catalytic process, that can augment the existing desulfurization processes such as HDS for increased techno-economic feasibility.

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Chapter 3

Chapter 3
Characterization Methods

In this chapter, characterization and analytical techniques involved in this research are discussed. Instrument details and procedures, specifically pertaining to Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDX), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction(XRD), Surface Area Analyzer, Micro Plasma Atomic Emission Spectroscopy (MP-AES), Inductive Coupled Plasma-Optical Emission Spectroscopy, Total Organic Carbon analyzer (TOC), Chemical Oxygen Demand analyzer (COD), Gas Chromatography - Flame Photometric Detector (GC-FPD), pH and Sulfur analyzer (TN-TS) have been elaborated.

3.1 Scanning electron microscope (SEM)

Scanning electron microscopy is used to enhance the resolution up to 1nm using high speed electrons in high vacuum (10^{-7} to 10^{-10}mbar). Design of SEM is similar to light microscope, except light is replaced by electrons and glass lenses are substituted by electromagnetic/ electrostatic lenses. The SEM has electron source, electromagnetic lenses, specimen holders and stages. Electrons are produced through thermionic emissions of tungsten filament, LAB6 crystal or ZrO/W Schottky source and generated low energy electrons are accelerated by providing high voltage between cathode (electron source) and anode. Magnetic field generation by electromagnetic lenses causes the electrons take circular path through the lens system. Strength of the magnetic field decides the focal width of the lens. Initially, lens performs as a condenser lens that determine the overall brightness of the beam followed by objective lens and projective lens which act in combination to project the final image on the CCD camera (photosensitive film)[1–3].

In this work, Stereoscan 440 software-controlled scanning electron microscope was used. The energy of the electron beam is adjusted in between 300V to 30kV and current is adjusted from 1 picoampere to 1 microampere. Instrument was operated in the environmental scanning electron mode (ESEM). The samples were prepared using the standard procedures and the characterization results were obtained in the form of morphology images of specific magnification.

3.2 Energy dispersive x-ray spectroscopy (EDX)

EDX is an analytical method for detection of elements present in the sample. EDX detector is usually connected with SEM or transmission electron microscope (TEM). This technique works on the principle of emissions of characteristic X-rays and their detection. Elements are identified on the basis of specific energy of characteristic X-rays related for each element. Intensity of peaks helps to quantify the elemental percentages present in the sample[4].

3.3 Fourier transform infrared spectroscopy (FT-IR)

FTIR spectra gives information about functional groups and provide supplementary information to identify the structure of molecule. Infrared spectroscopy works on the principal of vibration of atoms. Infrared radiations are passed through the samples and specific radiations are absorbed at corresponding vibrational energy of atoms and displayed in the form of absorbance spectra. Different modes of vibrations such as stretching, bending get recognized in IR and molecular dipoles is one of the factor which changes with interaction of IR radiation with materials. Factors such as combination and overtone bands, fermi resonance, coupling and vibration-rotation bands causes changes in infrared spectra. FTIR technique is a versatile, easy to operate and can characterize sample in all the physical states. Infrared spectroscopy consists of photoacoustic spectroscopy, micro spectroscopy, reflectance-based spectroscopy such as attenuated total reflectance, diffuse reflectance and specular reflectance. Different sources and detectors are used in FTIR spectroscopy depending on the application. In near-infrared, tungsten-halogen lamps are used as sources and sulfide photoconductors are used as a detector. In mid-infrared region Globar or Nernst are used as sources and pyroelectric device incorporating deuterium tryglycine sulfate are used as a detector. Mercury cadmium telluride detector is preferred in sensitive work[5–7]. Output from instrument is referred as spectrum which consists transmittance and wavenumber. Wavenumber is increasing from right to left. In this work, mid-infrared spectra (400 to 4000cm^{-1}) was used for the analysis.

3.4 X-ray diffraction (XRD)

XRD is a nondestructive diffraction technique. Incident x-rays falls on atomic crystals and interfere with one another and diffracted rays are detected by detector, this phenomenon is called as x-ray diffraction. It measures the average spacing between layers of atoms, determine the orientation of crystals, helps to identify the unknown materials and measure the size, shape and stress of crystalline regions. X-ray diffraction can be studied using single crystal xrd or powder xrd. In powder XRD, wide angle and small angle mode is used for characterizing the material. In this work, wide angle powder x-ray diffraction of all the samples was carried out in a PAN analytical X'pert Pro dual goniometer diffractometer (40kV and 30mA). The radiation used was Cu Kα (λ = 1.5418 Å) with a Ni filter and samples were scanned in 2θ range of 10−90° at scanning rate of 6.67°/min and scan step size of 0.0084[8,9].

Intensity Vs angle of diffraction (2θ) is recorded in the final output. The d spacing was estimated using the Braggs law and compared with International center for diffraction data (ICDD). Miller indices are estimated for each peak to identify unit cell parameters, structure orientation and stress.

3.5 Surface area analyzer

The instrument can provide data on the surface area, pore size and pore size distribution using nitrogen gas adsorption technique. Volume of gas filled in pores Vs pressure data can be used to estimate BET surface area (single point or multipoint)[10]. In this work, surface area, pore volume, pore size distribution in the material was determined by N_2 adsorption isotherm at 77 K using Quantachrome Autosorb automated gas adsorption system. Multi point Brunauer - Emmett - Teller (BET) method was used for surface area measurement, micropore surface area was evaluated using Dubinin-Radushkevich (DR) method and total pore volume and pore diameter was estimated using Barret- Joyner - Halenda method (BJH).

3.6 Microwave plasma atomic emission spectroscopy (MP-AES)

This technique works on the principle of determination of elemental composition by examining electromagnetic spectrum. MP-AES instrument consist nebulizer, spray chamber, monochromator, CCD detector, air generator. Nebulizer and spray chamber is used to create aerosol and after that aerosol is passed into the center of the hot plasma where decomposition and atomization take place. Atom continues to emit light of specific wavelength and returns to the lower state from excited state. Scanning monochromator is used to measure wavelength of emissions and CCD detector helps to image the wavelength range. MP-AES quantifies the concentration on the basis of comparison of emissions of known concentrations of elements. It has better performance and high sensitivity than conventional atomic absorption[12,13]. In this work, MP-AES of Agilent 4100 were used for determination of metal content.

3.7 Inductive coupled plasma-optical emission spectroscopy (ICP-OES)

ICP-OES is one of the most powerful technique for determination of elemental composition from solid, liquid and gases samples. This technique works on the similar principal like MP-AES, and includes emissions and detection of excited photons and ions. Optical emission spectroscopy(OES) plays an important role in collection of photons by lens or concave mirror. Wavelength selection device- monochromator helps to form an image on the entrance aperture and specific wavelength is converted to electrical signals by photodetectors[11]. In this work, ICP-OES of Spectro arcos, Model No- ARCOS-FHS-12 were used for determination of metal content.

3.8 Analysis of sulfur in fuel

The sulfur content was analyzed using total sulfur analyzer, TN-TS 3000 (Thermoelectron Corporation, Netherlands) and Gas Chromatograph (Agilent GC 7980A).

Block diagram of TN-TS 3000 is provided in Fig.3.1. Sample is introduced into the furnace through solid and liquid sample modules injectors. Conditioned gaseous stream enters into sulfur detector where pulsating light excites SO_2 molecules, then decay to lower energy state by emitting UV light of specific wavelength. Band pass filter allows the specific wavelength UV light to be detect by photo multiplier tubes. Amount of UV light emitted is proportional to SO_2 concentration. Chemiluminescence detector is used for detection of nitrogen content[14]. Two separate calibrations for sulfur measurement were used in TNTS. First calibration was in the range of 0 to 50 ppm and second in the range 50 to 500ppm. Total uncertainty was found as 2 ppm error in the range of 0-50ppm and up to 5ppm in the range 50-500ppm measurement with repeatability error within 1%, indicating complete reproducibility.

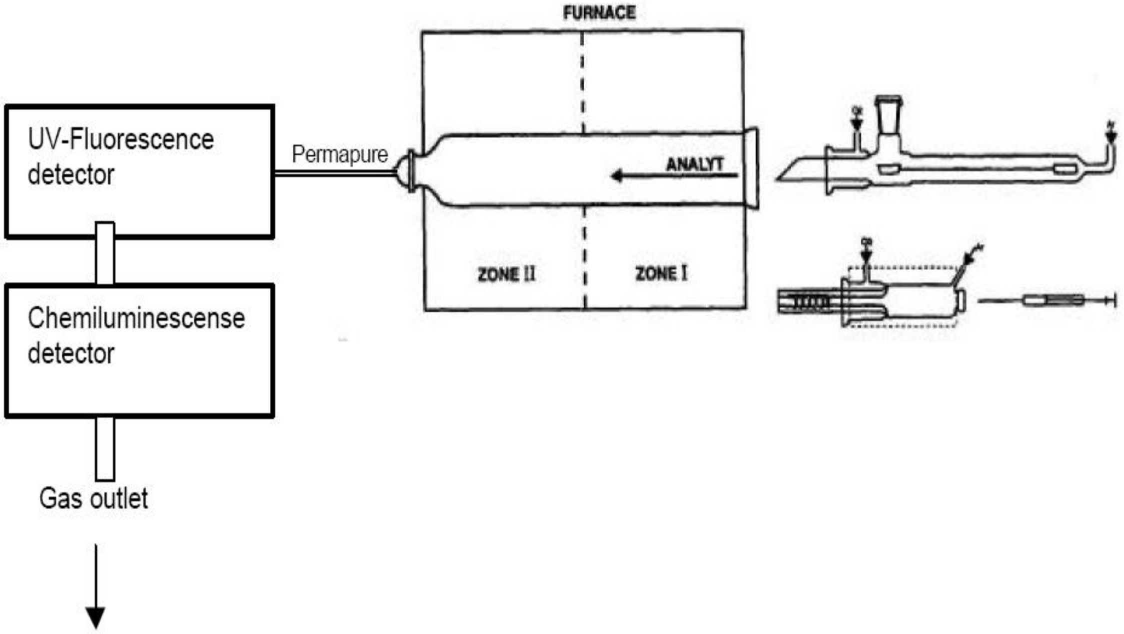

Figure 3.1: Block diagram of sulfur analyzer (TNTS-3000)[14]

The samples were also analyzed for sulfur compounds using Gas liquid chromatography (Agilent GC, 7890A). Gas liquid chromatography (GLC) involves vaporization of sample and enters into the chromatographic column then sample is carried through the column by the flow of inert gases like helium and nitrogen. Stationary phase present in the column helps to distribute the specific residence time for each compound present in the mixture. Flame photometric detector (FPD) is used for sulfur analysis in organic liquids.

Gas Chromatograph (Agilent GC, 7890A) equipped with CPSil 5CB sulfur column (30m× 320µm×4 µm) in conjunction with flame photometric detector (GC-FPD). Helium was used as a carrier gas with flow rate of 2 mLmin^{-1}and a split ratio of 10:1 was maintained. The injector temperature was 250°C with injection volume of 0.2µL and total analysis time of 25min. The oven temperature was ramped at 20°C/min from 40 to 100°C and 60°C/min to 230°C. Reproducibility was checked and was found satisfactory. Two separate calibrations for sulfur measurement were used for gas chromatography. Calibration ranges were in between 0-100 and 100-500ppm. Uncertainty in calibration measurement was estimated by considering the addition of uncertainty of calibration measurement capability, uncertainty in repeated measurements and uncertainty in resolution of instruments (1ppm). The error in the cross checking of the readings with GC was typically less than 2%.

3.9 Total organic carbon analyzer (TOC)

TOC analyzer is useful for determining total carbon content (TC), total organic carbon content (TOC) and inorganic carbon content (IC). TC is addition of TOC and IC. In this work, analysis was carried out using shimadzu TOCL-01086 TOC analyzer which had autosampler, furnace and platinum catalyst. The sample gets injected onto the platinum catalyst for combustion at 680°C in presence of externally supplied oxygen. The CO_2 generated passes through the moisture trap and halide scrubbers to remove water vapor and halides and finally is detected through non-dispersive infrared detector[14].

There are two ways for calibration of TOC. One is non-purge organic carbon (NPOC) method and other is traditional method for calibration (TOC). NPOC calibration directly provides quantitative estimation of TOC and traditional method gives quantitative information about TC and IC. In this work, NPOC calibration is done using potassium hydrogen phthalate as a calibration standard in water (1000ppm) and 2N HCl for acidification.

3.10 Chemical oxygen demand analyzer (COD)

Chemical oxygen demand (COD) measurements were done using spectroquant Pharo 100 spectrophotometer where spectroquant TR 320 was used as digestor. Standard calibration and procedures were used for COD measurement; addition of two different reagents followed by digestion for 2hrs at 148°C and measurement of COD.

3.11 pH analyzer

pH analysis was done using spectralab MP-5 pH meter. Calibration of pH meter was carried out at 3 different pH values 3, 7 and 9 using buffer solutions.

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Chapter 4

Nalinee B. Suryawanshi, Vinay M. Bhandari, Gayatri Sorokhaibam and Vivek V. Ranade. *Investigating adsorptive deep desulfurization of fuels using metal modified adsorbents and process intensification by acoustic cavitation.* Ind. Eng. Chem. Res, 58,18, 7593-7606 (2018) http://doi.org/10.1021/acs.iecr.8b04043 .

Chapter 4

Newer Insight into Adsorptive Deep Desulfurization of Fuels using Metal Modified Adsorbents and Process Intensification by Acoustic Cavitation

Abstract

The harmful impact on environment due to SO_x emissions from fuels and increasingly stricter norms over the years, have amplified deep desulfurization challenges, consequently enhancing attractiveness of adsorptive separations. The present work explores metal modifications of sulfur specific carbon adsorbents- both commercial (Shirasagi TAC and SRCx 4/6) and newer adsorbents derived from *Cassia fistula* biomass (CFP-450) and its impact on sulfur removal behaviour and selectivity. Single and double metal modifications were made using zinc, cobalt, nickel and copper. An attempt was made to investigate further improvements in sulfur removal using process intensification - acoustic cavitation coupled with adsorption. The removal of three refractory sulfur compounds *viz*. thiophene, benzothiophene, dibenzothiophene was studied using the newer adsorbents and the performance was compared with commercial TAC and SRCx 4/6 for both single and double metal impregnation and process intensification. The commercial carbon adsorbent TAC have high capacity for sulfur removal, up to 23mgS/g especially, for dibenzothiophene. In case of TAC, process intensification using cavitation coupled with adsorption improved sulfur removal to the extent of 100% for thiophene and for Ni-Cu modified TAC, capacity increase up to 38mgS/g for dibenzothiophene was obtained. The results indicate that combined effect of metal modification and process intensification can substantially improve the sulfur removal efficiency of carbon adsorbents.

4.1 Introduction

Air pollution has emerged as a serious problem in many parts of world and major contribution is from transportation fuels that release SO_x and other pollutants. As a consequence, Governments worldwide formulate stringent norms on fuel quality from time to time. According to US-EPA, maximum allowable sulfur concentration is 15 and 30ppm in diesel and gasoline respectively[1,2] while the new regulations of European Union mandate below 10 ppm sulfur levels in transportation fuels[3]. For futuristic developments such as Fuel Cell, where gasoline is considered as an ideal liquid fuel, even small traces of sulfur can poison the catalyst in the fuel cell and hence sulfur concentration well below 1 ppm is recommended. The three common liquid fuels: gasoline, diesel and jet fuel have different composition and content in terms of sulfur compounds which vary widely from lower end sulfur compounds such as sulfides, disulfides, mercaptans to higher end refractory compounds such as thiophene, benzothiophene, dibenzothiophenes and their alkylated derivatives. The huge differences in terms of reactivity of these compounds and differences in the nature and concentrations of variety of sulfur compounds make application of any single desulfurization technology difficult in techno-economically meeting the newer norms. Production of ultra-low sulfur fuels is difficult using the existing established methods, mainly based on reaction approach, such as hydrodesulfurization (HDS). HDS employs high pressures (3-7MPa), high temperatures (320-380°C) and catalysts such as Ni/Mo or Co/Mo supported on Al_2O_3[4]. Exploiting HDS in deep desulfurization implies substantially high capital investment and severe process changes in terms of catalyst and operating conditions. Alternative methods for desulfurization of liquid transportation fuels include adsorption[5], oxidation[6] or biodesulfurization[7]. Advanced oxidation processes such as photo assisted oxidation[8] ultrasound assisted oxidations and cavitation[6] have also been reported for desulfurization. Recently, hydrodynamic cavitation for desulfurization of fuels was reported without use of any catalyst[9–11]. Adsorptive deep desulfurization has been a subject of discussion for decades mentioning numerous adsorbents and modifications for improving the adsorption capacity, selectivity and for ease of regeneration. Adsorption can be an excellent supplementary process in the existing set-up, has potential in meeting ultralow sulfur levels at low costs and hence newer insight is required on various aspects ranging from adsorbent types to different modifications-material or process.

A wide variety of materials starting from activated carbon (AC)[5], silica based sorbents[12], zeolites[2], metal oxides[13], metal organic frameworks[14], graphene-like boron nitride[15] and metal exchanged/ impregnated activated carbon/ zeolites/ mesoporous materials have been reported in the past for adsorption. Carbon based adsorbents are preferred due to their manoeuvring capacity with a variety of starting materials for obtaining high surface area, controllable physical texture, high mechanical strength, possible surface modifications apart from availability of various sources such as coal[16], wood[17], polymer[17], biomaterials - rice husk [18], *Cassia fistula*[19], organic wastes[20], carbon cloth[21], carbon aerogels[22], resin derived carbon spheres[23], rubber[24] etc. Performance of adsorptive desulfurization can be improved by modifying carbonaceous matrix and/or modifying the nature of sulfur compounds using methods such as chemical, thermal, electrochemical, ozone, microwave, photon, cavitation, plasma treatment. Chemical treatments involving acidic, basic and metal modifications are most widely reported. Incorporating metal having positive charge can assist sulfur removal due to interactions with slightly polar and negative sulfur moiety. Single metal incorporation on carbon matrix is extensively studied by many researchers such as Fe[25], Zn[26], Co[25], Ni[26], Cu[25], Ag[27], Na[27], Al[5], Si[5], Mn[28], Mo[29], Pd[30], Ce[31] compared to limited study on bimetallic incorporation such as Ce-Fe[24], Co-Cu[32], Cu-Ni[33], Co-Mo[29]. The mechanism of such modifications in sulfur removal, however, is not well understood. Our earlier work indicated that incorporation of specific functional groups or active metals may provide new sites for sulfur adsorption [5,34].

Desulfurization capacity with majority of the metal impregnated carbon materials was substantially low implying necessity for newer strategy of materials developments, material modifications and process intensification. Further, multifunctional adsorbents have not been discussed in detail to exploit higher capacity due to enhanced interactions. It is instructive to evaluate these effects of metal modifications apart from extracting functionalities from newer biomass as a starting material for obtaining high sulfur removal capacity and for obtaining insight into sulfur removal which form the main objectives of this study. In the present study, single and double metal modifications of carbon adsorbents, using four different metals (Zn/Co/Ni/Cu) have been discussed in the context of deep desulfurization of transportation fuels, based on the premise that cations of transition metal are likely to improve adsorption capability. Another engineering modification in the form of process intensification using acoustic cavitation (ultrasonication), without oxidizing agent or catalyst, has been investigated in detail for improving adsorptive desulfurization. A newer biomass derived (*Cassia fistula*) adsorbent, was studied in detail for the removal of refractory sulfur compounds - thiophene, benzothiophene and dibenzothiophene and the results have been compared with those from using sulfur specific commercial carbon adsorbents.

4.2 Experimental

4.2.1 Materials

Analytical reagent (AR) grade thiophene (Loba chemicals, 99%), benzothiophene (Fluka, 95%) and dibenzothiophene (Sigma-Aldrich, 98%) were used as model organosulfur compounds. n-octane (Sigma-Aldrich, 98%) was used as a solvent to prepare the model fuel. A commercial sulfur specific carbon adsorbent-SHIRASAGI TAC and SRCx were obtained from Japan Enviro Chemicals Ltd., Japan. Another activated carbon, CFP-450,derived from *Cassia Fistula* biomass and treated by phosphoric acid in 1:1 ratio, was synthesized in the laboratory using the procedure reported elsewhere[19]. Nitric acid (Sigma-Aldrich,64-66%), hydrochloric acid (Emplura, 35%), cobalt chloride hexa-hydrate (Qualigens, 97%), zinc chloride (Qualigens, 95%), nickel nitrate hexa-hydrate (Merck, 97%), cupric nitrate tri-hydrate (Thomas Baker, 99.5 %) were used for the modification of adsorbents.

4.2.2 Analysis of sulfur in model fuel

Model fuel was prepared by dissolving known quantities of sulfur compounds in n-octane: thiophene in n-octane (MF-T), benzothiophene in n-octane (MF-BT), dibenzothiophene in n-octane (MF-DBT). Selectivity was studied in synthetically prepared model diesel consisting of equal sulfur concentrations of thiophene, benzothiophene, and dibenzothiophene in n-octane. Assuming conventional desulfurization process to yield fuel containing 100ppm sulfur and adsorption follows the conventional HDS process for deep desulfurization, a total sulfur concentration of 100ppm was employed in selectivity studies of mixtures. The sulfur content was analysed using total sulfur analyser, TN-TS-3000 (Thermoelectron Corporation, Netherlands) and also by using Gas Chromatograph (Agilent GC, 7890A) equipped with CPSil 5CB sulfur column (30m× 320µm×4µm) in conjunction with flame photometric detector (GC-FPD). Helium was used as a carrier gas with flowrate of 2 mLmin^{-1}and a split ratio of 10:1 was maintained. The injector temperature was 250°C with injection volume of 0.2µL and total analysis time of 25min. The oven temperature was ramped at 20°C/min from 40 to 100°C and 60°C/min to 230°C. Reproducibility was checked and was found satisfactory. Two separate calibrations for sulfur measurement were used for TNTS and Gas chromatography. For TN-TS analyser, the first calibration was in the range of 0 to 50ppm and second in the range 50 to

500ppm. For GC, the calibration ranges were 0-100 and 100-500ppm. Uncertainty in calibration measurement was estimated by considering the addition of uncertainty of calibration measurement capability, uncertainty in repeated measurements and uncertainty in resolution of instruments (1 ppm). For TN-TS sulfur analyser, the total uncertainty was found up to 2ppm in the range of 0-50ppm and up to 5ppm in the range 50-500ppm measurement with repeatability error within 1%, indicating complete reproducibility. The error in the cross checking of the readings with GC was typically less than 2%.

4.2.3 Preparation of modified adsorbents

4.2.3.1 Single metal modification (Zn/Co/Ni/Cu)

Zinc chloride and cobalt chloride hexahydrate were used as metal precursors for Zn and Co metal impregnation, respectively. 1M concentration of metal precursors (Zn/Co) in 0.5 M HCl solution was used for wet impregnation (120 g Carbon/L) at 60°C for 6h. Single metal modified adsorbents for metals Ni and Cu were synthesized using acidic solution of 0.5 M metal precursors of nickel nitrate or cupric nitrate in 0.1M HNO_3 and using wet impregnation method (120g Carbon/L) at 60°C for 6 h. The modified adsorbents were then filtered, washed with double distilled water, air dried and finally activated at 200°C for 16 h. Zn and Co modification were carried out only for TAC and are referred as TAC-Zn and TAC-Co respectively. The modified adsorbents Ni/Cu are referred as CFP-450-Ni, CFP-450-Cu, TAC-Ni, TAC-Cu, SRCx-Ni, SRCx-Cu (Table 4.1).

4.2.3.2 Double metal modification (Ni and Cu)

The double metal modified adsorbents were prepared from single metal modified adsorbents using the above-mentioned procedure and Ni was impregnated prior to Cu loading. Double modified CFP-450, TAC and SRCx are referred as CFP-450-Ni-Cu, TAC-Ni-Cu and SRCx-Ni-Cu respectively (Table 4.1). The uncertainty error due to all physical measurement was typically less than 2% and total error in the experimentation including the analysis is believed to be within 5 %.

4.2.4 Adsorption equilibrium studies

Batch adsorption equilibrium studies were carried out at ambient room temperature using known volume of model fuel with predetermined sulfur concentration and equilibrating with known weight of the adsorbent (0.05-0.75g per 10mL of the model fuel). Spectralab HM8T orbital shaker was used for equilibration time of 16h at an agitation speed of 130 rpm. Prior to each adsorption experiment, the adsorbents were activated in Nabertherm furnace (RT 50-250/11, ±5K/mm) at 200°C for a minimum period of 2h for removing moisture, if any. Uncertainty analysis in the adsorption isotherms is predicted by standard deviation for adsorption equilibrium capacity.

4.2.5 Process intensification studies using acoustic cavitation

Process intensification through acoustic cavitation was studied using the ultrasonication bath (PCi analytics, Model 9L250H) having ultrasonic power of 250 W and operating frequency of 33KHz. The samples of model fuel containing adsorbent were subjected to acoustic cavitation in 2 cycles of 15 min each. After the sonication, the samples were kept in orbital shaker for another 16h equilibration.

4.2.6 Adsorbent characterization

Qualitative information on morphological distribution of metals on the adsorbent surfaces was obtained by environmental mode Scanning Electron Microscope (E-SEM, Leo-Leica, stereoscan 440, Cambridge, UK). Powder X-ray Diffraction (XRD) for all the samples was carried out in a PAN analytical X'pert Pro dual goniometer diffractometer (40 kV and 30 mA). The radiation used was Cu Kα ($\lambda = 1.5418$ Å) with a Ni filter and samples were scanned in 2θ range of 10−90° at scanning rate of 6.67°/min and scan step size of 0.0084. Data collection was carried out by mounting the samples on a glass plate. Surface area, pore volume, pore size distribution of the different adsorbents was determined by N_2 adsorption isotherm at 77 K using Quantachrome Autosorb automated gas adsorption system. Multi point Brunauer – Emmet - Teller (BET) method was used for surface area measurement, micropore surface area was evaluated using Dubinin-Radushkevich (DR) method and total pore volume and pore diameter was estimated using Barret- Joyner-Halenda method (BJH). Surface functional groups on the

Table 4.1: List of modified adsorbents

No.	Metal used	Adsorbent for modification	Adsorbent code after metal impregnation	Metal loading before modification (wt%)	Addition of metal loading in modification (wt%)	Total metal loading on modified adsorbent (wt%)
1	Zn	TAC	TAC-Zn	0.46	-0.032	0.428
2	Co	TAC	TAC-Co	0	0	0
3	Ni	TAC	TAC-Ni	0	0.45	0.45
4	Cu	TAC	TAC-Cu	3.19	-0.05	3.14
5	Ni-Cu	TAC	TAC-Ni-Cu	Ni:0 Cu:3.19	Ni: 0.036 Cu: 0.268	Ni: 0.036 Cu:3.46
6	Ni	SRCx	SRCx-Ni	0	0.883	0.883
7	Cu	SRCx	SRCx-Cu	0.0062	0	0.0062
8	Ni-Cu	SRCx	SRCx-Ni-Cu	Ni: 0 Cu:0.0062	Ni:0.0019 Cu:1.09	Ni:0.0019 Cu:1.0962
9	Ni	CFP-450	CFP-450-Ni	0	0.59	0.59
10	Cu	CFP-450	CFP-450-Cu	0	1.52	1.52
11	Ni-Cu	CFP-450	CFP-450-Ni-Cu	0	Ni: 0.013 Cu: 1.95	Ni: 0.013 Cu: 1.95

modified carbon adsorbents were determined by Cary 600 FTIR (Agilent) using KBr pellet method in the range 400-4000cm^{-1}. Elemental analysis was carried out using Scanning Electron Microscope (Leo-Leica, stereoscan 440, Cambridge, UK) equipped with Energy Dispersive X-ray system (EDAX, XL-30) operating at 15-25 kV. The presence of transition elements in the carbon adsorbents was also confirmed and quantified by Microwave Plasma Atomic Emission Spectrometer (MP-AES) (Agilent 4100), also cross-checked using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Spectro arcos, Model No. ARCOS-FHS-12).

4.3 Results and discussion

4.3.1 Characterization of the adsorbent materials

E-SEM images of the adsorbents along with their single and double metal modified forms are shown in Figures 4.1, 4.2 and 4.3. Several changes in the morphology after post metal impregnation were observed. The images show disordered structure with pores of non-uniform sizes. SEM and BET characterization showed that, the adsorbents are highly porous and having wide distribution in pore sizes from micropores with nanometre size to macroporous in micrometre size. Metal deposition evidence can be seen from the white shiny patches on the grey surface and most of these metal particles of larger size can be seen as aggregates on the modified carbon surfaces[35]. The randomly distributed metal clusters are indicated by the SEM images of TAC-Ni and TAC-Cu (Fig. 4.1). SRCx has well defined structure of long cylindrical pores with pore size of 8 to 18 µm. After metal modification pore sizes reduced up to 2.7-0.5µm. The rupturing of the honey comb like structure along with reduction in pore size in virgin SRCx as one goes from single to dual metal modification (Fig. 4.2) is highly prominent. It is also seen that the morphologies of the laboratory synthesized CFP-450 adsorbents were greatly affected by the nature and extent of metal impregnation (Fig. 4.3). SEM-EDX analysis revealed the presence of other heteroatoms like Cu, Cr and Zn on TAC surface, Si and Al on SRCx surface. Random error in the EDX analysis is estimated for few samples by independent synthesis and characterization, in triplicate and relative error was estimated below 5%. The results of characterization indicate higher metal loading on the external surfaces only and a high loading of 14.2wt% of Zn and comparatively low Co loading of 1 % for TAC-Zn and TAC-Co respectively (Table 4.2) was observed. MP-AES and ICP-OES results (Table 4.1) indicated no increase in the Zn loading over that present already and absence of Co metal in the bulk carbon adsorbent which may be attributed to the fact that the commercial adsorbent TAC already contains Cu, Cr and Zn which reduces its capacity for further modification. Further, the higher concentration of hydrochloric acid (0.5M) was found to aid leaching of some of the inherent metal during the impregnation of Zn and Co and hence a lower acid concentration of 0.1M was employed for metal modifications of Ni and Cu. Similar to the observation above, only 0.45% (wt.) Ni loading on TAC was obtained which was confirmed by MP-AES analysis (Table 4.1). The metal loading on carbon gets altered in the process of double metal modification and Ni metal loading was reduced from 0.45% to 0.036% and Cu loading increased by 0.26% after double metal modification in TAC. As was the case for TAC, no appreciable metal contents were detected on the surface of CFP-450 and a reasonably high loading of 1.52% and 0.59% for Cu and Ni was obtained after single metal modification. In the double metal modification, Ni loading was reduced to 0.013% and Cu loading increased to 1.95%. SRCx, showed 1.98% and 0.88% of Cu and Ni loading respectively for single metal modification. After double modification, Cu loading was reduced to 1.09% and Ni loading reduced to 0.0019%. It can be seen that the metal loading is higher in presence of Cu, both in CFP-450 and SRCx. In CFP-450, the double modification with Ni and Cu impregnation had the maximum metal loading, while in SRCx, the single modification with Cu showed the maximum metal loading. It may be possible that oxidized carbon surfaces of CFP-450 (prepared by phosphoric acid oxidation) and SRCx which are capable to exchange more favorable with Cu ions present in the aqueous solution which resulted in better retention of Cu species on carbon surfaces of CFP-450 and SRCx. Also, Ni^{2+}(aq) can be considered to be more weakly adsorbed species and is likely to be displaced by Cu^{2+}(aq) as concentration of the solution increases[36].

In the case of double metal modifications, Ni doping was carried out prior to Cu loading. As a result, some of Ni on the surface gets displaced during double metal modification. From the MP-AES analysis, it is evident that in double metal modification, individual metal loading gets reduced as compared to single metal modification, though the combined/total metal loading on the surface was higher than single loading.

Structural properties of the adsorbents were evaluated by nitrogen adsorption and desorption isotherms and the results are given in Table 4.3. Surface areas of TAC, SRCx and CFP-450 were found to be 1300m^2/g, 1098m^2/g and 1113m^2/g, respectively. Reproducibility of nitrogen adsorption was checked thrice and variation was found within ± 3%. After Zn and Co modification on the surface of the TAC, reduction in the surface area of the adsorbent was observed. A reduction of ~ 34 % in the surface area from 1300 to 861m^2/g in TAC-Zn and ~2.5 % reduction corresponding to 1267 m^2/g, in TAC-Co was observed. Most of the nitrogen adsorption occurred at a relatively low pressure below 0.2 and plateau is reached at high pressure, particularly in the case of TAC-Co, indicating the increase in micro porosity with Co modification. However, Zn modification did not result in similar increase in micro porosity. Single and double metal modification by Ni and Cu generally reduces the surface area except for TAC-Cu. In the case of metal modification in SRCx and CFP-450, there is consistent reduction in the surface area for all single and double metal modifications that can be attributed to physical blocking of the pores due to presence of metals.

X-ray diffraction profiles (Fig. 4.4) of TAC and CFP-450 exhibited similar broad peak at around 24°. However, TAC showed additional sharp peaks at 2θ positions of 31°, 35° and 37° with residual peaks around 63°. TAC surface contains appreciable amount of copper and chromium, which was observed in the form of oxides at 2θ values of 36° and 37°. From the XRD pattern and SEM-EDX results of TAC, it was observed that there was significant presence of Cu (15.3%) and Cr (7.1%) in TAC. XRD peaks at 2θ values of 35.7° and 38.5° are characteristic of CuO[37], which is observed on the commercial sample of TAC and modified TAC, with the degree of crystallinity being more in TAC-Cu as evident from the sharper and intense peak corresponding to CuO at these positions. The diffractions patterns are also similar for the double modified TAC-Ni-Cu but of very low intensity. The peaks corresponding to Cu^{2+} ions are broader and of lower intensity in the doubly modified form, TAC-Ni-Cu suggesting the presence of small Cu particles with low degree of crystallization. TAC-Zn and TAC-Co spectra show less intense peaks at similar position of 2θ like TAC. As elemental analysis shows, there is no appreciable presence of Zn and Co on TAC and comparative high concentration of acid during the modification possibly reduced its crystalline nature.

CFP-450 and SRCx showed broad peaks or humps and the absence of sharp peak indicating predominantly amorphous structure as shown in Fig. 4.4. The absence of other prominent phases was indicated by the absence of sharp peaks corresponding to oxides/minerals phases except for Si (0.34%) and Al (28.16%), which were present as trace amounts as indicated in EDX data (Table 4.1). It also implied that Al and Si present in the modified adsorbent were well dispersed in the carbon matrix of SRCx and its metal functionalized forms[34]. Diffraction peaks belonging to SiO_2 at 20.8 and 26.7 (JCPDs 46-1045) were diffused in the

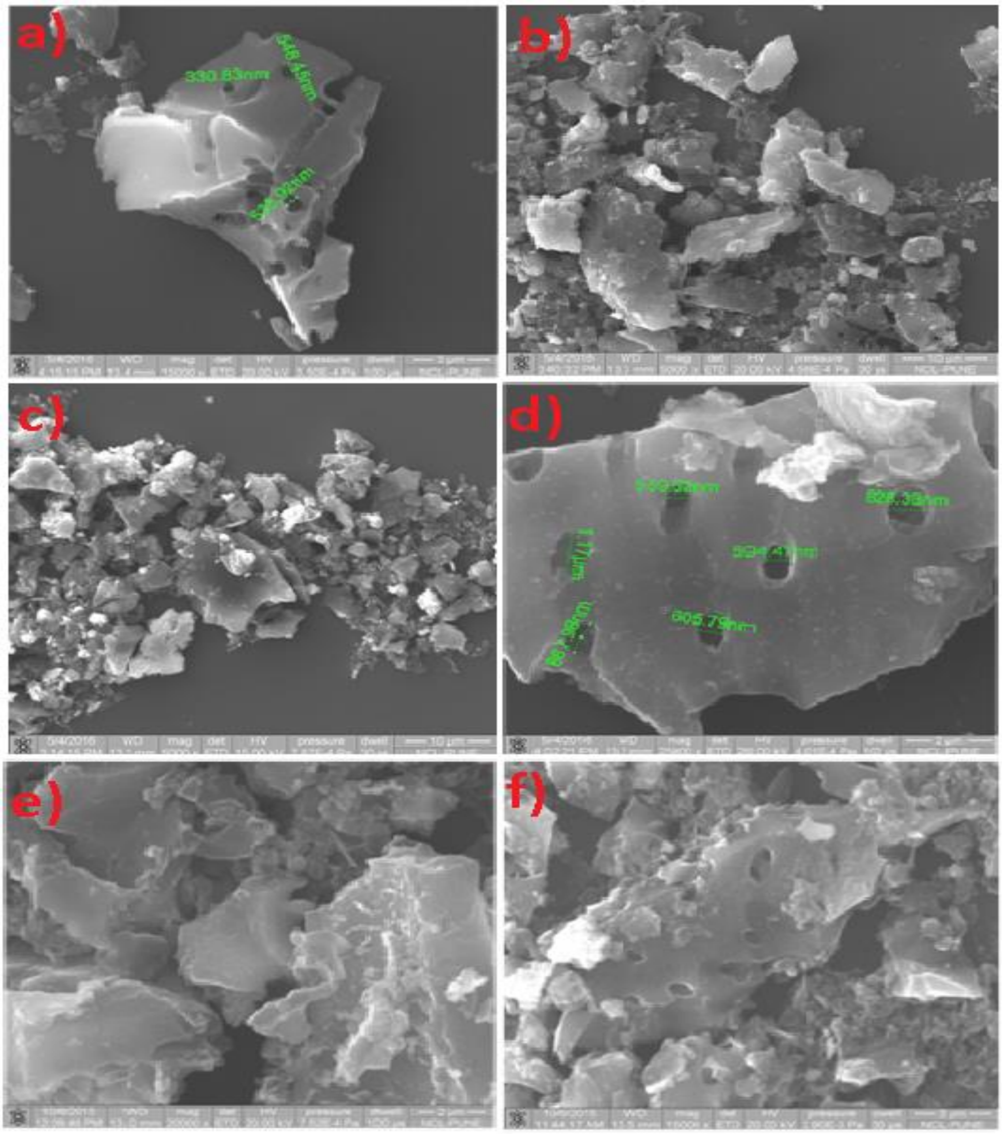


Figure 4.1: E-SEM images (a) TAC (b) TAC-Ni (c) TAC-Cu (d) TAC-Ni-Cu (e) TAC-Zn (f) TAC-Co

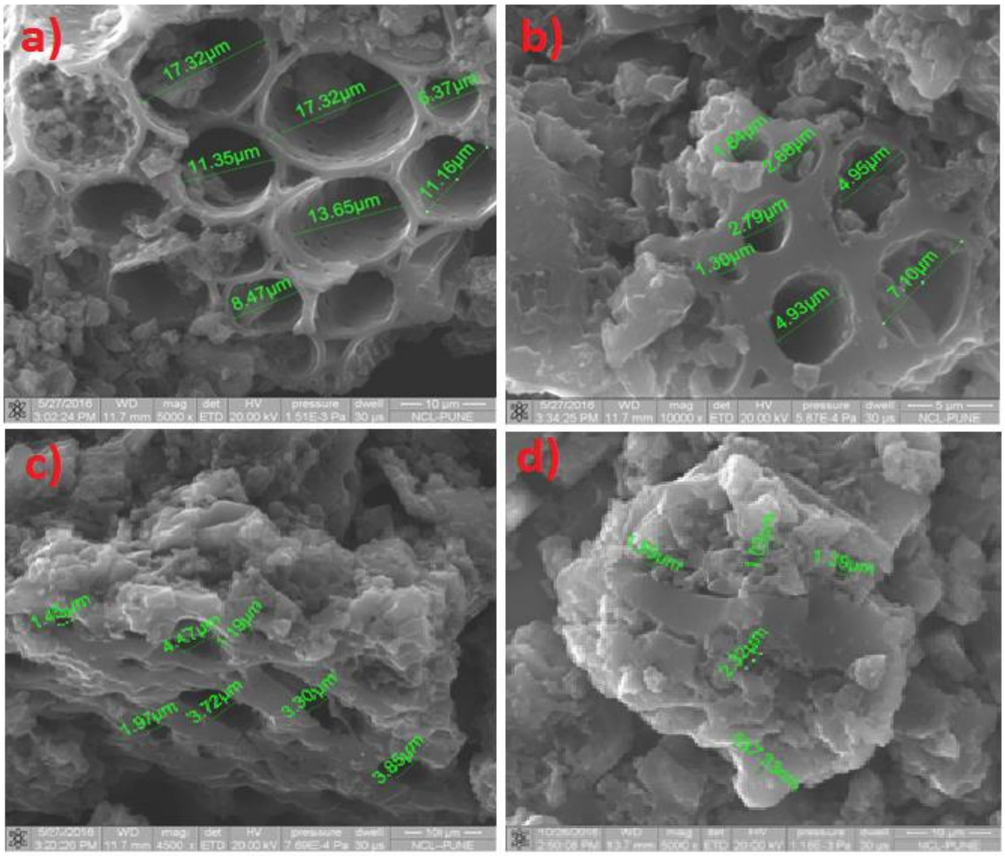


Figure 4.2: E-SEM images (a) SRCx (b) SRCx-Ni (c) SRCx-Cu (d) SRCx-Ni-Cu

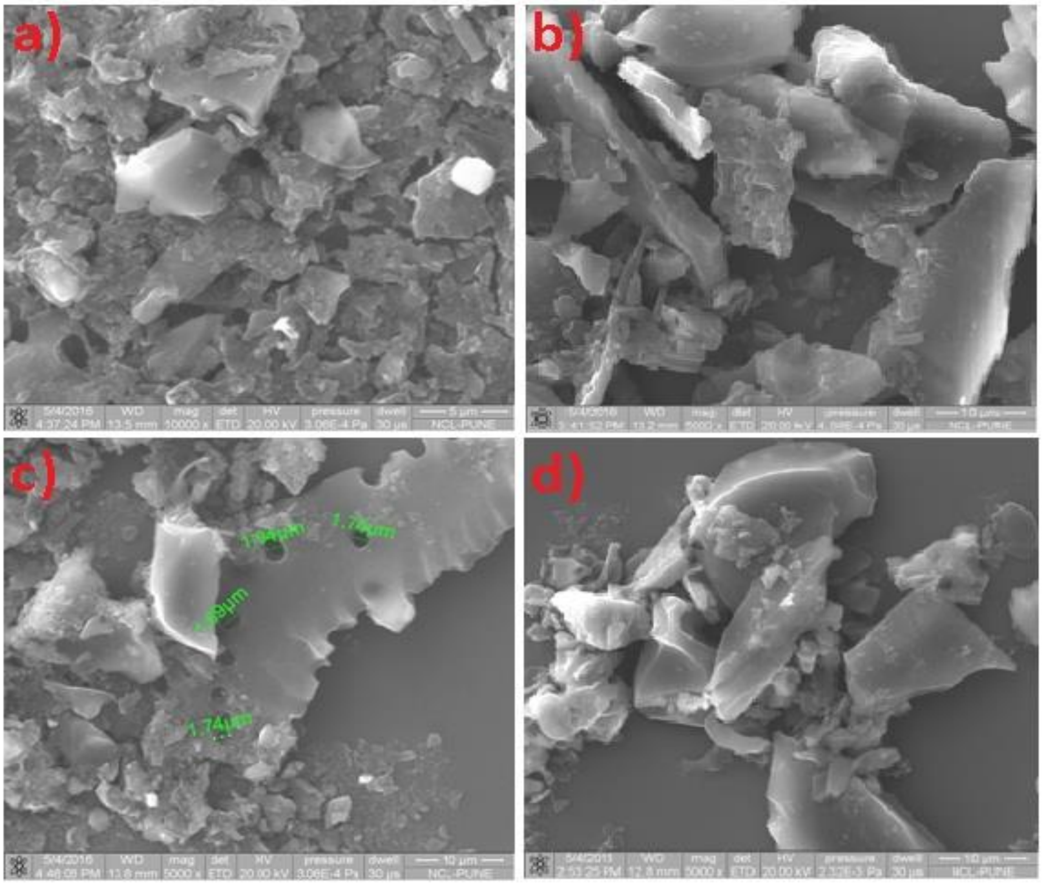


Figure 4.3: E-SEM images (a) CFP-450 (b) CFP-450-Ni (c) CFP-450-Cu (d) CFP-450-Ni-Cu

Table 4.2: Elemental composition of commercial and modified adsorbents from EDX data

Adsorbent	Element (wt. %)									
	C	**O**	**Cu**	**Cr**	**Ni**	**Zn**	**P**	**Co**	**Si**	**Al**
TAC	53.0	22.2	15.3	7.1	0	2.2	0	0	0	0
TAC-Ni	58.2	20.6	12.6	5.5	1.5	1.5	0	0	0	0
TAC-Cu	60.7	19.9	13.1	4.1	0	1.4	0	0	0	0
TAC-Ni-Cu	59.4	22.5	10.8	5.3	0.6	1.1	0	0	0	0
TAC-Zn	29.4	19.1	6.1	5.9	0	14.2	0	0	0	0
TAC-Co	61.3	34.2	1.6	0.6	0	0	0	1	0	0
SRCx	74.7	15.5	1.85	0	0	0	0	0	0.33	1.84
SRCx-Ni	71.6	19.7	2.13	0	2.13	0	0	0	0.3	0.29
SRCx-Cu	76.7	15.8	2.82	0	1.37	0	0	0	0.29	0.25
SRCx-Ni-Cu	74.8	16.7	3.32	0	1.16	0	0	0	0.29	0.32
CFP-450	56.2	40.0	0	0	0	0	3.2	0	0	0
CFP-450-Ni	60.5	36.5	0	0	1.7	0	0.8	0	0	0
CFP-450-Cu	58.2	35.6	4.7	0	0	0	1.2	0	0	0
CFP450-Ni-Cu	58.0	36.9	3.8	0	0.5	0	0.5	0	0	0

Table 4.3: Surface area and porosity of the modified adsorbents

Adsorbent	**BET Surface area (m^2. g^{-1})**	**Total pore volume (cm^3.g^{-1})**	**Micropore Volume (cm^3.g^{-1})**	**Average Pore Diameter (nm)**
TAC	1300	0.90	0.66	2.88
TAC-Ni	779	0.46	0.43	2.40
TAC-Cu	1320	0.82	0.68	2.49
TAC-Ni-Cu	824	0.50	0.45	2.42
TAC-Zn	861	0.64	0.44	3.01
TAC-Co	1267	0.74	0.63	2.45
SRCx	1098	0.71	0.552	2.58
SRCx-Ni	868.95	0.51	0.53	1.20
SRCx-Cu	876.41	0.52	0.54	1.18
SRCx-Ni-Cu	906.71	0.53	0.52	1.17
CFP-450	1113	0.14	0.15	2.01
CFP-450-Ni	379	0.20	0.21	2.13
CFP-450-Cu	352	0.18	0.20	2.14
CFP-450-Ni-Cu	355	0.18	0.20	2.13

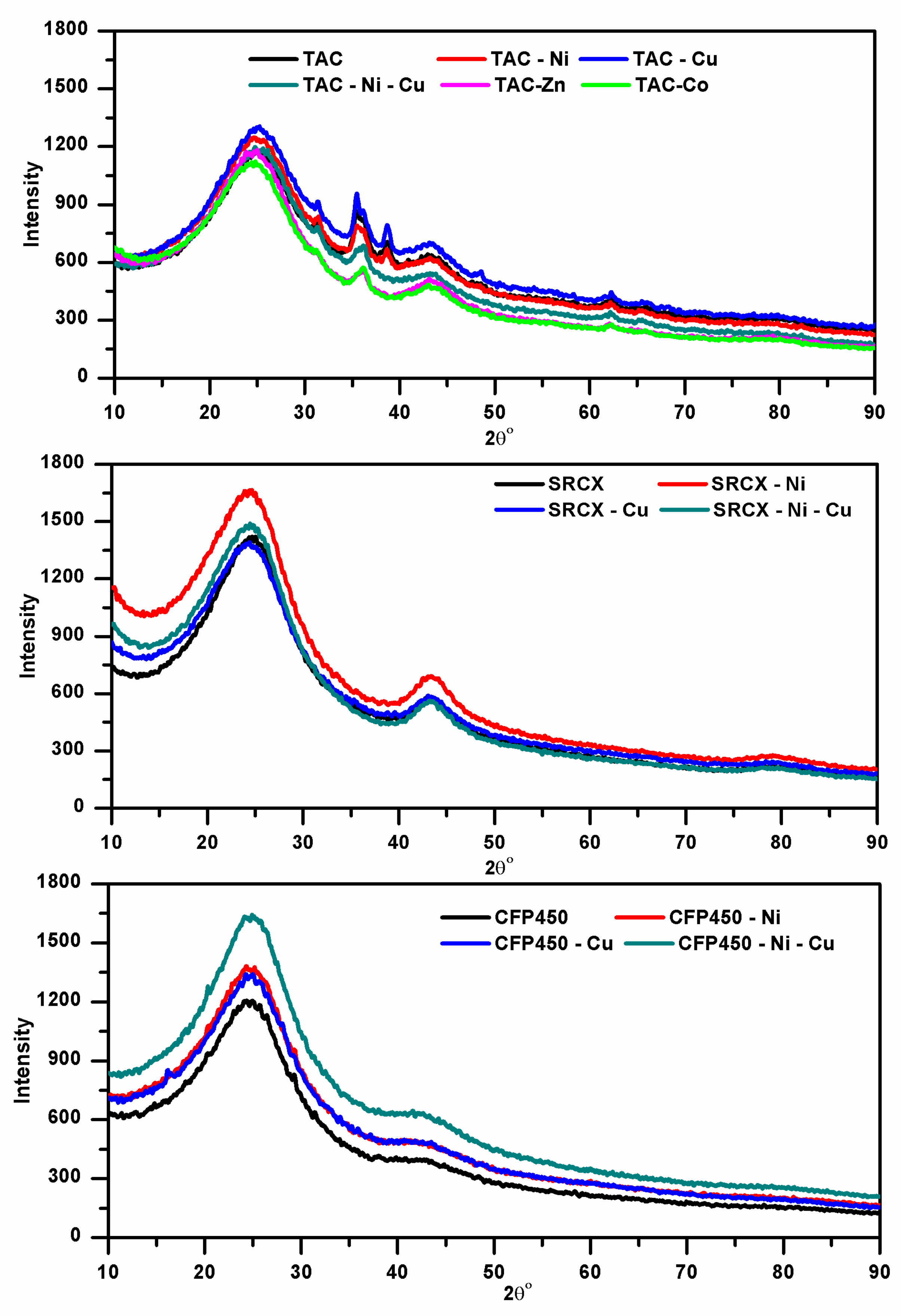


Figure 4.4: XRD pattern of the modified adsorbents: TAC, SRCx and CFP-450

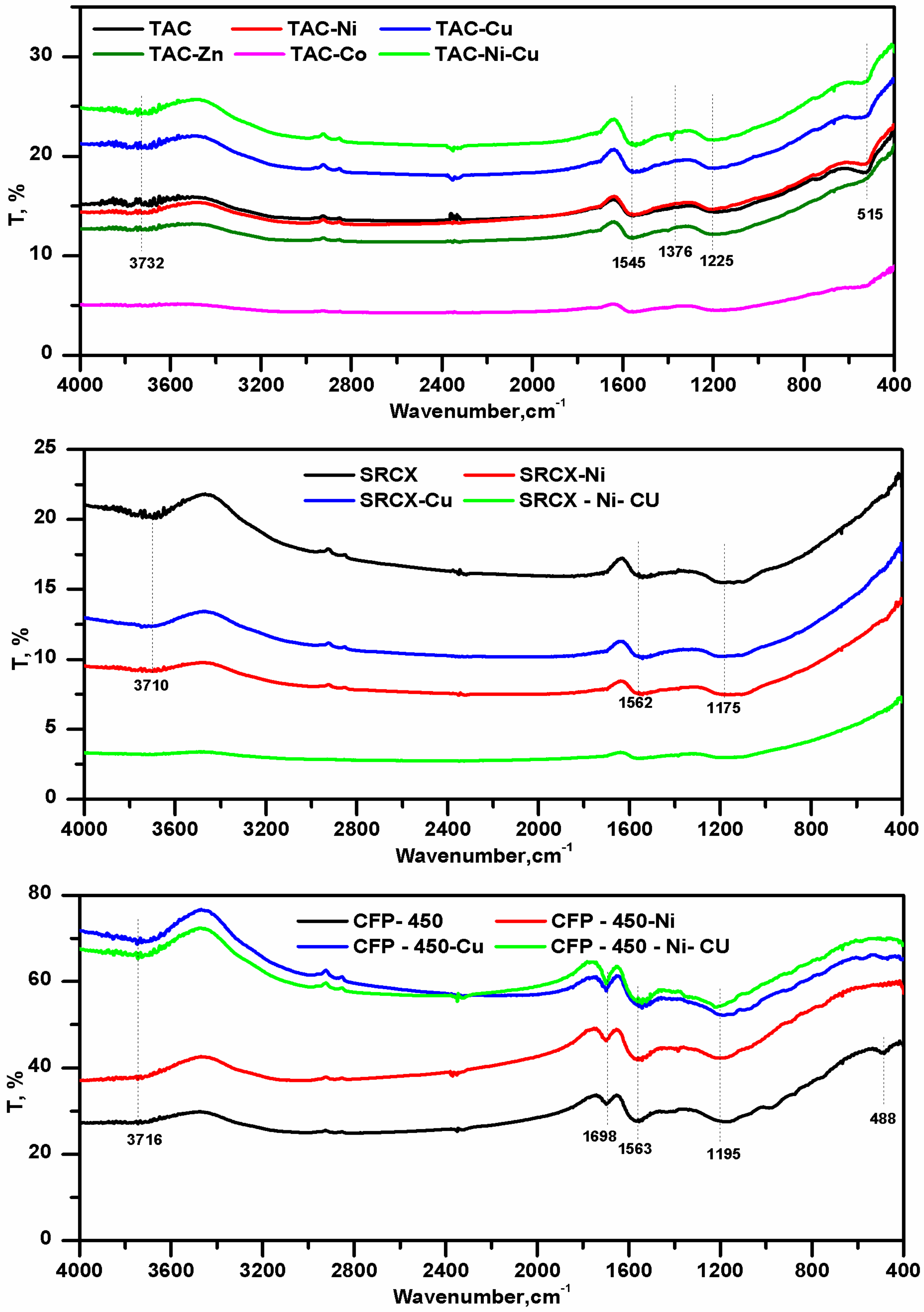


Figure 4.5: FTIR spectra of the modified carbon adsorbents: TAC, SRCx and CFP-450

broad peaks of activated carbon. The lower content and more dispersed nature of Si and Al are also responsible for the absence of prominent peaks associated with these metals.

The XRD spectrum of CFP-450 and its subsequent metal modification indicated presence of hump at 24.25° and 44.7° relating to the graphite like structure of activated carbons. The broad peak is an indication of amorphous nature of the carbon surface and possible increase in crystallinity can be visualized with rising height of the peak with Ni and Cu loading. The increase in metal loading with double modification in CFP-450-Ni-Cu is evident with the maximum peak intensity which is also in agreement with the MP-AES data showing maximum metal loading with double modification. However, the presence of these metals and their respective peak could not be clearly identified in the XRD spectra of the single or double metal (Ni/Cu or Ni-Cu) modified CFP-450 indicating the possibility of highly dispersed Ni/Cu on CFP-450 surface without formation of large aggregates.

FTIR spectra of the CFP-450, commercial TAC, SRCx and modified carbons of TAC, SRCx and CFP-450 are given in Fig. 4.5. In these adsorbents, broad peak is observed at 3700 cm^{-1} which indicate the presence of OH group on the surface of the adsorbent. The peak near 1563 cm^{-1} in CFP-450 and SRCx and their modified forms may be ascribed to (COO-) stretching vibrations which indicated the presence of oxygen containing functional group as a result of chemical activation[19]. The peaks around 1175-1195 cm^{-1} in CFP-450 and SRCx may be considering C-C functional groups and at 1698 cm^{-1} in CFP-450 and metal modified forms may be attributed to the stretching vibration of C=O respectively[19]. Again, these acidic functional groups could have been a result of chemical treatment which led to oxidized acidic groups. The presence of amide functionality can be confirmed in TAC and metal modified forms from the peak at 1545 cm^{-1}. The broad band centered at 1225 cm^{-1} in TAC and its modified forms may be ascribed to acetate like vibrations.

4.3.2 Adsorptive deep desulfurization of fuels

4.3.2.1 Effect of metal modification/impregnation

Deep desulfurization experiments were carried out to evaluate the effect of metal loading on the performance of desulfurization of transportation fuels. The adsorption equilibrium for sulfur compounds T, BT, and DBT on TAC, SRCx and CFP-450 adsorbents are shown in

Fig.4.6, 4.7 and 4.8 respectively for sulfur concentrations up to 500 ppm. Uncertainty estimation for the adsorption isotherms is predicted by standard deviation in adsorption equilibrium capacity. Standard deviation error bars are shown for the representative data sets of thiophene and dibenzothiophene for TAC and CFP-450 in Fig 4.6 and 4.8. Maximum standard deviations for sulfur compounds were obtained below 1.75ppm.

It was observed that the modified adsorbents have a good capacity for refractory sulfur compound, in general, and DBT in particular. An adsorption capacity of ~2, 12 and 23mgS/g of the adsorbent was obtained for T, BT and DBT respectively using TAC as an adsorbent (Fig. 4.6). The capacity observed with the activated carbon - Shirasagi TAC is significantly higher than most of the carbonaceous activated carbons or zeolites reported, though some zeolites with Ni modification may show up to 41mgS/g[2]. Further, it is interesting to note that the extent of sulfur removal improves as the refractory nature or molecular weight of sulfur compound increases.

Fig. 4.9 shows the selectivity difference of sulfur compounds in model diesel comprising mixture of sulfur compounds (thiophene, benzothiophene and dibenzothiophene; Initial S concentration of 100 ppm, and equal S concentration of each component). The selectivity difference is quite large and the observed higher capacity for DBT is particularly significant since the commercial fuels have higher concentrations of the refractory sulfur compounds (DBT in the present case) than thiophene. The order of selectivity for TAC was:

thiophene < benzothiophene < dibenzothiophene

The single component adsorption and adsorption in mixture was found to be consistent and even at lower total sulfur concentration, the selectivity for dibenzothiophene was the highest, indicating practically complete removal of the refractory sulfur compounds. Similar trend for selectivity was also reported by Saleh and co-workers and it was believed that the double benzene ring in DBT increases the probability of adsorption on the active sites of carbon due to the dispersive interaction between delocalized π electrons within the benzene rings of DBT and electron rich region of the aromatics ring of the carbons[38]. The removal of benzothiophene gets suppressed to some extent in the mixture probably due to higher selectivity for DBT. The large variation in the selectivity clearly highlights the fact that it is not just sulfur specific adsorbent that is required in desulfurization, but it also needs to have high selectivity towards specific sulfur compounds of interest. Thus, even when TAC has apparently good sulfur removal capacity, in case of only thiophene sulfur, it may not be a good adsorbent.

The mechanism of carbon modification using metal addition can be quite complex. The basic objective is to promote removal of slightly polar, negatively charged sulfur moiety through electrostatic interactions of positively charge bearing metal species. The nature of these associations can be π-complexation, by Yang et al.,2003 or stronger bonding as suggested by Bhandari et al.[1,2]. Knowing well from the literature reports that these types of interactions with various metals such as Ag, Ni, Co, Zn, Cu can increase the adsorption capacity and therefore sulfur removal, to what extent a metal can be loaded on carbon adsorbent is still a question difficult to answer since higher incorporation of metals have not proportionately enhanced the capacity of the modified adsorbents, no matter which metal is used. The modification philosophy is schematically explained in Fig. 4.10. Some metals are more favorable on the carbon supports which correspondingly affect the aggregation and dispersion. Thus, nature of carbon, nature of metal, structure of porous matrix, surface area available for modification, metal-metal interactions in multiple metal modifications, repulsive forces due to similar charges and its impact on subsequent metal modifications, partial displacement of one metal by another on the basis of affinity grading and such many complexities associated with metal modification of carbons have posed serious limitations in *a priori* prediction of metal modifications and its impact on desulfurization. As a consequence, experimental investigations have become imperative for gaining more insight.

A closer analysis of the improvements and useful insight could be obtained using the comparison of various metal effects, presented in Fig. 4.11. An improvement in the sulfur removal was seen in both TAC-Co and TAC-Zn modification. This, however, is believed to be mainly because of acid modification of the surface rather than metal modification since the metal content in these adsorbents was not high. Interestingly, compared to other sulfur compounds, a very high increase in thiophene adsorption was obtained for Zn (~15%) and Co (~30%) modified TAC at 0.5 % loading (Fig. 4.11a). As can be seen from the equilibrium data, the removal of thiophene was found to be more difficult and only up to 30% removal was possible for higher adsorbent loading of 7.5% as compared to near complete removal for other refractory compounds. There is a relatively higher sulfur removal of benzothiophene and dibenzothiophene (~80 % removal of BT and ~92 % removal of DBT at 7.5 % loading) with or without metal modification in case of TAC. The negligible impact of metal modification (Zn and Co) of TAC for the removal of BT and DBT can be attributed to high capacity for these refractory compounds. Further low loading of Zn and Co on TAC can be attributed to prior presence of other metals as seen from EDX data which reduces probability for additional metal modification. Effect of metal modification was more prominent in thiophene removal.

In order to attempt an increased loading of metals, certain changes in the preparatory method of metal impregnation were explored by changing the transition metals from Zn and Co to Ni and Cu, and concentration of the acidic medium. There was, however, no significant increase in the adsorption capacity for single metal modified forms such as Ni and Cu on TAC (Fig 4.6) and the capacities obtained were - thiophene from 1.8 to 2.5mgS/g; BT similar capacity in the range of 9 to 12 mgS/g and for DBT only slight increase up to 25mgS/g. This is consistent with the reasoning given above for the TAC which appears to be already functionalized/modified adsorbent for specific sulfur removal and further modification with such sulfur specific commercial adsorbents may be difficult. These observations are also consistent with the reported literature on sulfur removal using single metal modified commercial adsorbents such as GH2x and SRCx[34]. Recently Thaligari et al.[39] reported a capacity of 14.4 mgS/g for Zn modified commercial granular activated carbon (2% Zn loading, w/w). Moosavi et al.[40] reported that for 4-6 DMDBT, capacity could be increased upto 23mgS/g, using Cu^+ modification of activated carbon fiber. Thus, the limited literature on this subject demand systematic evaluation of the impact of metal modification using indigenously synthesized activated carbons and also possible double metal modification. Ni+ Cu combine double modification of TAC showed a notable difference only in DBT adsorption where significant increase in the capacity from 23 to 32 mg/g of S was obtained. From the above analysis, it is evident that modification of carbons using Zn and Co addition in matrix improves the removal and the nature of sulfur compounds affects the removal behaviour largely due to increased bonding with slightly polar sulfur.

The values of equilibrium capacity for SRCX were 5, 14.8 and 22mgS/g, for T, BT and DBT respectively. The selectivity difference is quite large and the high capacity for DBT is particularly important since commercial fuels have higher concentrations of refractory sulfur compounds than thiophene. It was observed that effect of metal modification is more pronounced for dibenzothiophene adsorption on SRCx. It is clear from the adsorption isotherm

(Fig. 4.7) that the adsorption capacity was improved from 20 to 34mgS/g as result of Ni modification on SRCx. The order of improvement follows

SRCx-Ni > SRCx > SRCx-Ni-Cu > SRCx-Cu.

The results are in agreement with the earlier report[36] where Cu modified forms of SRCx did not show significant improvement in the removal capacity. Sulfur adsorption capacity for thiophene and benzothiophene can be seen to be affected after metal modification. The amounts of sulfur adsorbed at lower concentrations of initial sulfur was low for metal modified forms, however there was significant improvement in adsorption capacity with increasing initial concentration.

It is instructive to evaluate these effects on laboratory synthesized activated carbon, CFP-450 which was prepared using the method described elsewhere[19]. The carbon was derived from the whole fruit of Golden shower tree (*Cassia fistula*). The prepared carbon, CFP-450 was further modified by Ni and Cu loading by wet impregnation method as described above. The adsorption capacities of CFP-450 (Fig. 4.8) for T, BT and DBT were ~2.5, 6.2and 12.7mgS/g, respectively. A possible increase in thiophene adsorption can be observed with single metal modification of CFP-450 by Cu and Ni, which can be further improved by using the double modification. For benzothiophene, single metal modification showed only marginal improvement, however, the improvement with double modification was significant. In fact, for thiophene and benzothiophene, ~100% improvement was observed after double metal modification. For DBT, interestingly single metal modifications of Cu and Ni were highly effective in increasing the sulfur removal capacity; however, the double metal modification here actually resulted in the reduction in the sulfur removal capacity as compared to unmodified as well and single metal modified carbons. This contradiction in the sulfur removal behaviour only in the case of DBT can be attributed partly to the steric effect that result in reduced access to DBT due to double metal loading.

The studies on the commercial sulfur specific adsorbent, laboratory synthesized biomass derived newer sulfur specific adsorbent, single metal modifications and double metal modifications along with the sulfur removal studies on three different sulfur compounds (T, BT and DBT) strengthen some of the findings reported in the literature, especially on the sulfur removal by sulfur specific adsorbents and provide newer insight into the sulfur removal

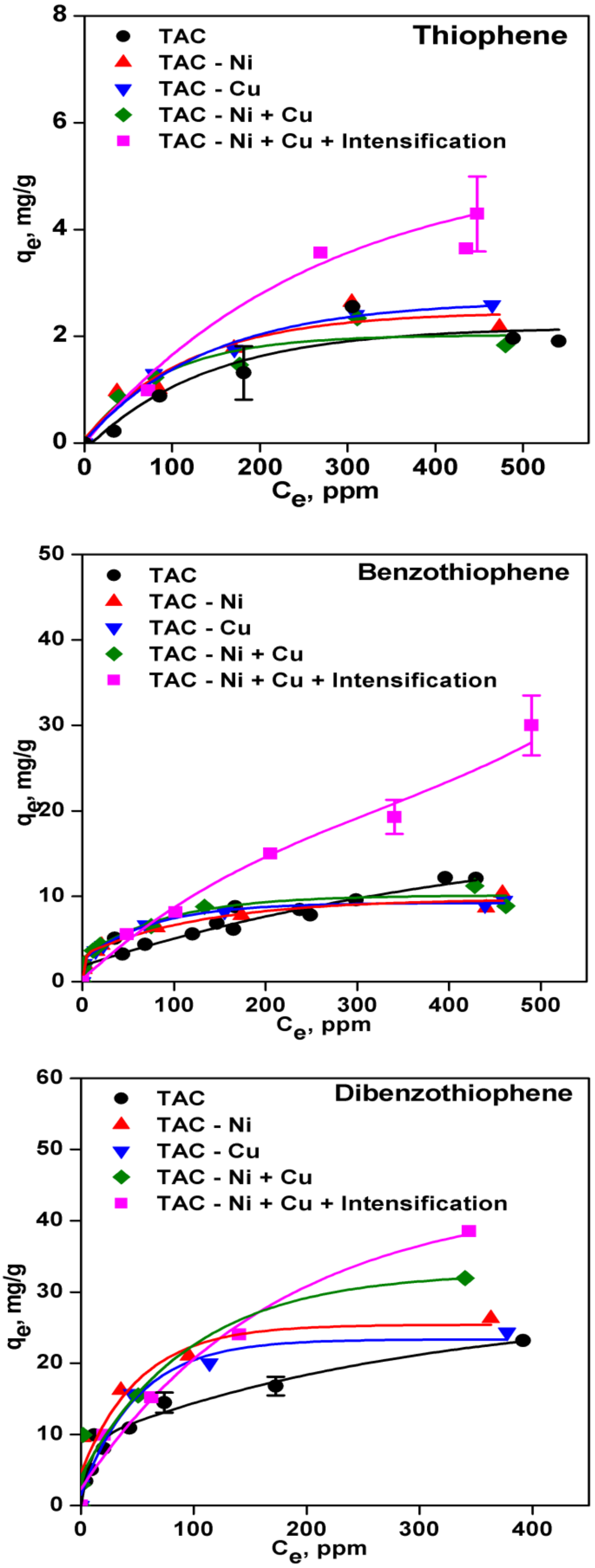


Figure 4.6: Adsorption isotherms: Effect of metal modification and intensification on TAC

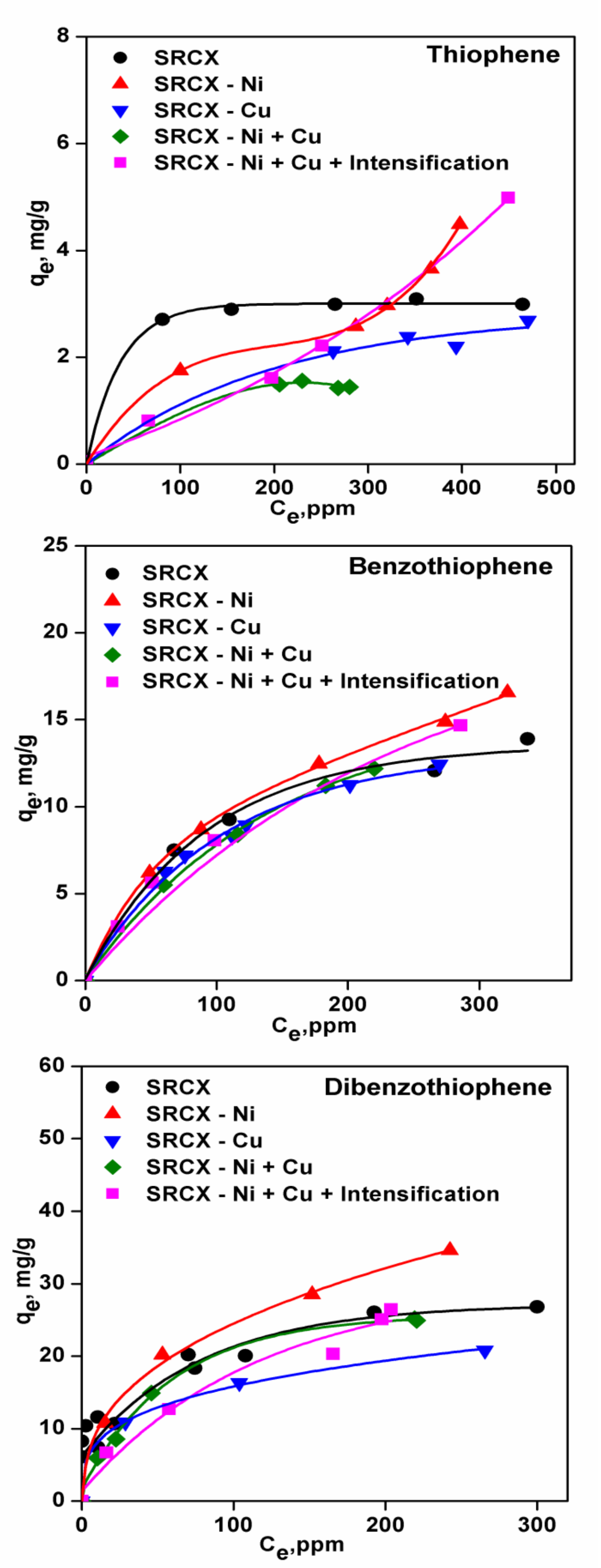


Figure 4.7: Adsorption isotherms: Effect of metal modification and intensification on SRCx

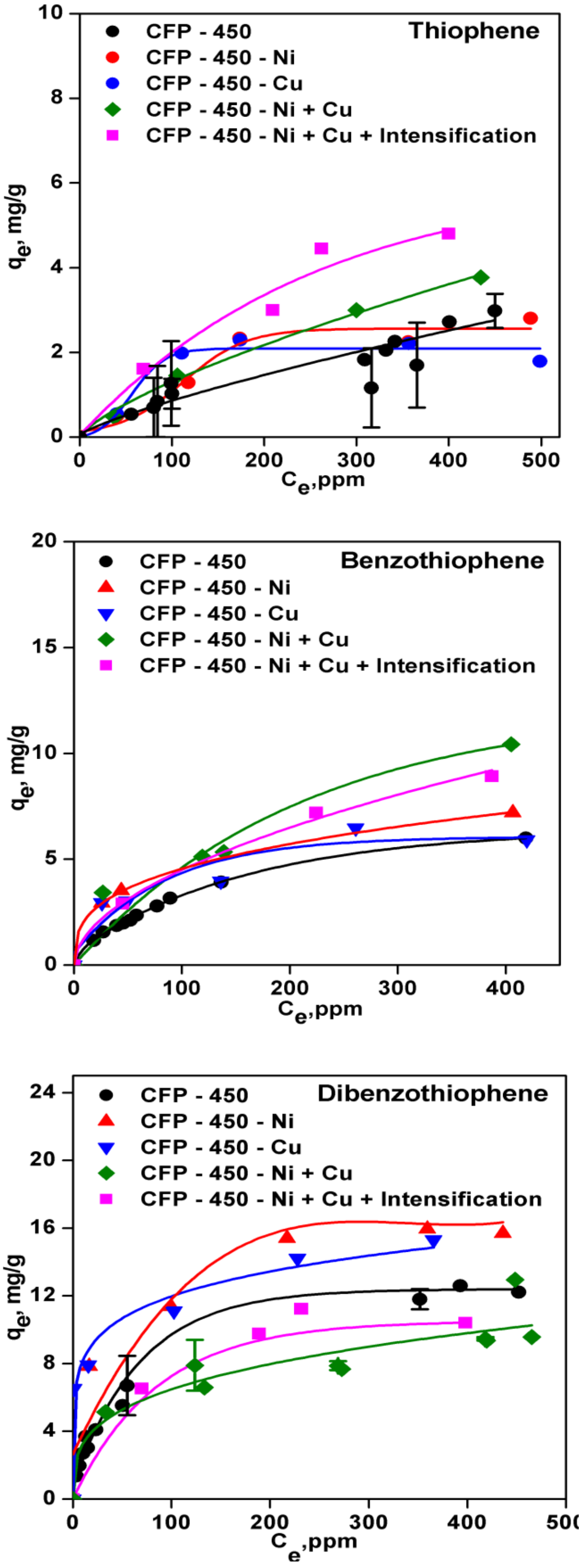


Figure 4.8: Adsorption isotherms: Effect of metal modification and intensification on CFP-450

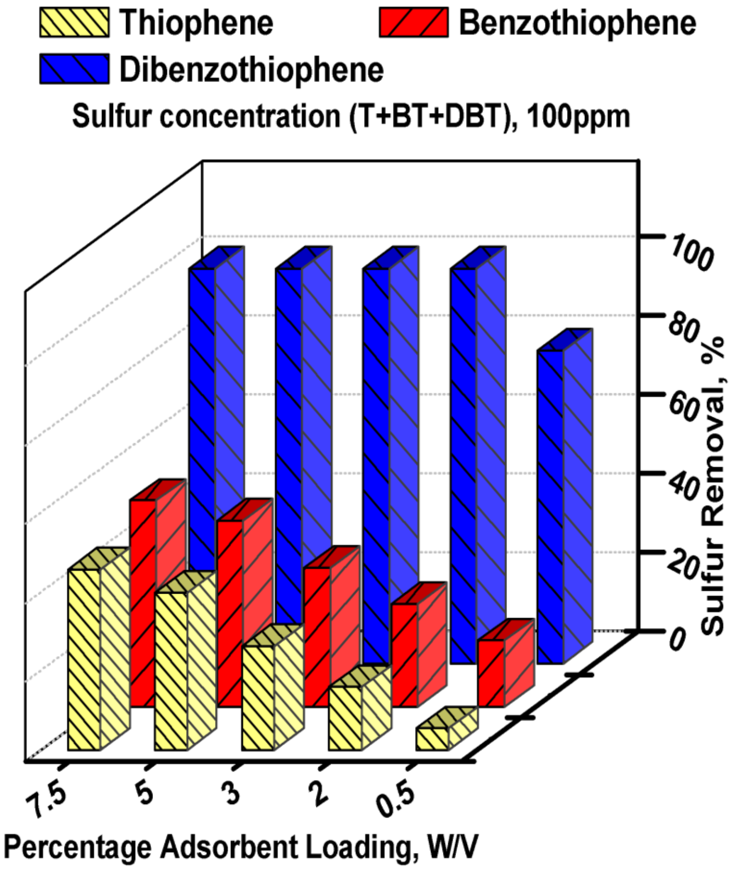


Figure 4.9: Sulfur removal on TAC: Selectivity in mixture

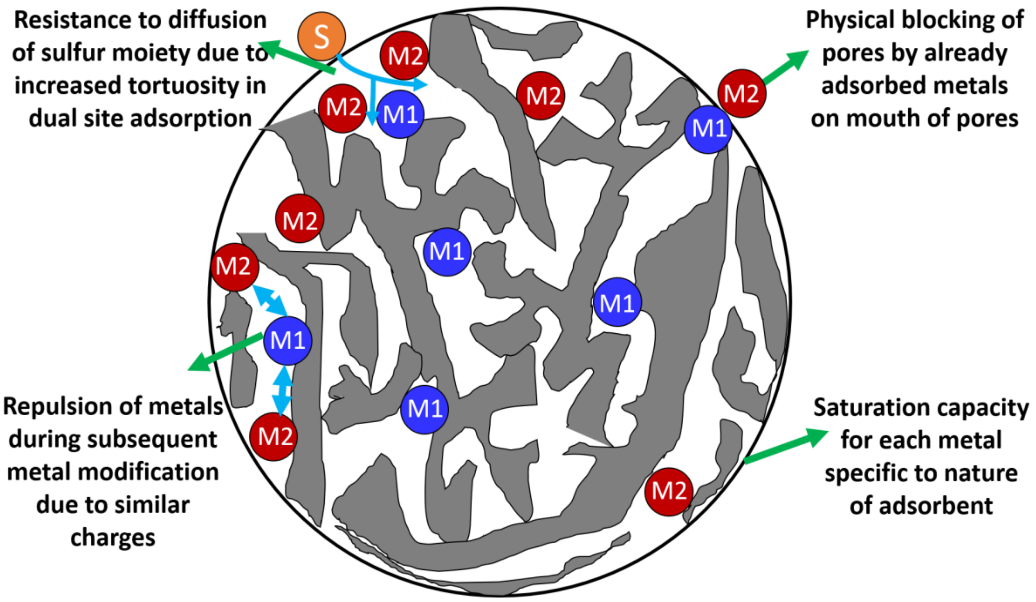


Figure 4.10: Schematic of metal modification of adsorbents and impact on sulfur removal

behavior by single and double metal modifications. The study also provides insight into the selectivity behavior for different sulfur compounds which varies widely depending on the nature of the sulfur compounds - more refractory compounds (BT and DBT) being preferred over thiophene, which is in accordance to that observed for oxidation reactions[41].

4.3.2.2 Effect of process intensification using acoustic cavitation/ultra-sonication

It is expected that the cavitation process can alter the adsorption behaviour either through disintegration of larger molecules to smaller fragments or through surface modification/pore opening to facilitate the adsorption process. Ultrasound assisted oxidative desulfurization has been widely reported for desulfurization of fuels. In order to exploit the molecular level changes due to cavitation, the influence of acoustic cavitation on adsorptive desulfurization using metal modified adsorbents was investigated, as a proof of concept, for the two sulfur specific adsorbents, commercial/modified Shirasagi TAC, SRCx and laboratory synthesized adsorbent (CFP-450). Adsorption with acoustic cavitation was carried out, essentially at ambient conditions, for 30 min using ultrasound power of 250W. The results of the process intensification are presented in Fig. 4.12, and overall comparison of this effect is also provided in Fig. 4.6, 4.7 and 4.8. Representative standard deviation error bars for intensification results are shown in Fig 4.6. The impact of process intensification is highest with thiophene, which otherwise has low selectivity compared to BT and DBT. An improvement of close to 100%can be obtained for thiophene removal. The effect of intensification for the adsorption of BT and DBT was marginal, largely due to the fact that there is high selectivity for these even in conventional adsorption. The impact due to cavitation is both physical and chemical. Primarily, the physico-chemical changes occur due to the generation of intense temperature (~10,000K) and pressure (~1000atm) conditions at pico-scale as a result of implosion of cavities in the cavitation process, that subsequently can cleave the molecules or impact pore diffusion/surface adsorption[42]. The effects of acoustic cavitation have been exploited extensively in catalytic oxidative desulfurization processes that typically employ acid catalysts and sulfones that are formed in the process get extracted in suitable solvent such as water. It is evident that the mechanism of intensified adsorption process presented in this work is quite different from the catalytic oxidative desulfurization process though both employ acoustic cavitation. Ultrasound is reported to improve mixing and adsorption capacity through cavitation and streaming[43]. In addition, enhanced adsorption was also reported as result of changes in pore transport, increase in pore volume and surface area due to acoustic cavitation[44]. It is instructive to

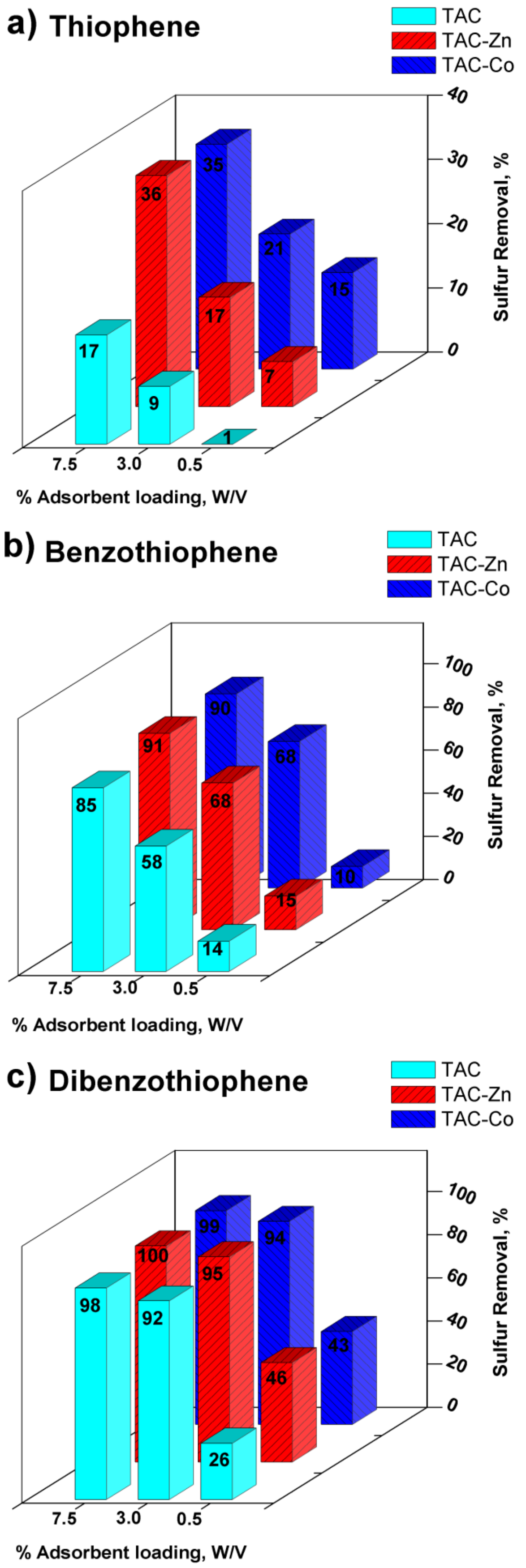
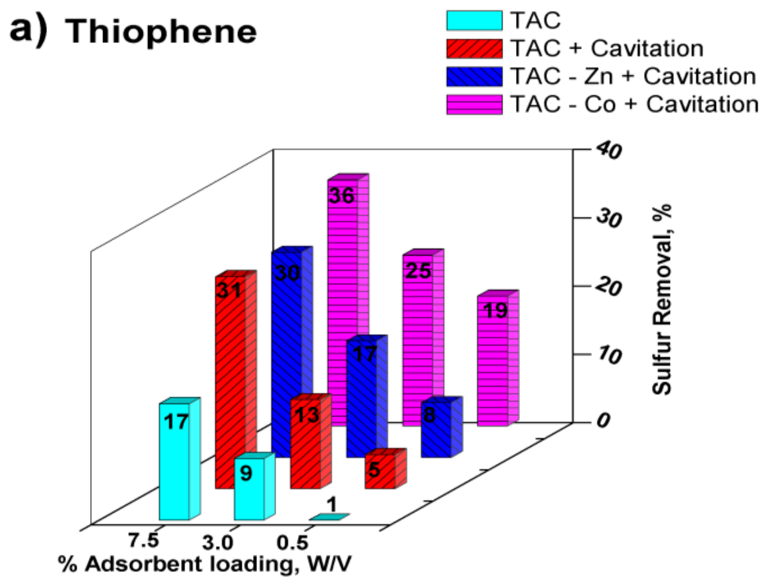
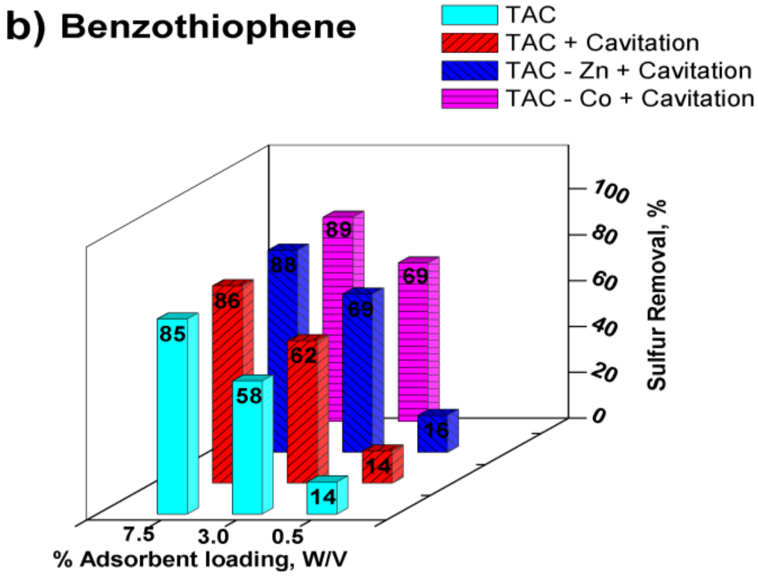


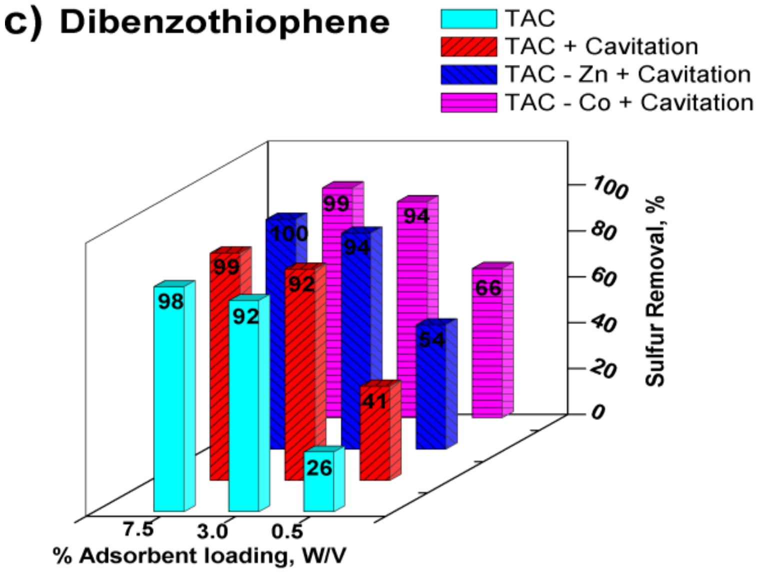
Figure 4.11: Comparison of metal modification on TAC for sulfur removal



a) Thiophene



b) Benzothiophene



c) Dibenzothiophene

Figure 4.12: Effect of metal modification and intensification for TAC

evaluate the effect of intensification for metal modified adsorbents as well. The studies on Zn and Co modified commercial TAC showed appreciable effect of intensification mainly for TAC-Co again in the case of thiophene removal (Fig. 4.12). It may be noted that, metal modification reduced the surface area but at the same time increases the acidic oxygen functional groups on the carbon surface (Table 4.2 and 4.3). In the case of double metal modification, the effect of acoustic cavitation assisted adsorption was appreciable in case of TAC-Ni-Cu for the removal of all the refractory sulfur compounds: T, BT and DBT from the model fuels (Fig. 4.6). In case of SRCx, effect of process intensification is more dominant in thiophene (Fig.4.7), while process intensification with CFP-450-Ni-Cu showed further improvement for T and BT (Fig. 4.8). The significant increase in the sulfur removal capacity can be appreciated from the fact that for TAC the adsorption capacity increased from 2 to 4.3, 12 to 31.6 and 23 to 38mgS/g for T, BT and DBT, respectively using intensified Ni-Cu double modified adsorbent. Among the various metal modifications, cobalt modification was most effective for thiophene removal and intensification further improved the sulfur removal.

4.3.3 Isotherm models

Adsorption isotherms provide valuable insight into the adsorbate- adsorbent interaction, degree of affinity of the adsorbents and nature of adsorbent surface. The adsorption equilibrium data was fitted for three different models for isotherms namely Langmuir[45], Freundlich[46] and Temkin[47] for the three adsorbents, TAC, SRCx and CFP-450. Linear form of isotherm equations (Table 4.4) were used for prediction of theoretical data. The values of regression correlation coefficient were close to unity.

Langmuir isotherm is based on assumption of monolayer adsorption on homogenous surface with definite active adsorption sites. Langmuir constant was estimated by plotting Ce versus Ce/qe. It provides information about affinity of the binding sites with adsorbates. Separation factor (R_L) in Langmuir isotherm shows favorability of adsorption process. For the values of R_L in the range 0 and 1, adsorption can be considered as favorable. R_L less than 0 indicates that infinite adsorption sites are available for adsorption while R_L greater than 1 signifies adsorption is irreversible and unfavorable. Freundlich adsorption isotherms are based on multilayer adsorption on surface with non-uniform heat distribution of adsorption on heterogenous assumes heat of adsorption decreases linearly rather than logarithmic with coverage on the surface. Parameters of this isotherm can be estimated by plotting q_e versus ln C_e. The constants, b and A_T are for the heat of adsorption and binding constant. The parameters estimated from various model isotherms are given in Table 4.5 and Figs. 4.13, 4.14 and 4.15 show fit of the data for TAC, SRCx and CFP-450, respectively. In general, SRCx showed good fit of Langmuir model for thiophene, benzothiophene and dibenzothiohene adsorption. The selectivity was highest for DBT and least for thiophene in case of all the adsorbents. The commercial adsorbents, TAC showed good fit for thiophene, benzothiophene and dibenzothiophene for all isotherm models. However, experimental data of thiophene adsorption onto CFP-450 indicated Freundlich (R^2= 0.98) and Temkin (R^2= 0.94) as the best fit models. Benzothiophene and dibenzothiophene adsorption is well explained by all three isotherm models. Langmuir isotherm model is best fit model for adsorption of all sulfur compounds on TAC, SRCx and CFP-450 except thiophene adsorption on CFP-450. The Langmuir monolayer capacities for T, BT and DBT, increase in the following order:

Thiophene - CFP-450 (no fit) < TAC (2.33mgS/g) < SRCx (3.06mgS/g)
Benzothiophene - CFP-450 (7.75mgS/g) < SRCx (14.7mgS/g) < TAC (17.21mgS/g)
Dibenzothiophene-CFP-450 (14.7mg/g) < SRCx (25.6mg/g) < TAC (28.5mg/g)

4.3.4 Regeneration of Adsorbents

Commercialization of any adsorption process depends on the regeneration ability of the adsorbent material. Generally, the regeneration of adsorbents after desulfurization has been reported using solvent elution method which is costlier and environmentally hazardous route than thermal regeneration. Table 4.6 summarizes some important results on regeneration of sulfur saturated metal modified carbon adsorbents. Successful regeneration of metal modified carbon depends on the interaction between sulfur compounds and metal and most of the studies report random selection of regeneration method and selection of operating condition without sufficient justification.

In solvent regeneration method, number of solvents such as toluene, methanol, CCl_4, DMF, methyl naphthalene, tetralin, dichloromethane, n-hexane, o-xylene, phenol, n-octanol, n-pentanol have been reported. Thermal regeneration is another route for effective regeneration and one of the study by Saleh et al., 2018 showed the evidence for regeneration of double metal modified sulfur saturated carbon adsorbent, where thermal regeneration was carried out at 330°C for 3h in an inert atmosphere under the flow of H_2. However, most of the literature studies have focused on adsorptive desulfurization and adsorbent modifications rather than regeneration, probably due to emphasis on increased capacities for the adsorbents lack of which naturally neutralizes importance of regeneration [30,33,35,48]. However, the strategies reported in the literature can be considered to be useful from application point of view for the regeneration of similar materials/adsorbents.

In view of the literature report (Table 4.6), in the present work, regeneration of sulfur saturated (BT) SHIRASAGI TAC was carried out using toluene as one representative case study. The regeneration study indicated ~ 25 ml/g solvent requirement and only 36% sulfur from BT could be eluted at ambient conditions. The results however indicate application of solvent regeneration method for the adsorbents in desulfurization.

Table 4.4: Adsorption isotherm equations

Adsorption Isotherm	**Equation**
Langmuir	$\frac{\mathrm{Ce}}{\mathrm{qe}} = \frac{1}{\mathrm{q_{max}k_L}} + \frac{\mathrm{Ce}}{\mathrm{q_{max}}}$ $\mathrm{R_L} = \frac{1}{1 + \mathrm{k_L c_0}}$
k_L- Langmuir adsorption constant	
c_e - Equilibrium concentration	
q_e - Equilibrium adsorption capacity	
q_{max} - Maximum adsorption capacity	
c_0 - Initial concentration	
Freundlich	$\mathrm{logq_e} = \mathrm{logk_F} + \frac{1}{\mathrm{n}}\mathrm{logc_e}$
k_F - Freundlich constant	
n - Heterogeneity factor	
c_e - Equilibrium concentration	
q_e - Equilibrium adsorption capacity	
Temkin	$\mathrm{q_e} = \mathrm{BlnA_T} + \mathrm{BLnC_e}$ $\mathrm{B} = \frac{\mathrm{RT}}{\mathrm{b}}$
$A_{T(L/g)}$ and B(J/mol) - Temkin constants	
A_T - Equilibrium binding constant	
R - Molar gas constant	
T - Adsorption temperature in K	
b - Constant associated with heat and adsorption	
c_e - Equilibrium concentration	
q_e - Equilibrium adsorption capacity	

Table 4.5: Values of adsorption isotherm model constants

			Langmuir				**Freundlich**			**Temkin**		
		Q_{exp}	**R^2**	**q_{max}**	**k_L**	**R_L**	**R^2**	**1/n**	**k_F**	**R^2**	**b**	**A_T**
TAC	**T**	2.1	0.99	2.33	0.009	0.14	0.98	0.30	0.28	0.96	5422	0.12
	BT	12	0.94	17.21	0.005	0.21	0.97	0.56	0.44	0.98	636	0.05
	DBT	23	0.94	28.5	0.017	0.093	0.98	0.44	2.0	0.90	493	0.30
SRCx	**T**	2.8	0.99	3.06	0.12	0.016	0.84	0.057	2.14	0.85	15588	298249
	BT	13.5	0.96	14.7	0.025	0.069	0.98	0.29	2.48	0.89	1272	1.85
	DBT	27	0.97	25.6	0.06	0.028	0.81	0.25	6.05	0.84	631	1.68
CFP-450	**T**	2	0.74	6.63	0.0014	0.36	0.98	0.75	0.025	0.94	2398	0.02
	BT	6.2	0.99	7.75	0.007	0.16	0.98	0.53	0.26	0.97	1568	0.085
	DBT	13	0.97	14.7	0.021	0.076	0.95	0.84	0.84	0.90	866	0.28

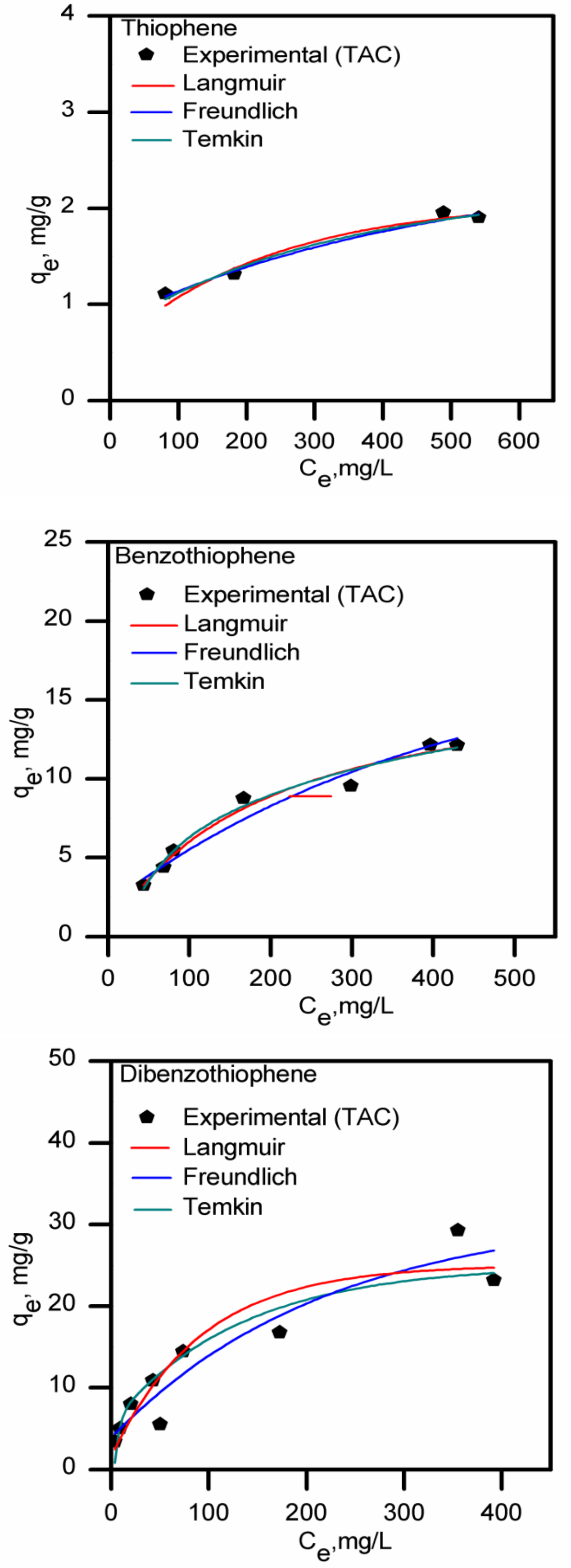


Figure 4.13: Fit of the adsorption isotherm: TAC

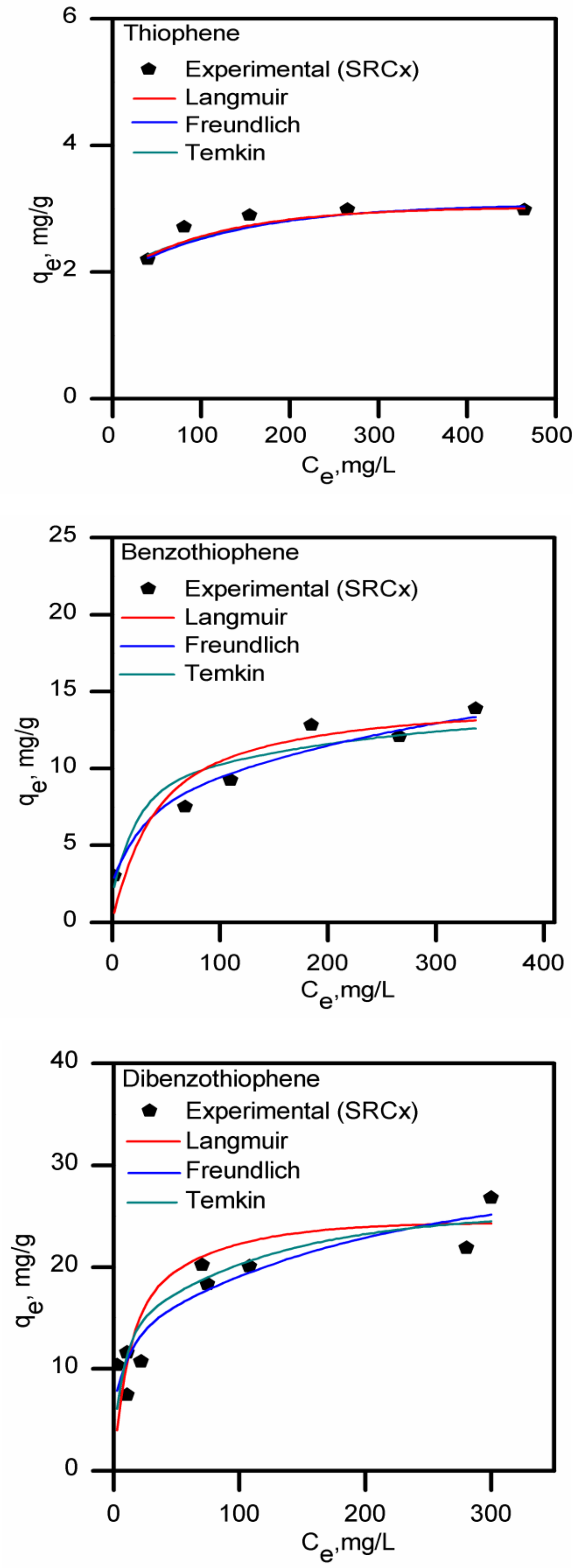


Figure 4.14: Fit of the adsorption isotherm: SRCx

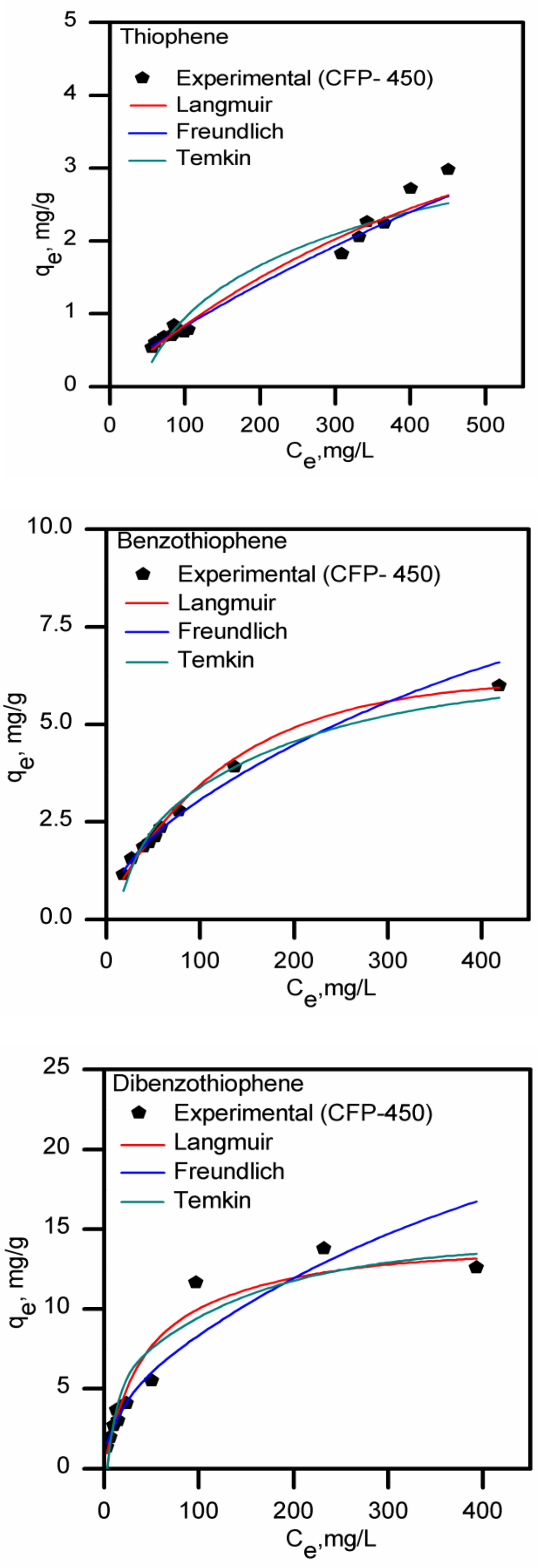


Figure 4.15: Fit of the adsorption isotherm: CFP-450

Table 4.6: Literature reports on regeneration of sulfur saturated metal modified carbon adsorbents

Metal and carbon	**System**	**Regeneration**	**Capacity, mg/g**	**Ref**
AC (Source-Rubber) Co-Cu/AC	85% hexane and 15% toluene T BT DBT MBT, MDBT 4,6-DMDBT (50ppm each)	Regenerated using 50/50 vol% methanol/toluene followed by bed heating upto 180ºC in N_2 flow (Stability upto 5 cycles)	1.84mgT/g 2.12mgBT/g 3.52mgDBT/g 2.48mgMBT/g 3.44mgMDBT/g 3.4mgDMDBT/g	[32]
AC Mn-AC2 Mn-AC4 Mn-AC6 Mn-Ac8 (numbers indicate the concentration of manganese chloride)	DBT in commercial diesel 835–11,890mg/kg	Regenerated for Mn-AC4 using n-hexane, toluene, o-xylene, phenol, n-Octanol or n-Pentanol at 65C n- hexane was better regenerate with 66.4% and 85.2% of DBT eluted at 20◦C and 65◦C, respectively	18.4mg DBT/g 25.8 mg DBT/g 43.2 mg DBT/g 41 mg DBT/g 29.6 mg DBT/g	[28]
AC-Co-Mo	T, BT, MBT, DBT, MDBT, DMDBT in hexane and toluene mixture (50ppm each)(Thermal coprecipitation method was used for metal impregnation)	Thermal regeneration method at 330ºC for 3h in an inert chamber under flow of hydrogen	2.2mgT/g 2.32mgBT/g 2.72mgMBT/g 3.68mgDBT/g 3.64mgMDBT/g 3.72mgDMDBT/g	[29]
AC ACO(oxidized) AC-Ce	DBT in petroleum ether(500ppmS) adsorption from model fuels (Classical soaking impregnation method)	Reported Regeneration using toluene (reused for three cycles)	(10.2)mgS/g 7.62(12.2)mgS/g 8.15(14.2)mgS/g	[31]

4.4 Conclusions

The present study highlights the importance of developing sulfur specific adsorbents for deep desulfurization of fuels under ambient conditions. Both, single and multiple metal modifications can be employed for increasing the sulfur removal efficiency which was found to depend on the nature of the metal and matrix used for modification. The important conclusions are:

1. Sulfur specific adsorbents, commercial Shirasagi TAC, SRCx and laboratory synthesized CFP-450 have high capacity for sulfur removal. A sulfur removal close to 100% can be obtained for refractory sulfur compounds (BT and DBT) for Shirasagi TAC carbon adsorbent.
2. Huge difference in selectivity was observed for the three sulfur compounds, thiophene, benzothiophene and dibenzothiophene, clearly highlighting the dependence on the nature of sulfur compounds. Selectivity for thiophene was lowest and near complete removal of benzothiophene and dibenzothiophene was obtained.
3. Metal modification, in general, increases sulfur removal capacity. Cobalt metal modification of the adsorbent, especially for thiophene removal, was found to be more effective than Ni, Cu and Zn. Double/multiple metal modification was also effective to a certain extent.
4. A significant increase in thiophene adsorption was observed with single metal modification of CFP-450 by Cu and Ni, which can be further improved by using the double modification.
5. Process intensification using acoustic cavitation could significantly enhance the adsorptive sulfur removal and close to 100% improvement could be obtained for thiophene removal. Modification of carbons and process intensification, combined together, can substantially improve sulfur removal.

Thus, tailoring/surface modification of carbon adsorbents along with process intensification appears to be a promising approach in adsorptive deep desulfurization of fuels.

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Chapter 5

Nalinee B. Suryawanshi, Vinay M. Bhandari, Laxmi Gayatri Sorokhaibam, and Vivek V. Ranade. *Non-catalytic Deep Desulfurization Process using Hydrodynamic Cavitation*. Scientific Reports. 6, 33021 (2016); http://doi.org/10.1038/srep33021

Chapter 5
A Non-Catalytic Deep Desulfurization Process using Hydrodynamic Cavitation

Abstract

A novel approach is developed for desulfurization of fuels or organics without use of catalyst. In this process, organic and aqueous phases are mixed in a predefined manner under ambient conditions and passed through a cavitating device. Vapor cavities formed in the cavitating device are then collapsed which generate (*in-situ*) oxidizing species which react with the sulfur moiety resulting in the removal of sulfur from the organic phase. In this work, vortex diode was used as a cavitating device. Three organic solvents (n-octane, toluene and n-octanol) containing known amount of a model sulfur compound (thiophene) up to initial concentrations of 500 ppm were used to verify the proposed method. A very high removal of sulfur content to the extent of 100% was demonstrated. The nature of organic phase and the ratio of aqueous to organic phase were found to be the most important process parameters. The results were also verified and substantiated using commercial diesel as a solvent. The developed process has great potential for deep desulfurization of various organics, in general, and for transportation fuels, in particular.

5.1 Introduction

Deep desulfurization or reducing sulfur content of various organics, in general, and transportation fuels, in particular to very low level (~10 ppm) is a demanding but essential operation, especially from pollution point of view. In the case of transportation fuels, Governments worldwide mandate sulfur concentration to the level of 15ppmw and 30ppmw in diesel and gasoline respectively[1–3]. For fuel cell applications, the sulfur levels are required to be much lower (less than 1ppmw) to avoid poisoning of the catalyst. For organics such as turpentine, removal of sulfur can be important in organic synthesis such as production of camphor.

Deep desulfurization during petroleum refining operations has been a challenge mainly due to the difficulties associated with removal of refractory sulfur compounds and also due to varying nature of compounds in different fuel fractions[4]. A catalytic process of hydrodesulfurization (HDS) commonly used in refineries, is considered as a satisfactory method for lowering sulfur content up to 350 ppm and thereafter pose limitations due to low reactivity of the remaining refractory compounds and increased cost of operation[5,6]. The conventional HDS process employs catalyst such as Co-Mo or Ni-Mo, requires high temperatures of the order of 450°C, and high pressures of the order of 20–40 atm. Employing HDS process to meet the new standards is expected to require 3 fold increase in the catalyst volume/reactor size adversely affecting economic viability apart from adversely affecting quality of fuel[4]. A number of alternative processes have been investigated which include adsorptive desulfurization[1,7–11], biodesulfurization[4,12] and oxidative desulfurization[13,14]. Adsorptive deep desulfurization appears to hold promise and a number of sorbents starting from simple activated carbons[15] to π-complexation adsorbents, where Cu-Y and Ag-Y zeolites were shown to exhibit good capacity for thiophene sulfur removal from benzene and n-octane mixtures[3,16]. Recently, a more complex process by combining oxidation and extraction has been reported–extractive and catalytic oxidative desulfurization (ECOD) that employs catalyst for oxidation and suitable extractant for removing oxidised products as an alternative to the existing HDS process[17,18]. Acid treated activated carbons have also been considered to promote oxidation in oxidative desulfurization[19].

There are some reports of using cavitation coupled with catalysts for desulfurization. Ultrasound assisted oxidative desulfurization has been discussed to a certain extent essentially in presence of various catalysts[20–23]. Jin et al. [24] reported sulfur removal in coal tar pitch by oxidation with hydrogen peroxide using trichloroacetic acid as catalyst and using ultrasound waves. A U.S. patent[25] discloses process with hydrodynamic cavitation-catalyzed oxidation of sulfur-containing substances that requires presence of at least one oxidizing agent like hydrogen peroxide. Thiophene has been considered to be one of the most difficult and refractory organic sulfur compounds in oxidative desulfurization as compared to benzothiophene and other sulfur derivatives[26,27].

In this work, we present a new process based on hydrodynamic cavitation for deep desulfurization of fuels and organics without employing any catalyst and under mild operating conditions. Thiophene was chosen as a model sulfur compound mainly due to limitation of conventional oxidation processes in its removal. We believe that the presented results demonstrate the applicability of proposed method based on hydrodynamic cavitation for sulfur removal and demonstrate its great potential for deep desulfurization of various organics, in general, and for transportation fuels, in particular.

5.1.1 The process: desulfurization using hydrodynamic cavitation with vortex diode as cavitating device

In the proposed approach, sulfur containing organic phase is mixed with water under ambient conditions and passed through a vortex diode[28]. Vapor cavities are formed in the diode and are transported to the downstream region where these cavities collapse. The cavity collapse generates localized very high pressure and temperature[29] as well as hydroxyl radicals. Interaction of hydroxyl radicals under these locally extreme conditions result in removal of sulfur from the organic phase without any catalyst under apparently ambient conditions of bulk. A schematic of vortex diode functioning, possible steps in desulfurization using cavitation process and photograph of the experimental set-up for carrying out the experiments of the developed process are shown in Fig. 5.1. Details of experiments are discussed in the following sections. Key results and some comments on possible application for large scale sulfur removal are included after that.

5.2 Experimental

5.2.1 Materials and methods

AR grade thiophene (Sigma-Aldrich, > 99%) was used as a model sulfur compound. n-octane (Loba chemie, 98%), n-octanol (Loba chemie, 99%), toluene (Merck, > 99%) were used as organic medium and for preparing model fuel. A commercial diesel was obtained locally. Organic phase is separated from solution and sulfur analysis of organic phase was carried out on Total Sulfur analyser TN-TS 3000 (Thermoelectron Corporation, Netherlands) and Gas chromatograph (Agilent 7890A) equipped with CPSil 5CB for sulfur as column (30 m × 320 μm × 4 μm) in conjunction with flame photometric detector (FPD). Helium was used as a carrier gas with flow rate of 2 mL/min and split ratio of 10:1 (20 mL/min flow rate). The injector temperature employed was 250°C with injection volume of 0.2 μL and total analysis time of 25 min. The oven temperature was ramped at 20°C/min from 40°C to 100°C and at 60°C/min from 100°C to 230°C. Reproducibility of the experimental results was checked and was found satisfactory.

5.2.2 Experimental set-up

A schematic of experimental set-up for deep desulfurization using hydrodynamic cavitation is shown in Fig. 5.2. The experimental data was collected on this set-up using vortex diode as a cavitating device (nominal rated capacity, 1 m^3/h). The setup has a holding tank of 60 L capacity, high pressure vertical multistage centrifugal pump (China Nanfang Pump, Model CDLF 2-17; SS 316, 1000 LPH at 152 MWC, 2.2 kW, 2900 rpm, 415 V AC, 3 phase, 50 Hz motor), control valves, and cavitation reactors. The flow through vortex diode was controlled using the bypass valve. Temperature was maintained using cooling coils inserted in the tank and with cooling system (JULABO, FP50). Flow transmitter (KROHNE, H250), pressure transmitters (Honeywell, ST700), resistance temperature detector (RTD) (Eureka Engg. Enterprises, India) were used for the measurements. The entire set-up was fabricated in SS-316.

A known volume of 12 to 20 L was used for each experiment by appropriately measuring the organic and aqueous phase volumes. Initial sulfur concentration in the feed was adjusted to predetermined concentration. Experiments were carried out to evaluate effect of various parameters such as pressure drop between P_2 to P_3, initial concentration, ratio of organic to aqueous phase (in terms of % organic phase) etc. Samples were collected at regular intervals of time and sulfur content was analyzed in the organic phase using TN-TS 3000 Total sulfur analyser. The results were also cross-checked using gas chromatograph with FPD for sulfur analysis.

Some experiments were also carried out to ensure that sulfur removal is not via extraction. For establishing this, sulfur containing organic phase was mixed vigorously with liquid-water in agitated vessels (stirred tank with turbine impeller, rpm > 200) and samples were analysed at regular time intervals. The samples were also checked for changes in pH and COD using Spectralab MP-5 pH meter and Spectroquant Pharo 100 spectrophotometer (Merck Limited) where Spectroquant TR 320 was used as digester for digestion of samples for 2h at 148°C

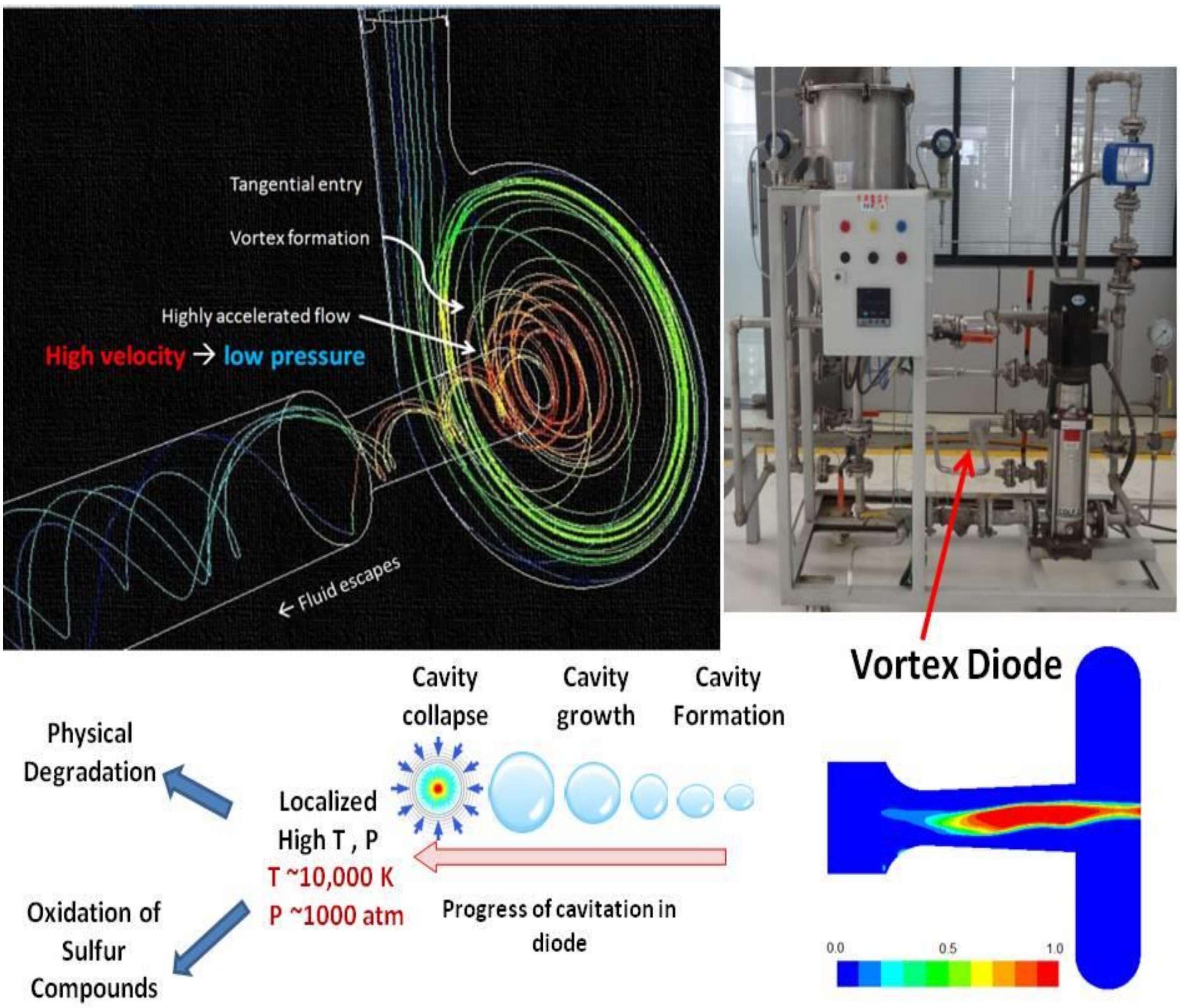


Figure 5.1: Schematic of vortex diode and cavitation process

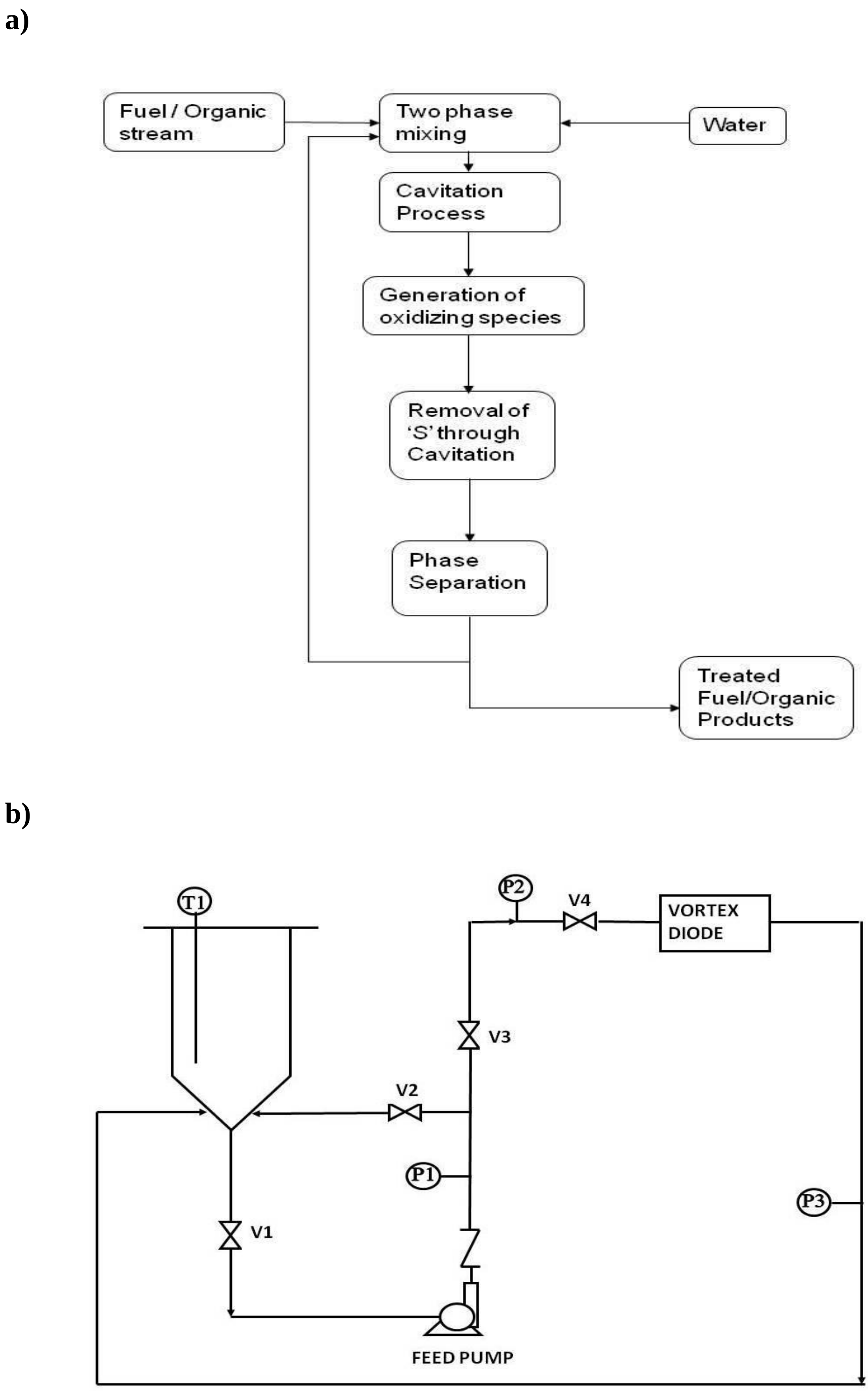


Figure 5.2: Block diagram of the process and schematic of experimental set-up

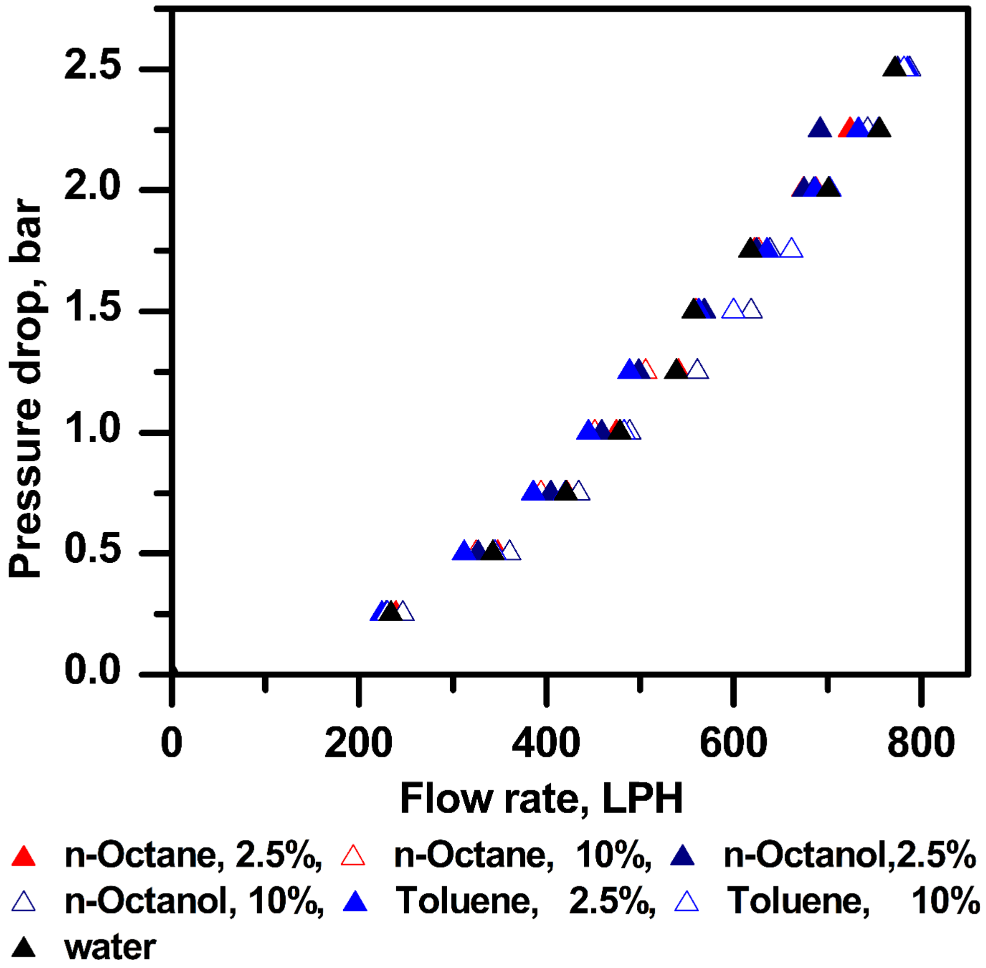


Figure 5.3: Effect of nature of solvent;

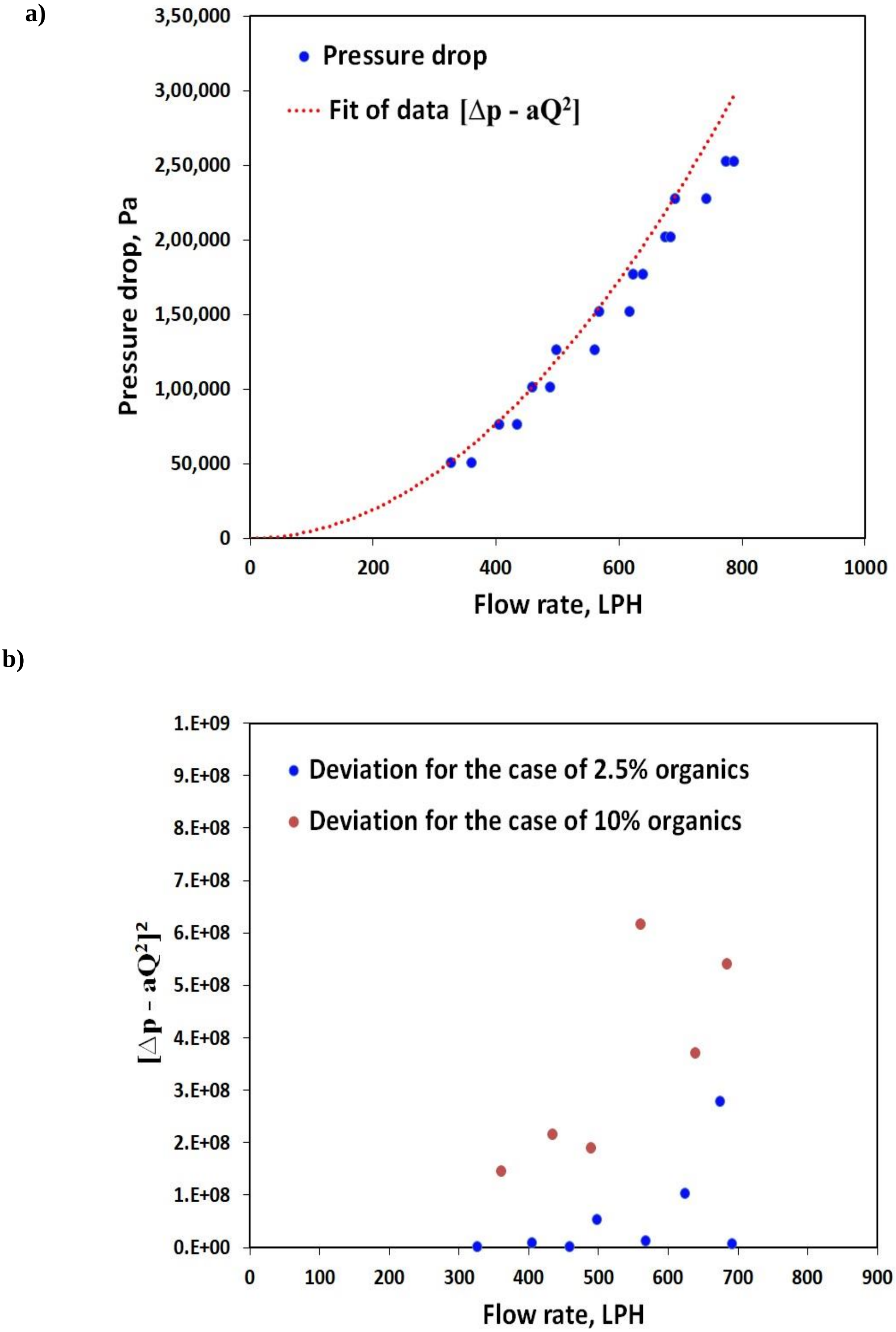


Figure 5.4: (a) Calculations to demonstrate cavitation occurring at a Δ P of 0.5 bar; (b) Prediction of inception of cavitation based on deviation from square law.

5.3 Results and discussion

5.3.1 Hydrodynamic cavitation for sulfur removal

Initial experiments were carried out to identify point of cavitation inception. Pressure drop measurements as a function of flow rate of two phase mixture (organic phase and water) were carried out. The contribution of bypass valve in the overall cavitation can be considered to be insignificant due to its partial closing in most cases (especially at very low pressure drop across vortex diode) and also due to the fact that mere cavity formation is not sufficient and requires effective cavity collapse for cavitation phenomenon as depicted in Fig.5.1. It was established in earlier studies that cavitation inception can be identified from the deviation of measured pressure drop from the usual square law (ΔP proportional to square of flow rate or mean velocity[30,31]. It was established that for the case of octanol-water mixture (up to 10% volume percent of octanol), the cavitation inception occurs just before the pressure drop across vortex diode reaches 0.5bar. The details of pressure drop and identification of inception point are provided in Fig. 5.4. All the further experiments were carried out at two values of pressure drop across vortex diode (0.5bar and 2bar with flow rate of ~330 and 680 LPH respectively).

The initial sulfur content of organic phase (e.g. octanol) was adjusted to predetermined concentration (e.g. 300 ppm) by adding appropriate quantity of thiophene. The thiophene containing organic solvent was mixed with measured quantity of water to generate two phase mixtures with organic solvent volume fraction of 2.5% and 10%. The sulfur content in organic phase (obtained by separating organic layer from the treated mixture) was monitored as a function of time. The experiments were carried out to quantitatively understand influence of various process parameters. Some of these results are discussed in the following to elucidate influence of key process parameters.

5.3.1.1 Influence of pressure drop, initial concentration and volume fraction

For the developed process, the effect of parameters such as pressure drop, initial concentration of the sulfur compound, organic volume fraction and nature of organic phase/solvent is believed to be most crucial and some important results pertaining to these are given in Fig. 5.5. Model fuel and initial sulfur concentration (ppm) used in experimentation is shown in legends of all figures. Pressure drop across the vortex diode or for that matter any cavitating device, is an important parameter that contributes towards the extent of cavitation. The number density of cavities and effective intensity of cavity collapse are governed by pressure drop across cavitating devices (for a specified configuration of device and downstream piping). It is evident from Fig. 5.5a and 5.5a1, that the effect of pressure drop was found to be rather negligible, especially at low values of organic to aqueous phase volume ratio. Influence of initial concentration (100ppm and 300ppm) on sulfur removal is also shown in Fig. 5.5b, 5.5b1, 5.5b2 and 5.5b3. It was observed that sulfur removal was generally better when initial sulfur concentration was low for high organic phase volume. The trend depends on nature of organic solvent and ratio (Fig. 5.5), though as seen from the figures, a very high removal close to 100% can be obtained at low organic fraction of 2.5%. In the developed process, there are two distinct liquid phases viz. aqueous and organic (containing sulfur compounds). Influence of nature of organic phase is expected to be important. Realized cavities and cavity collapse intensities are expected to vary with respect to the nature of organic phase and volume ratio of organic to aqueous phase. Experiments were therefore carried out for different organic solvents and using different volume ratios of organic to aqueous phase. Sample of results obtained with three different organic phases for different organic volume fractions are shown in Fig. 5.5c, Fig.5.5c1 and Fig.5.5c2. It can be seen that the removal of sulfur compounds is drastically different with different organic phases. A very high removal of sulfur was observed with n-octanol compared to other solvents. The order of sulfur removal with respect to the three organics studied in this work was as below:

Toluene < n-Octane < n-Octanol

The initial concentration of sulfur in the organics and effectiveness of the developed process at low pressure drop have important bearing from the view point of commercial operations. Since conventional hydrodesulfurization process has limitations in bringing down sulfur levels below 350 ppm, a process that can take care of sulfur removal from this point can be highly beneficial. The results of this work clearly indicate effectiveness for initial concentrations up to 500 ppm. Further, effective deep desulfurization at low pressure drop of just 0.5 bar across the cavitating device indicates lower cost of operation and significant ease of operation. Another important aspect of the process is that it is effective without using any catalyst or requiring high temperatures/pressures.

It is also important to note that the insolubility of the thiophene in water and the huge difference with respect to the organic solvent practically eliminates possibility of physical transfer of the thiophene in the aqueous phase. In order to establish that sulfur removal is because of hydrodynamic cavitation and not because of vigorous contact with aqueous phase, the results of stirred tank experiments were also compared. The measured sulfur content of the different organics samples collected from these tanks (Initial sulfur concentration: 300 ppm; without cavitation) and those using hydrodynamic cavitation are shown in Fig. 5.6.

Hydrodynamic cavitation is known to generate hydroxyl radicals through cleaving of water molecules- an active oxidant and this can be effectively utilized for removal/degradation of organics[32,33]. A plausible mechanism for the removal of sulfur would require cleavage of the sulfur bond with the attack from the oxidant and release of sulfur dioxide. Alternatively, it can also form other oxidation products such as sulfone that would go in the aqueous phase, thereby effecting sulfur removal. A postulated mechanism can be thought to involve mainly reaction of the free radicals with the sulfur compounds resulting into removal of sulfur as SO_2 and mineralization of the organic skeleton to final products as carbon dioxide and water.

It is also possible that the cavitation here works as a specific form of extractive, but not catalytic, oxidative desulfurization with water as a solvent and without employing any conventional catalyst of the type reported in the literature for ECOD. A number of other possibilities such as formation of SO_2, HSO_3, H_2SO_4 etc. may also be listed. No change in the pH of the aqueous solution was observed during or after hydrodynamic cavitation experiments, indicating that formation of acid or acidic species may not occur. The aqueous phase after the cavitation was analysed for increase in the organic carbon using COD/TOC test. It was observed that when toluene was used as the organic phase in cavitation, there was practically no increase in the COD/TOC values during the progress of cavitation indicating that no organic species entering into the aqueous phase due to cavitation. However, there was increase in the COD/TOC when n-octane was used as solvent in cavitation experiments, though the COD values were not high, but showed approximately 4 times increase (from 130 ppm to 650 ppm) indicating presence of organics in the aqueous phase which can be attributed to mainly organic solvent though possibility of entering solubilised forms of organic sulfur (e.g. sulfones) in the aqueous phase cannot be ruled out. Preliminary analysis of organic phase using gas chromatography, however, indicated no presence of any other compound than the solvent or thiophene. FTIR analysis of the aqueous samples (Fig.5.6) indicated no appreciable presence of sulfones in the aqueous phase.

Details of mechanisms have been reported in the case of oxidative desulfurization in presence of various catalysts such as hydrogen peroxide and other acid catalysts[26,27]. The conventional approach involves reaction of hydrogen peroxide with the acid resulting into formation of acid peroxide which subsequently reacts with the organic sulfur resulting into formation of sulfone or sulfoxide. Otsuki et al.[27] reported formation of sulfones in the organic phase during oxidative desulfurization using IR spectra analysis. The sulfone/sulfoxide, thus formed, can be extracted in different phase. It is important to note that the authors indicated difficulty in oxidising thiophene at 50°C due to low electron density though benzothiophene or dibenzothiophene could be easily oxidised using hydrogen peroxide and formic acid mixture as catalyst. Thus, in the developed method, removal of organic sulfur is possible by both mineralization as well as oxidation mechanism (Fig.5.7). However, since the process here does not employ acid catalyst, the contribution of later mechanism may not be significant. In principle, the cavities of organic, water or both (mixture) can form, the contribution of which would depend on the nature, vapour pressure of the organic solvent and composition. In the present work, the solvents, including water have vapour pressure in the range of 0.2–38 mmHg at 30°C; e.g. octanol (0.21), octane (17.65), toluene (37.7) and water (32) while thiophene has vapour pressure close to 92.6 mmHg at 30°C. However, in view of very low mole fraction of thiophene, its partial vapour pressure in the aqueous-organic two-phase mixture of this study is significantly low. The probability of cavity formation for any phase is expected to increase with increase in its relative volume percent. However, even if organics cavities are more in number on the basis of low vapour pressure of the solvent, the degradation of sulfur species is believed to be difficult, if oxidative reaction by hydroxyl radical is assumed. The mechanism here is certainly much more complex and needs to be investigated in detail. In this context also, it is instructive to evaluate inception of the cavitation under different conditions/solvents and this can be done using the data of Fig. 5.4 for water alone and using different solvents for the two solvent ratios. The data on inception of cavities with addition of different solvents and with different ratios did not reveal significant difference from that of water alone, indicating that the role of solvent can be viewed predominantly as facilitator in oxidative interfacial reactions through effective transfer of sulfur moiety in cavities that provide predominantly oxidising species. However, this again needs further detailed investigation.

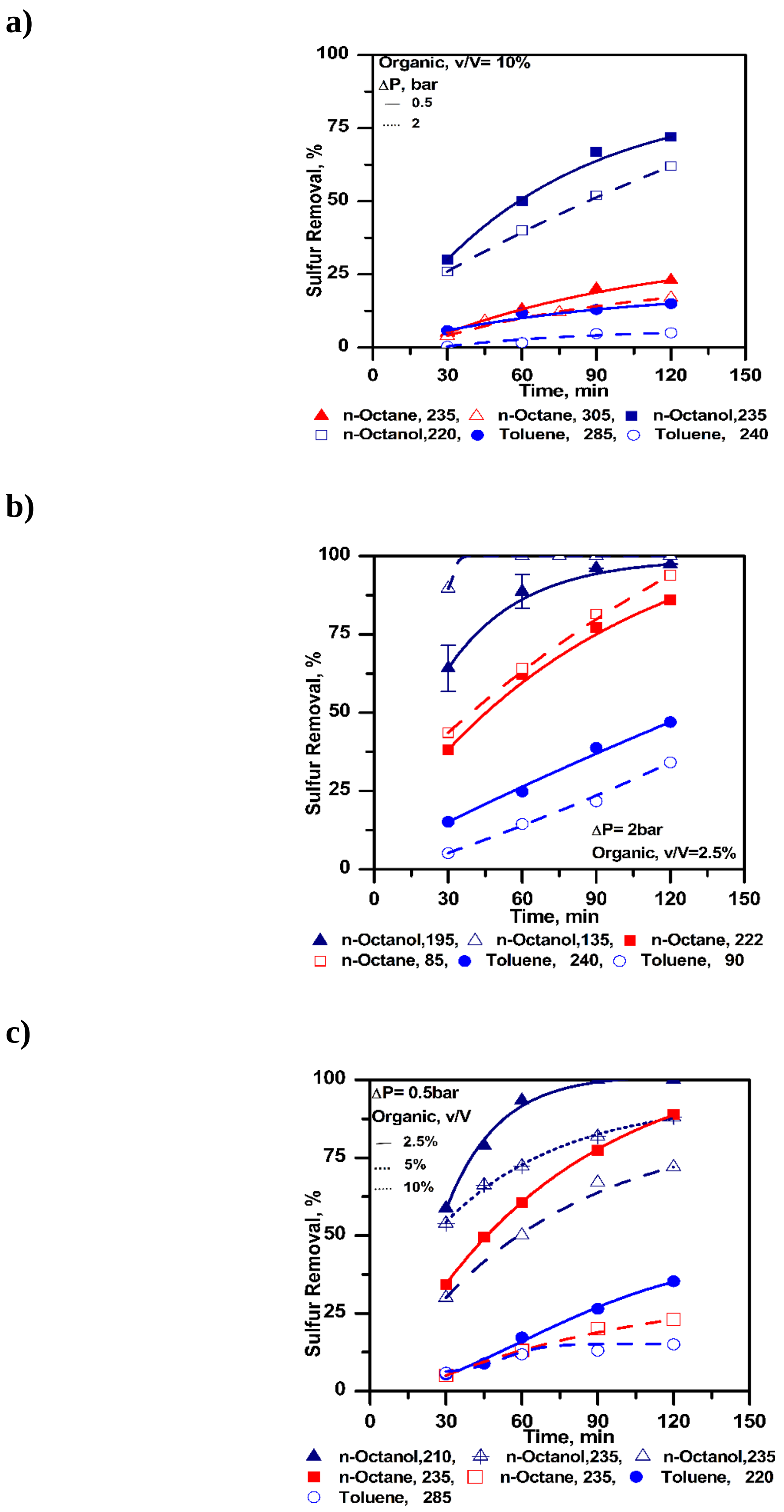


Figure 5.5: Effect of different parameters on desulfurization by hydrodynamic cavitation; (a) Pressure drop; (b) Initial concentration; (c) Volume fraction.

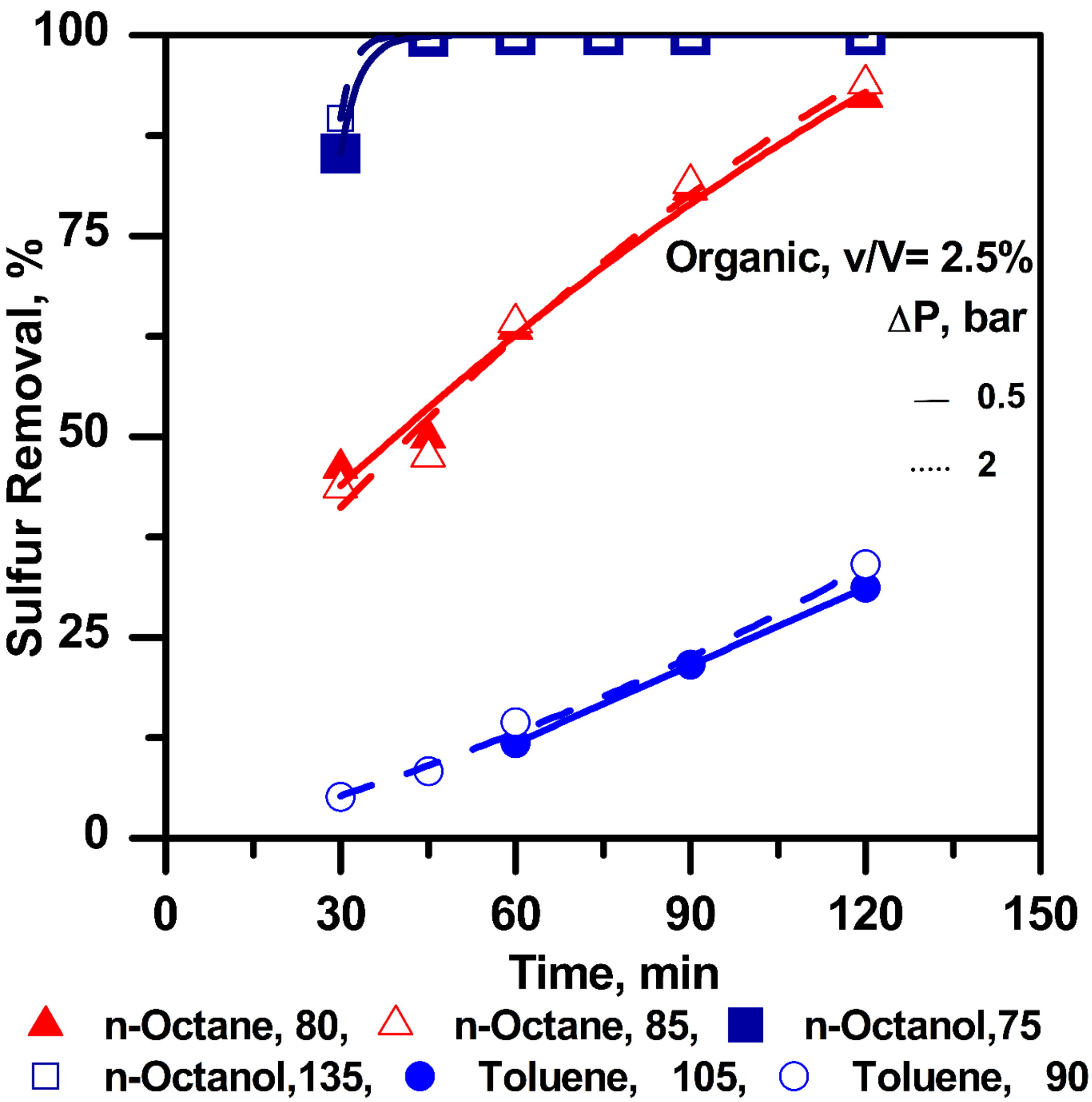


Figure 5.5a1: Effect of pressure drop at low initial sulfur concentrations

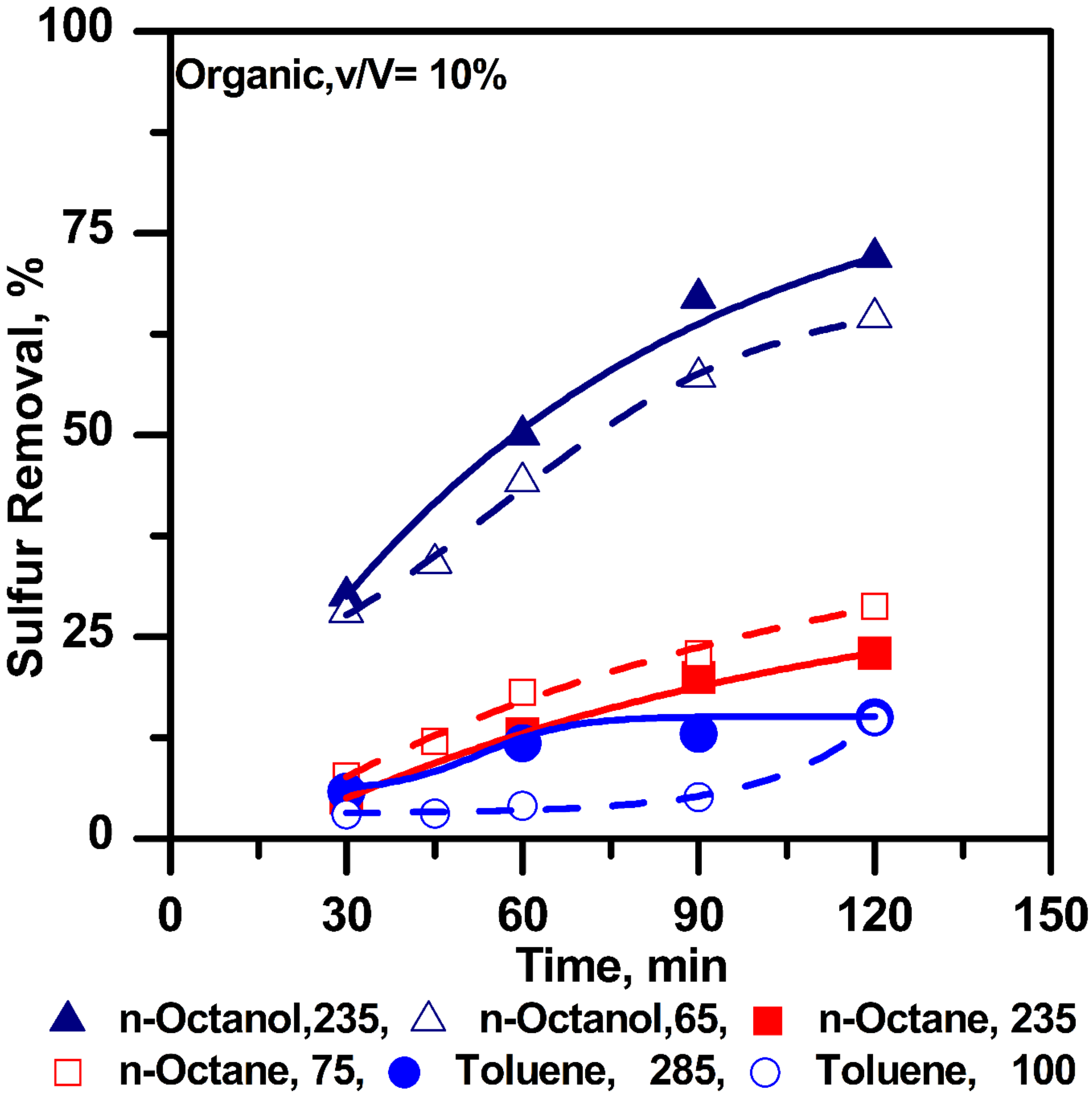


Figure 5.5b1: Effect of initial concentration at 10% organic phase volume (ΔP= 0.5 bar)

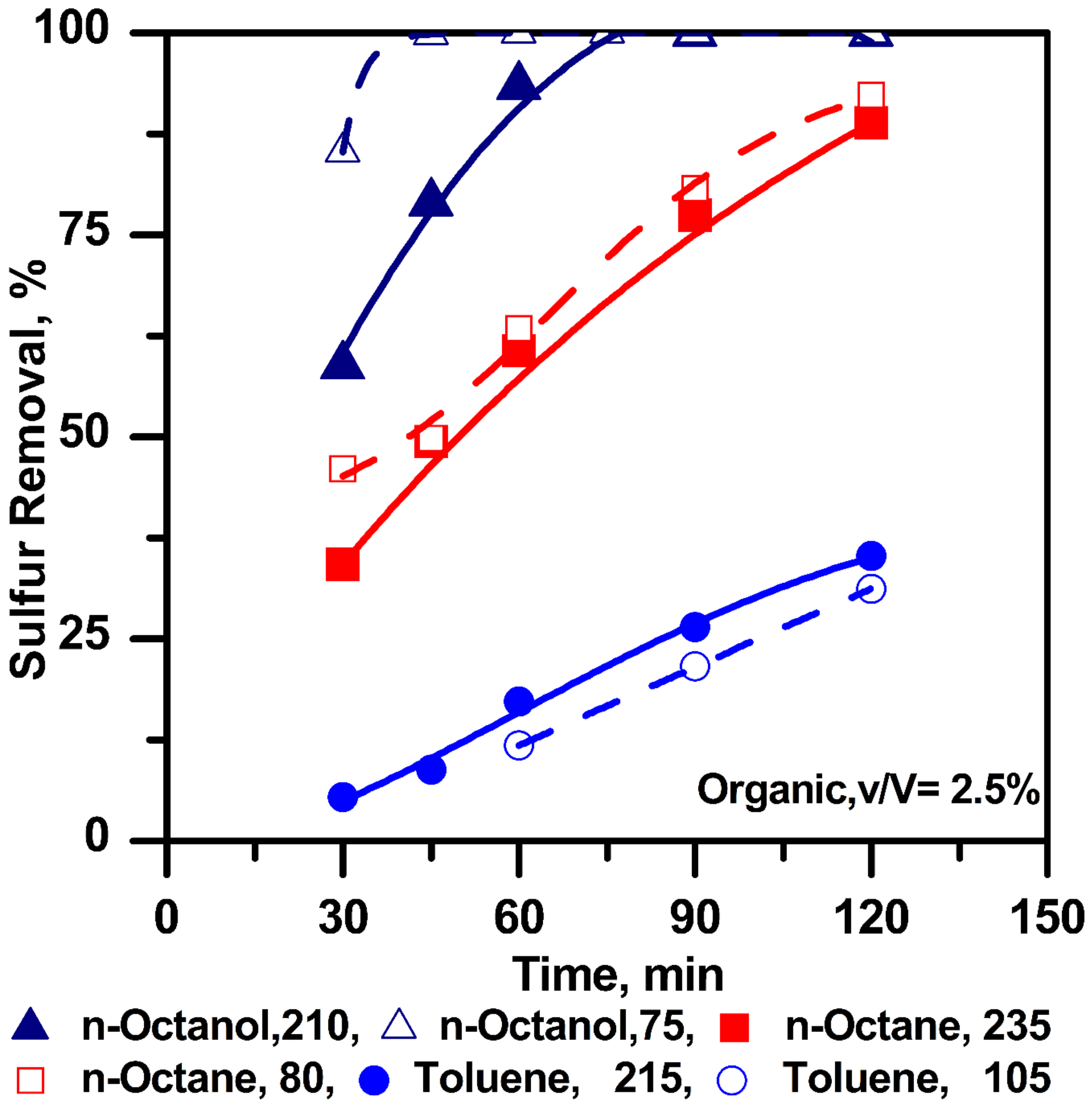


Figure 5.5b2: Effect of initial concentration at 2.5% organic phase volume (ΔP= 0.5 bar)

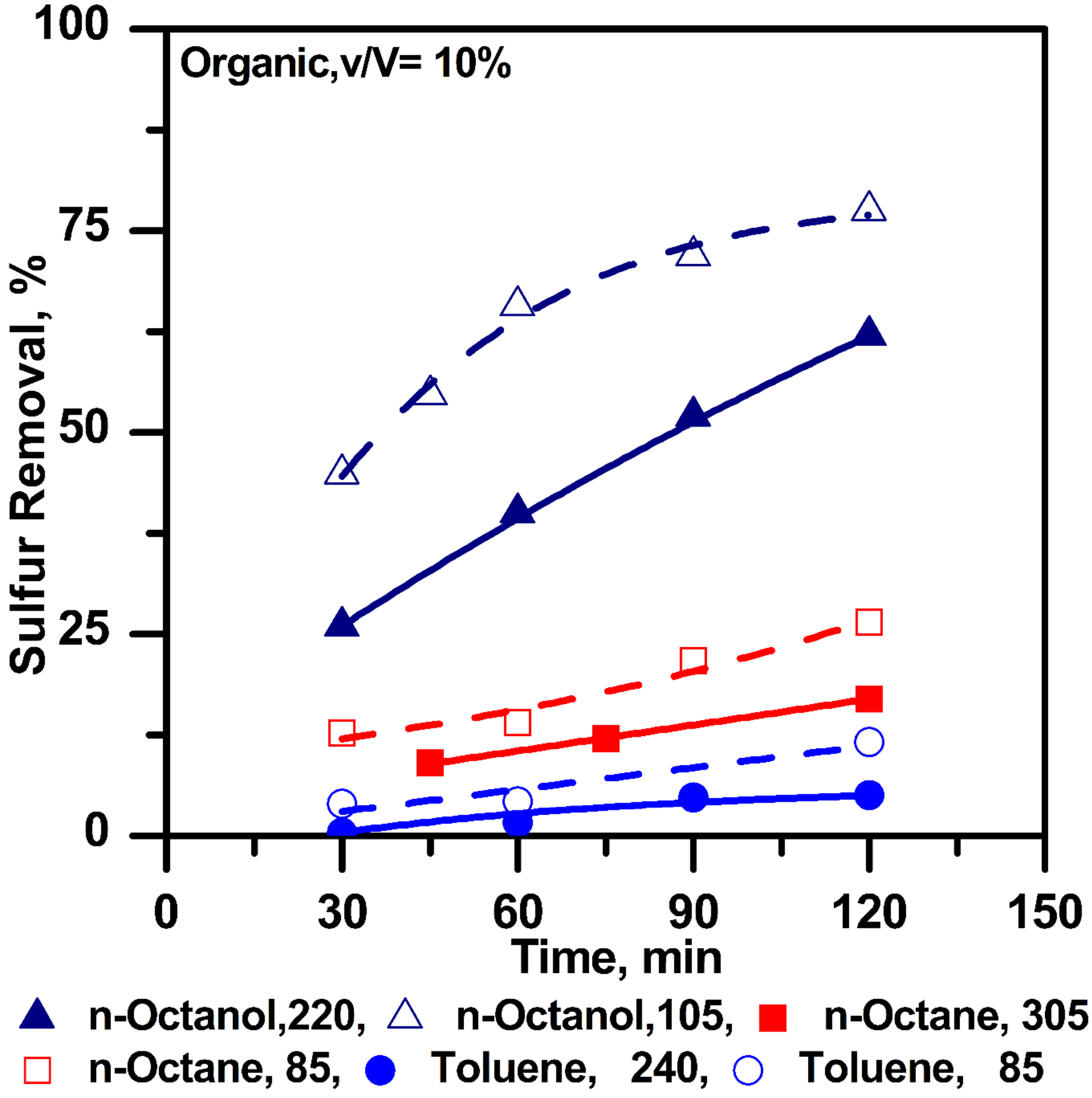


Figure 5.5b3: Effect of initial concentration at 10% organic volume (ΔP = 2 bar)

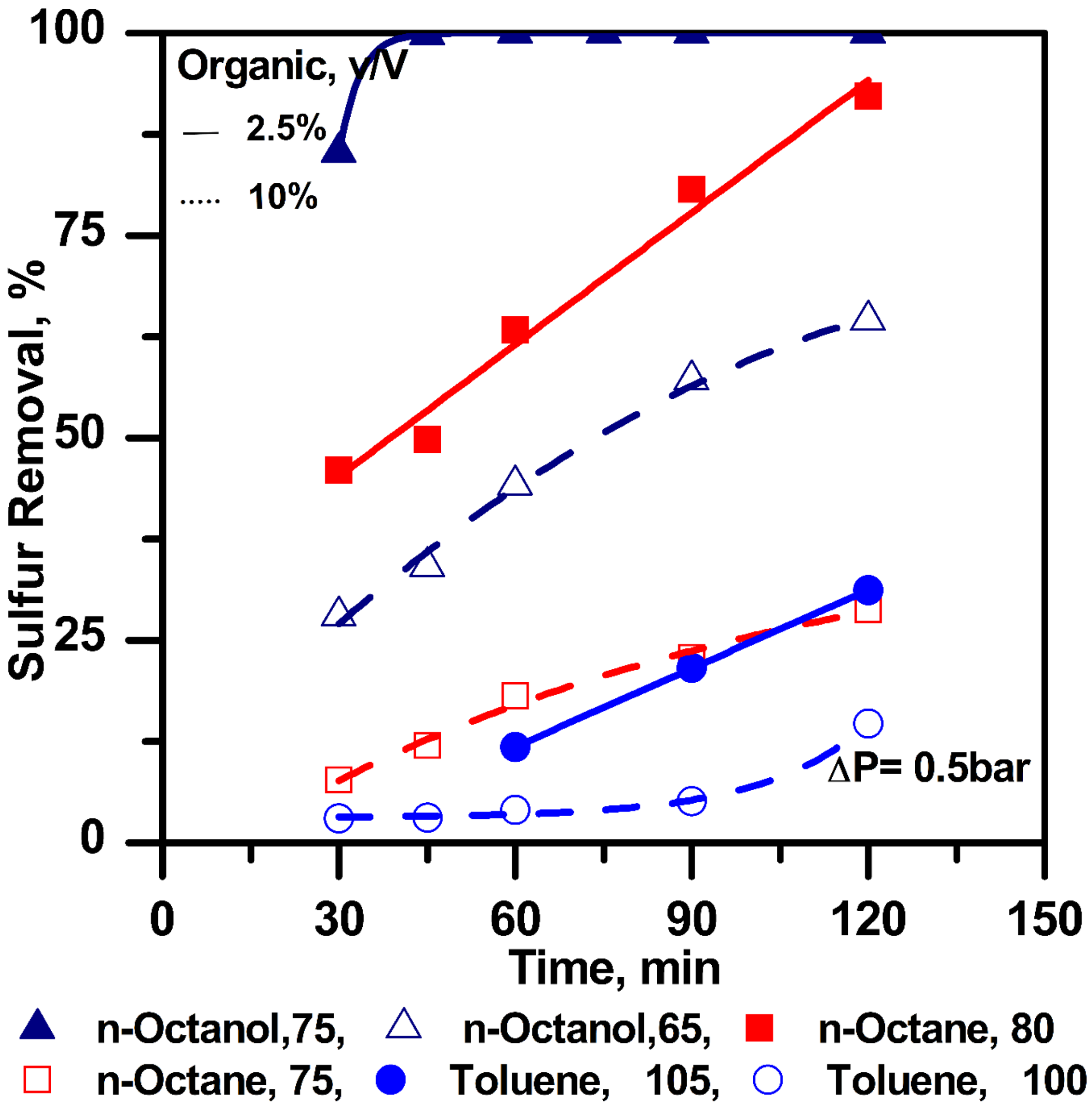


Figure 5.5c1: Effect of solvent ratio on sulfur removal at low initial concentrations (ΔP= 0.5 bar)

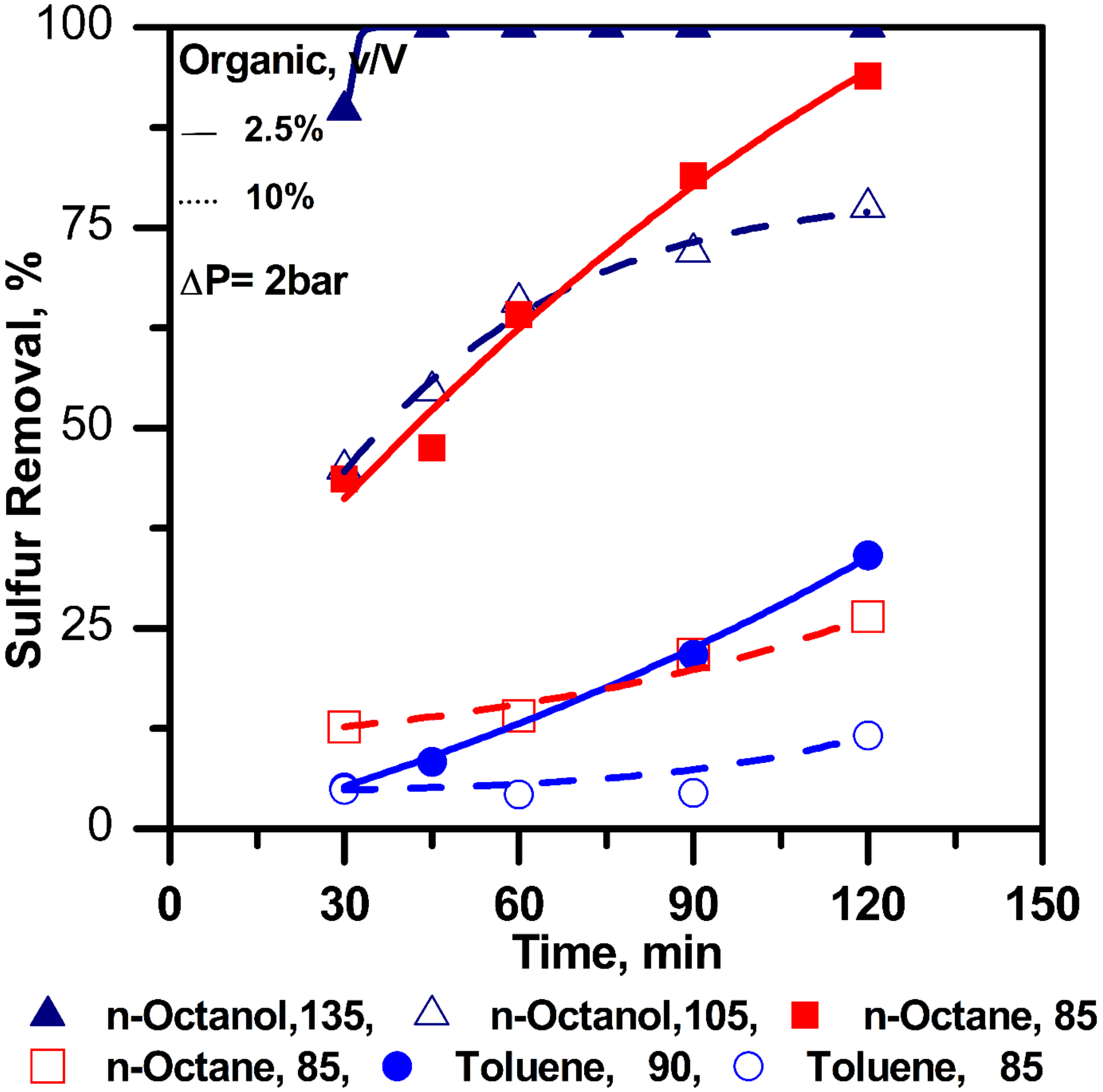


Figure 5.5c2 Effect of solvent ratio on sulfur removal at low initial concentrations (ΔP = 2 bar)

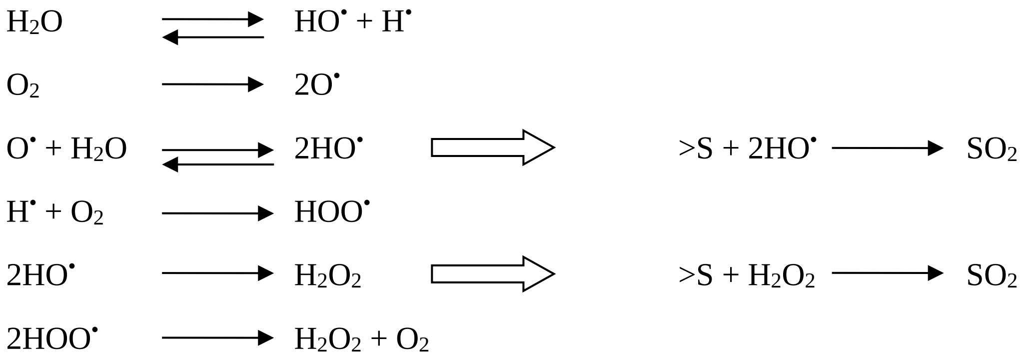


Figure 5.7: Proposed cavitative oxidation mechanism for desulfurization

5.3.1.2 Results with diesel

It is instructive to evaluate the impact of nature of solvent from commercial application point of view for deep desulfurization of fuels. For this purpose, a commercial diesel was tested for the removal of sulfur (thiophene) similar to that discussed in the study. The commercial diesel had initial sulfur content of 30 ppm (probably in the form of refractory sulfur compounds). A known amount of sulfur using thiophene was added in this diesel and the effect of cavitation process was studied for pressure drop and for the extent of sulfur removal. The results of sulfur removal (thiophene in diesel) for the two-different pressure drop conditions and using an intermediate organic to aqueous ratio (Organic phase, 6.5%) are shown in Fig. 5.8 along with a comparison with other organic solvents (Fig.5.8b, Fig.5.8b1 and 5.8b2). The results indicate a very high removal of sulfur even from the commercial diesel which is a mixture of aliphatic and aromatic organic compounds. Similar to that observed in certain cases earlier, here, the removal was better at higher pressure drop condition of 2bar as compared to 0.5bar. The results clearly demonstrate that proposed method is successful in removing sulfur from commercial diesel.

The proposed method can be effectively employed to reduce sulfur content of transportation fuels or other organic streams. The aqueous phase used in the proposed method can be recycled after removing a purge stream (with corresponding make-up water). The proposed method can be implemented in a compact set-up with effective removal of sulfur. The process may be further intensified using a number of ways e.g. aeration, catalyst etc. Hydrodynamic cavitation usually improves performance with scale-up. Therefore, the proposed method can be effectively implemented for large scale deep desulfurization operation.

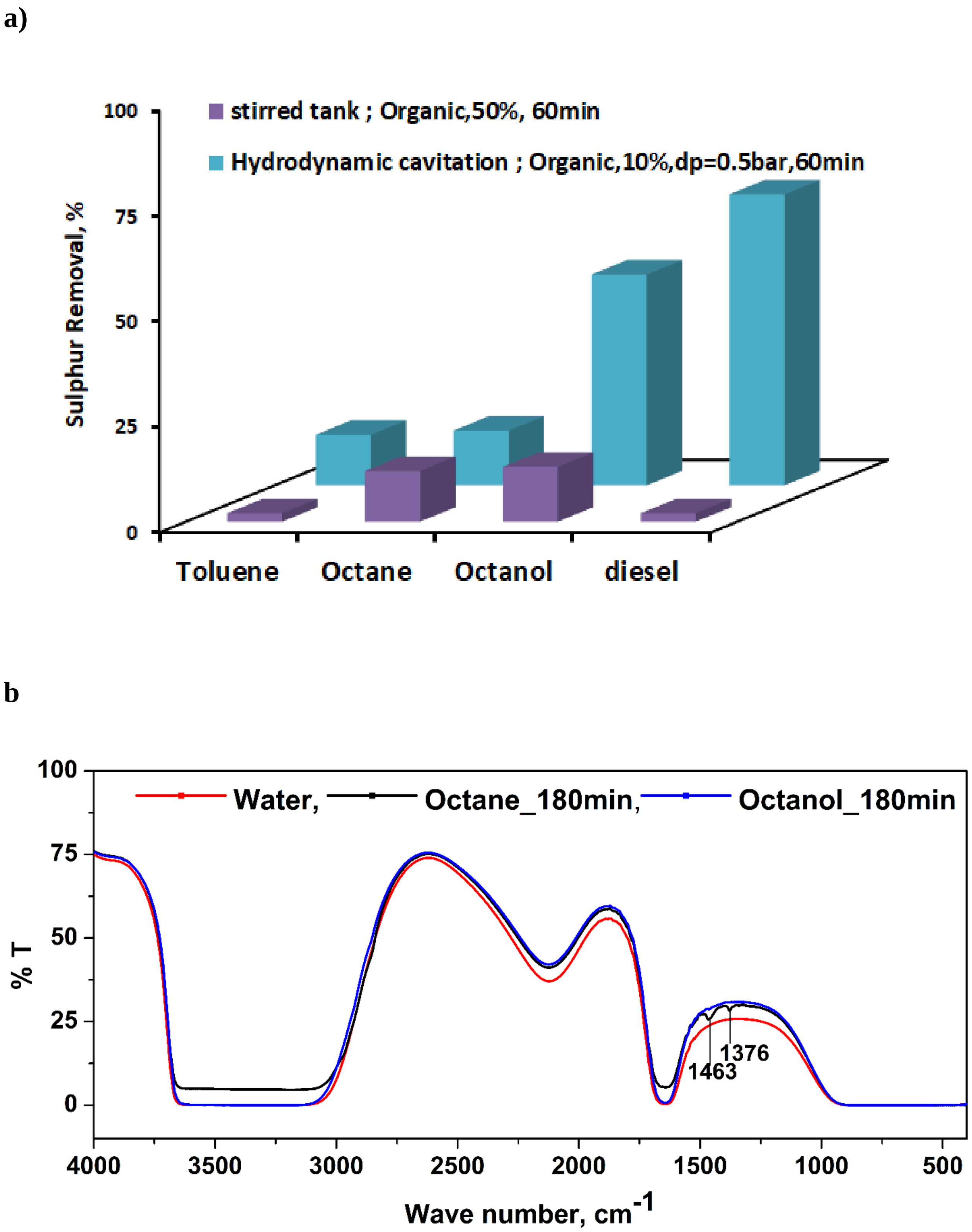
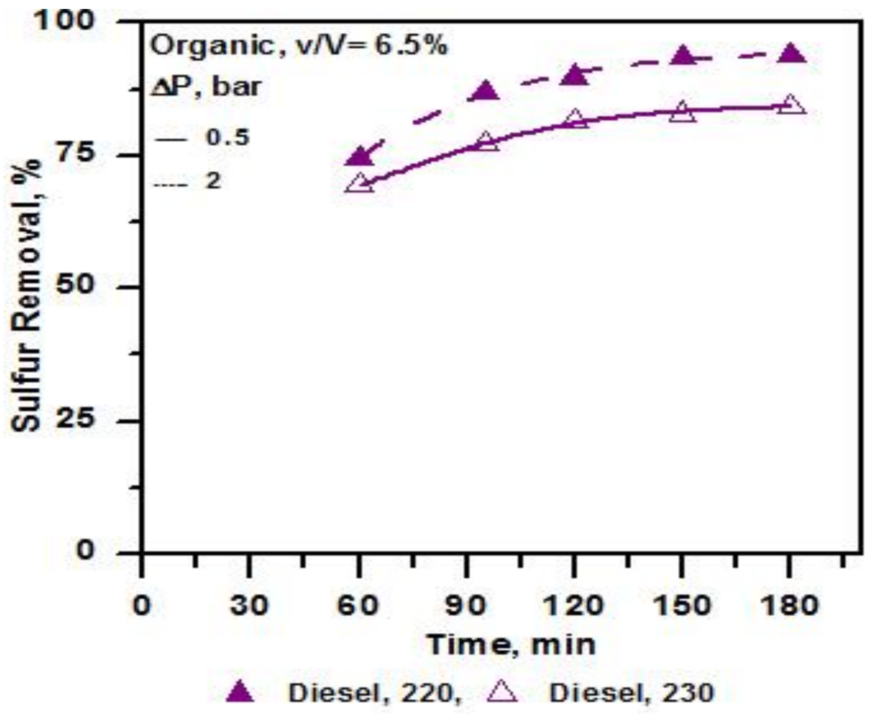


Figure 5.6: Cavitation is essential for reduction of sulfur content; (a) Sulfur removal using cavitation (Initial S:300 ppm); (b) FTIR spectra of aqueous phase after cavitation

a)



b)

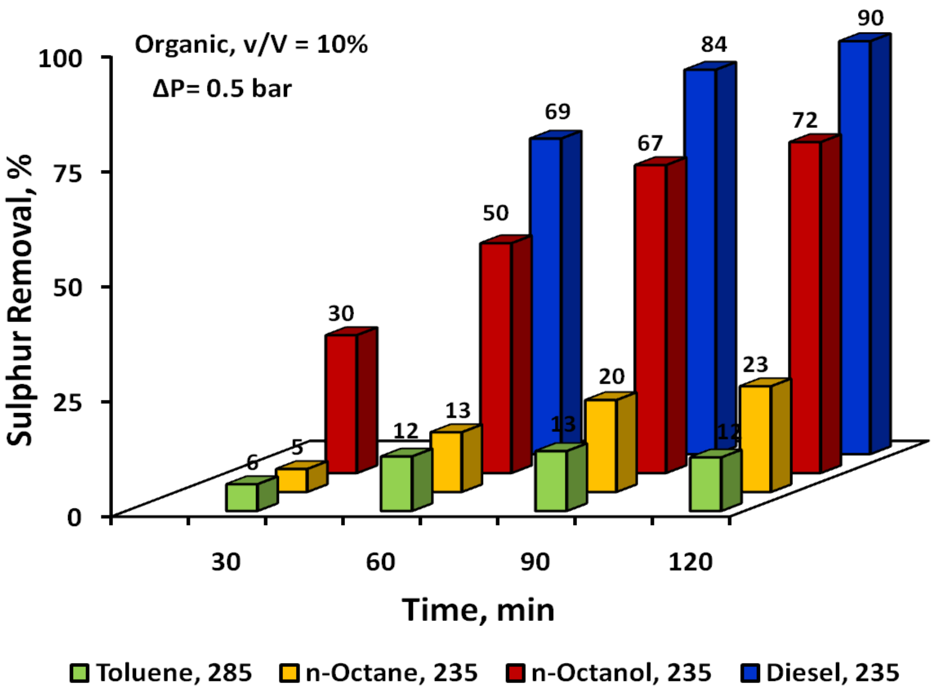


Figure 5.8: Comparison of deep desulfurization results using commercial diesel; (a) commercial diesel; (b) comparison with other organics.

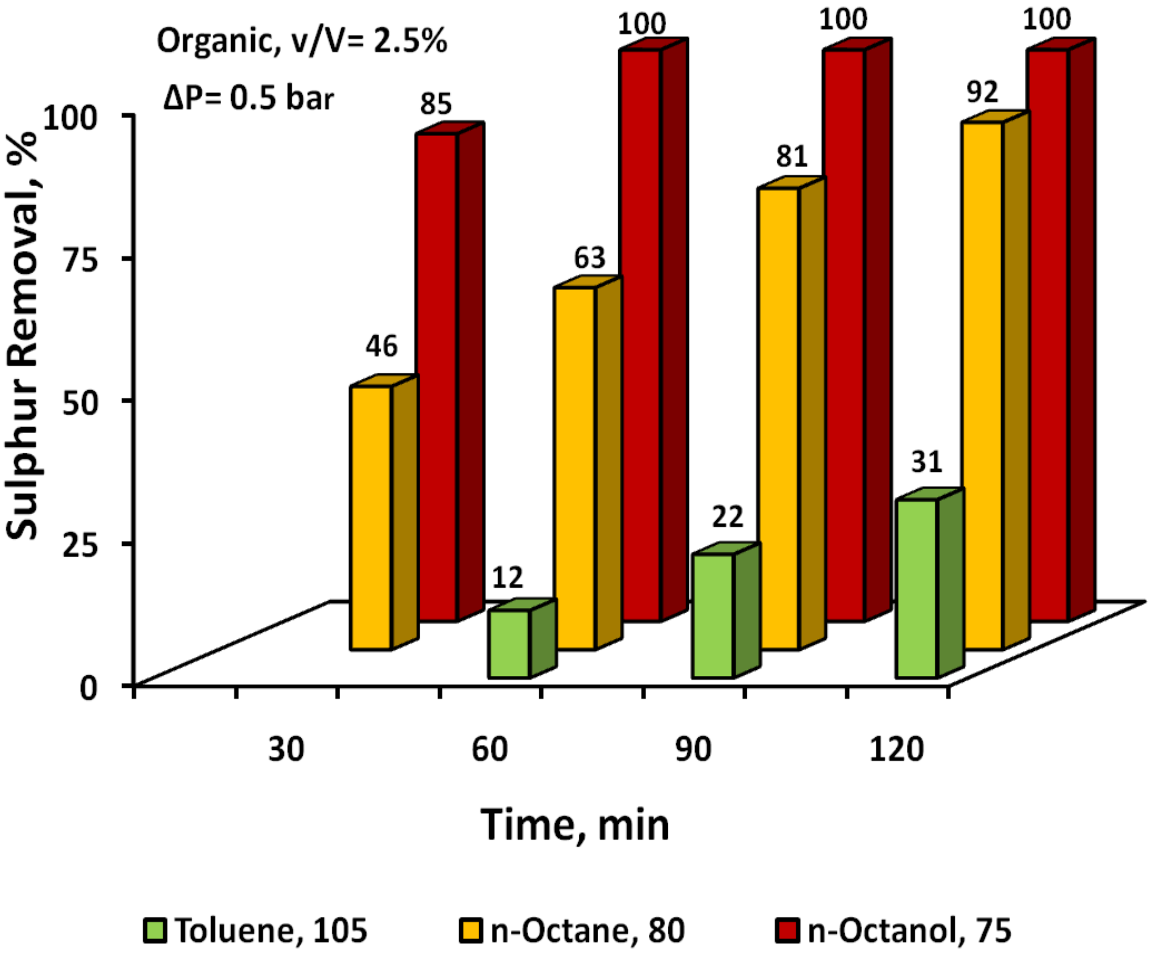


Figure 5.8b1: Comparison of effect of nature of solvent for low initial sulfur concentrations at ΔP= 0.5 bar

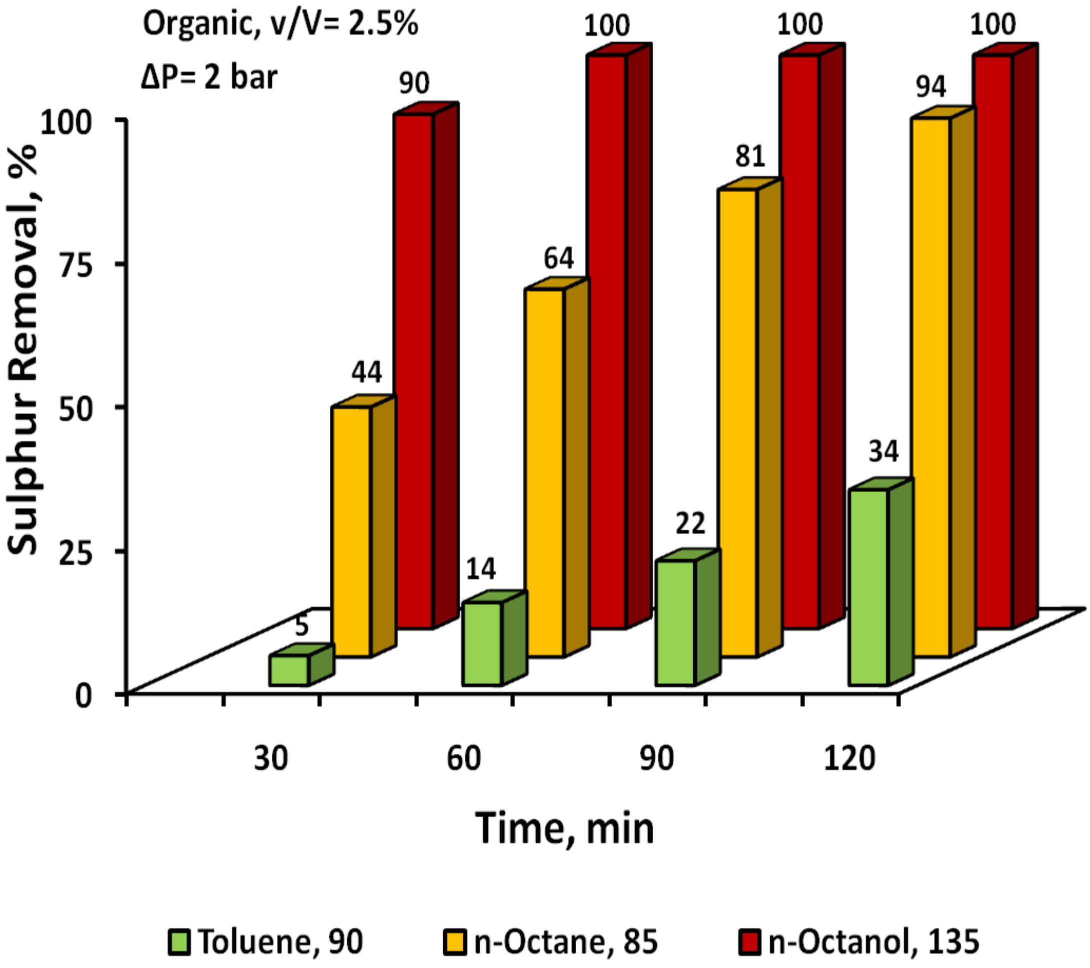


Figure 5.8b2: Comparison of effect of nature of solvent for low initial sulfur concentrations at ΔP=2 bar

5.4 Conclusions

A new multiphase non-catalytic process is developed for deep desulfurization of fuels or organics using hydrodynamic cavitation with vortex diode as a cavitating device. The process can completely remove thiophene sulfur from organic streams with considerable ease of operation and under mild operating conditions. Deep desulfurization of fuels to the extent of 100% was demonstrated for thiophene in model fuel. The removal efficiency depends strongly on nature of organics e.g. alcohols, aromatic solvents, aliphatic solvents or their mixtures apart from organic to aqueous ratio, pressure drop, and initial concentration of sulfur. A very high sulfur removal using commercial diesel was also demonstrated.

The aqueous phase used in the proposed method can be recycled after removing a purge stream (with corresponding make-up water). Hydrodynamic cavitation usually improves performance with scale-up and hence the proposed method can be effectively implemented for large scale deep desulfurization operations.

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Chapter 6

Nalinee B. Suryawanshi, Vinay M. Bhandari, Gayatri Sorokhaibam and Vivek V. Ranade. *Developing techno-economically sustainable methodologies for deep desulfurization using hydrodynamic cavitation*. Fuel, 210, 482–490 (2017).

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Chapter 6

Developing Techno-economically Sustainable Methodologies for Deep Desulfurization using Hydrodynamic Cavitation

Abstract

The present work, for the first time, describes the efficacy of the cavitation process and compares the cavitation yield for two types of cavitation devices-one employing linear flow for the generation of cavities and other employing vortex flow. The process involves pre-programmed mixing of the organic and aqueous phases, and can be carried out using simple mechanical cavitating devices such as orifice or vortex diode. The process essentially exploits in situ generation of oxidising agents such as hydroxyl radicals for oxidative removal of sulfur. The efficiency of the process is strongly dependent on the nature of device apart from the nature of the organic phase. The effects of process parameters and engineering designs were established for three organic solvents (n-octane, toluene, n-octanol) for model sulfur compound-Thiophene. A very high removal to the extent of 95% was demonstrated. The results were also verified using commercial diesel. The cavitation yield is significantly higher for vortex diode compared to the orifice. The process has potential to provide a green approach for desulfurization of fuels or organics without the use of catalyst or external chemicals/reagents apart from newer engineering configurations for effective implementation of hydrodynamic cavitation in industrial practice and also appears to be economically sustainable.

6.1 Introduction

6.1.1 Desulfurization

Air pollution due to burning of fossil fuels is a major challenge and removal of sulfur from transportation fuels is an essential operation in petroleum refineries for reduced pollution due to SO_x emission. The vehicular pollution in many major cities in many parts of the world has reached alarming proportion, forcing Governments worldwide to continuously enforce increasingly stricter norms for sulfur content in fuels for improved environmental sustainability. Euro-VI norms demand sulfur concentration in diesel and petrol to be less than 10 ppm[1], compared to earlier norms of 350 and 500 ppm in diesel and gasoline, subsequently lowered to the level of 15 ppm and 30 ppm in diesel and gasoline respectively[2–4]. Increased focus on newer developments such as fuel cell applications also demand more stringent limits on the sulfur levels (less than 1 ppm) to avoid poisoning of the catalyst. Biodiesel also can contain appreciable amounts of sulfur that requires processing in terms of sulfur reduction for sustainable applications[5].

The existing refinery operations have limitations with respect to satisfactory sulfur removal apart from the economics of the processes pertaining to the sulfur removal. There are a number of sulfur compounds in fuels that have varying concentrations and most importantly these vary in their reactivity as far as catalytic desulfurization is concerned demanding severe process conditions in terms of high temperature/pressures or newer catalysts. Conventional hydrodesulfurization (HDS) though suitable for lowering sulfur content up to 350 ppm, requires supplementary processes such as oxidation, adsorption or newer forms of processes that are capable of removing remaining refractory compounds to desired levels[6–8]. In view of the fact that huge volumes of fuels have to be processed techno-economically, there appears to be limited options for replacing the conventional HDS process that employs catalyst such as Co-Mo or Ni-Mo and requires high temperatures of the order of 450^{o}C, along with high pressures of the order of 20–40 atm. Thus, it is apparent that though the HDS process can meet the new standards with certain modifications such as increased (~3 fold) catalyst volume/reactor size and increased cost of operation, a more suitable practice would be to employ greener routes that can be integrated into the existing plant for better techno-economic feasibility and sustainability. The alternative can be in the form of adsorptive desulfurization using conventional adsorbents to π-complexation adsorbents[4,9–14], biodesulfurization[6,15] and oxidative desulfurization[16,17]. Recently, oxidation processes in different forms have been increasingly discussed for desulfurization of fuels which also include processes that combine oxidation and extraction (Extractive and catalytic oxidative desulfurization or ECOD). In these, more thrust is placed on developing/ evaluating various catalysts for oxidation and suitable extractants for removing oxidation products[18–20]. Cavitation, which is also one form of advanced oxidation process, has also been discussed largely using catalysts for desulfurization. Commonly, ultrasound assisted oxidative desulfurization is reported in presence of various catalysts for different substrates[21–25], while hydrodynamic cavitation is rarely used, that too using catalyst such as hydrogen peroxide[26]. Different fuel fractions such as gasoline, jet fuel and diesel have different compounds from lower end compounds of sulfides, disulfides, mercaptans to refractory compounds such as thiophene, benzothiophene, dibenzothiophene and such alkylated derivatives of thiophene. Different desulfurization processes have varying degree of success in removal of these varied forms of sulfur compounds and face severe challenges in satisfactory and efficient removal of refractory sulfur compounds. Thiophene is one of the most difficult and refractory organic sulfur compound as far as oxidative desulfurization is concerned and hence its effective removal is crucial[27–29].

Recently, a non-catalytic process for deep desulfurization of fuels employing hydrodynamic cavitation with vortex diode for generating vortex flow for cavitation was reported[27] with a very high sulfur removal for thiophene. It is instructive to study, the impact of the engineering designs of cavitating devices and also evaluate techno-economic sustainability. In this work, the main objective is to report extensive studies on hydrodynamic cavitation for deep desulfurization of fuels and organics without employing any catalyst and under mild operating conditions, but using linear flow for cavitation, orifice as a cavitating device, compare the performance with that of vortex diode and finally evaluate economic feasibility. Thiophene was chosen as a model sulfur compound mainly due to the limitation of conventional oxidation processes in its removal[30] and also for ease of comparison of the different processes in this regard. Cavitational yields have been discussed in different forms of cavitation apart from establishing the applicability of cavitation method based on hydrodynamic cavitation for sulfur removal, especially by obtaining insight into the sulfur removal behaviour not just for different cavitating devices, but also for different process parameters, more importantly on the nature of organic phase by evaluating three different solvents viz. n-octanol, n-octane and toluene, apart from real diesel. We believe that the present route offers a greener and a sustainable approach to deep desulfurization of various fuels with significant ease of operation along with techno - economic feasibility.

6.2 Experimental

6.2.1 Materials and methods

AR grade thiophene was obtained from Sigma-Aldrich (> 99%). Organic solvents viz. n-octane (Lobachemie, 98%), n-octanol (Lobachemie, 99%), toluene (Merck,>99%) and commercial diesel (obtained locally) were used as such for making the synthetic/model fuel. Sulfur analysis was carried out on Total Sulfur analyser TN-TS 3000 (Thermoelectron Corporation, Netherlands) and Gas chromatograph (Agilent 7890A) equipped with CPSil 5CB for sulfur as column (30 m× 320 μm×4 μm) in conjunction with flame photometric detector (FPD) with helium as a carrier gas, flow rate of 2 mL/min, split ratio of 10:1, Injector temperature of 250 °C, injection volume of 0.2 μL and total analysis time of 25 min. The oven temperature was ramped at 20 °C/min from 40 °C to 100 °C and at 60 °C/min from 100 °C to 230 °C. Reproducibility of the experimental results was checked and was found satisfactory. Two different cavitating devices, orifice (single hole, 3 mm) and vortex diode (66 mm chamber diameter) were employed for the cavitation studies.

6.2.2. Experimental set-up

The hydrodynamic cavitation process involves predefined mixing of sulfur containing organic phase with water under ambient conditions and pumping the mixture through the cavitating device such as orifice or vortex diode[31]. A schematic showing the different flow patterns in the two cavitating devices and the cavitation process is shown in Fig.6.1. In the inset of Fig.6.1, experimental set-up for the desulfurization studies is shown. Essentially, irrespective of the type of cavitating device, the cavitation process progresses through the formation, growth and implosion/ collapse of the cavities and as a result of implosion, extreme temperatures (~10,000 K) and pressures (~1000 atm) get generated at highly localized points of the cavity collapse, which consequently cleave water to generate, in situ, oxidising species such as hydroxyl radicals or hydrogen peroxide[rf]. Oxidation of the sulfur compounds is expected to take place under these conditions resulting in the removal of sulfur from the organics/fuels, without actually employing any external catalyst/reagent or externally employing high temperatures/ pressures.

A photograph of the experimental set-up for deep desulfurization using hydrodynamic cavitation is shown in the inset of Fig.6.1 indicating the two cavitation reactors namely orifice and vortex diode. The details of the set-up along with the schematic of experimental set-up and process flow sheet were given in Chapter 5 [27]. However, for immediate reference and clarity, some of the details are reproduced here. The experimental set-up (Stainless Steel SS 316) has different reactors as a cavitating device (nominal rated capacity, 1 m^3/h), a holding tank of 60 L capacity, high pressure vertical multistage centrifugal pump (China Nanfang Pump, Model CDLF 2-17; SS 316, 1000 LPH at 152 MWC, 2.2 kW, 2900 rpm, 415 V AC, 3 phase, 50 Hz motor), control valves and flow/pressure and temperature controls. Flow transmitter (KROHNE, H250), pressure transmitters (Honeywell, ST700), Resistance Temperature Detector (RTD) (Eureka Engineering Enterprises, India) were used for the measurements. Typically, 12–20 L volume was used for each experiment by appropriately measuring the organic (e.g. n-octanol, n-octane, toluene and commercial diesel) and aqueous phases. The initial sulfur content in the organic phase was adjusted to a predetermined concentration typically in the range of 100–300 ppm by adding known quantity of thiophene. The two-phase mixture: thiophene containing organic solvent and water, was then passed through the cavitating device e.g. orifice at a predetermined condition of pressure drop for any specific experiment. The sulfur concentration in the organic phase was measured at periodic intervals of time by separating the organic layer from the treated mixture. The experiments were typically carried out for 2 h and effect of various process parameters were studied for pressure drop in the range 2–10 bar, initial sulfur concentration (100–300 ppm), organic phase volume (% organic phase in the range 2.5–10%) etc. The sulfur content was analysed in the organic phase using total sulfur analyser (TN-TS 3000) and the results were also cross-checked using gas chromatograph with FPD (Flame Photometric Detector) for sulfur analysis, as per the details mentioned in the earlier section.

6.3 Results and discussion

6.3.1 Identification of cavitation inception point in hydrodynamic cavitation

It is essential that the cavitation process be performed for conditions of cavity generation, growth and collapse. Identification of cavitation point is crucial in this regard, since above the cavitation point, cavitation is expected to take place and this information can be obtained using

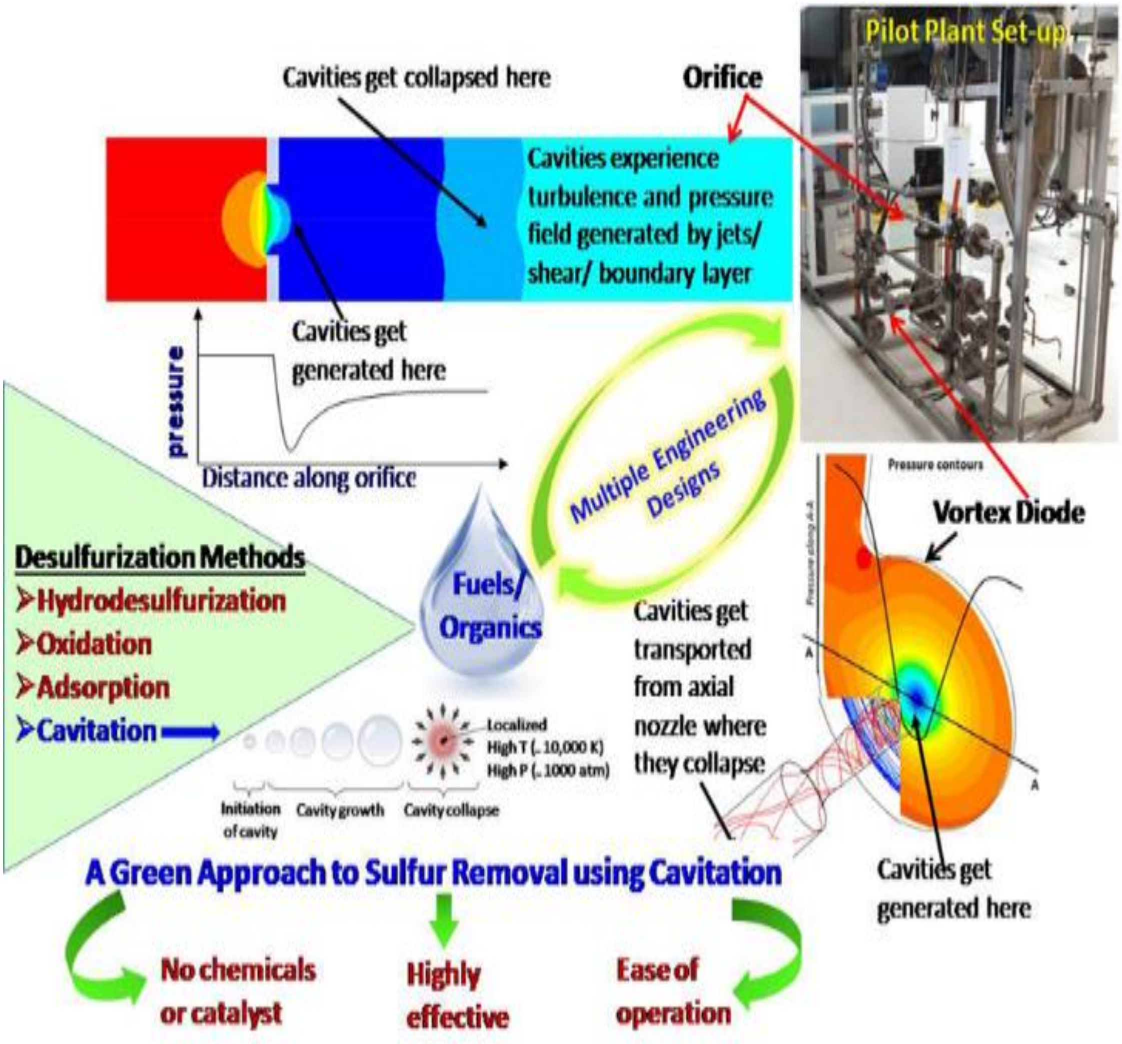

Figure 6.1: Schematic representation of cavitation process in orifice and vortex diode

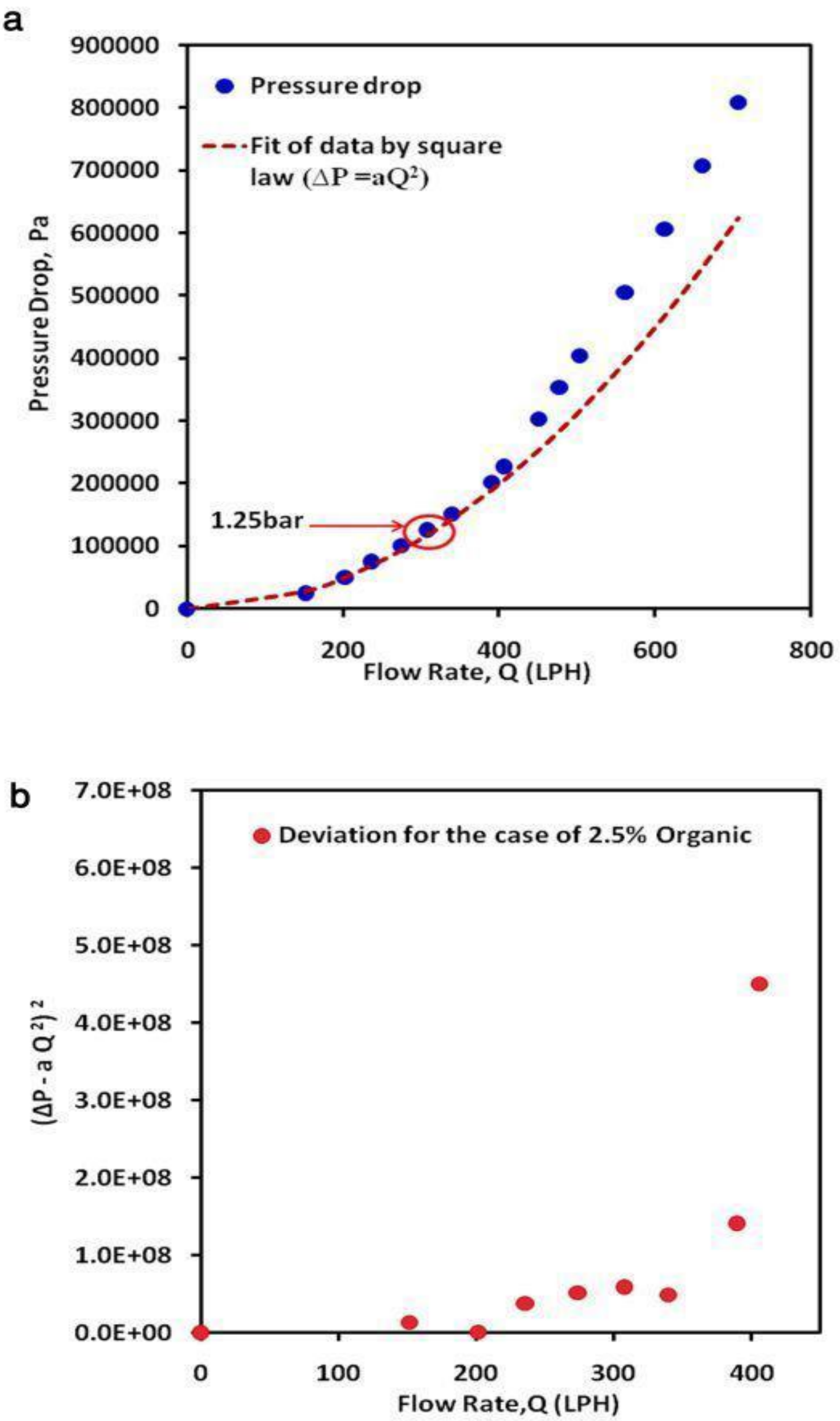

Figure 6.2: Inception of cavitation (a) Calculations to demonstrate cavitation occurring at a ΔP of 1.25 bar (b) Prediction of inception of cavitation based on deviation from square law

data pertaining to pressure drop measurements as a function of flow rate of two phase mixture (organic phase and water). The cavitation inception can be identified from the deviation of measured pressure drop from the usual square law (ΔP proportional to the square of flow rate or mean velocity), as already established from the earlier studies for vortex diode and similar observations can be made for orifice. From Fig.6.2, it is evident that while the cavitation inception in vortex diode occurs just before the pressure drop reaches 0.5 bar (~0.48 bar), for orifice the inception of cavitation is at a substantially higher pressure drop and occurs at ~1.25 bar. The major cavitation effect is however seen at ΔP 1.6 bar or higher. In view of these observations, the experiments were carried out at a pressure drop across orifice at 2 bar and above (2 bar, 5 bar and 10 bar with flow rate of ~ 390, 560 and 785 LPH).

6.3.2 Effect of pressure drop

The pressure drop across the orifice/ vortex diode or for that matter any cavitating device, is an important parameter that determines whether cavitation can take place and to what extent, apart from the cost of the operation. As is well established, the number density of cavities and intensity of cavity collapse are governed by the pressure drop across cavitating devices for a specified configuration of device and downstream design/piping. In order to establish the behaviour of desulfurization in the case of the orifice as against reported data on the vortex diode on desulfurization, experiments were carried out at three different pressure drop conditions, viz. 2, 5 and 10 bar. The results are shown in Fig.6.3-6.4. Model fuel and initial sulfur concentration (ppm) used in experimentation is shown in legends of all figures. Interestingly, similar to that reported for vortex diode, the effect of pressure drop was found to be rather negligible, especially at low values of organic to aqueous phase volume ratio.

It is evident from the Figure 6.3 and 6.4, the highest sulfur removal was observed to be above 90% at the pressure drop of 2 bar and 5 bar for 2.5 % organic volume (~92 and 95% for n-octanol), while for diesel it was ~90% in 2 hours. A lower extent of removal (~37%) was obtained for toluene as an organic phase under similar conditions. The effect of pressure drop is similar even when the organic volume is increased to 10%. It appears that low to medium ΔP values are satisfactory and removal efficiency can be significantly improved by using suitable organic solvent. The reason for this could be increased cavitation effect in the range of ΔP 2 to 5 bar, while above 5 bar ΔP, the cavities probably coalesce resembling choking which subsequently reduces the impact of cavitation. The overall effectiveness is proportional to the product of number of cavities and intensity of cavity collapse. Near the inception, cavity collapse intensity is higher since the medium is almost incompressible. However, number density of generated cavities is low. At very high pressure drop, though number density of cavities increases, the collapse intensity decreases significantly because of increased compressibility of the medium (due to the presence of a large number of bubbles). The overall effectiveness, therefore, exhibits maxima in terms of pressure drop. This aspect of cavitation in orifice is also evident from the analysis of Fig. 6.2 that deviation will continue to increase as flow rates (pressure drop) increase, however, the effect of cavitation will go from maxima since higher cavitation with higher flow rates (indicated by higher deviation) will lose effectiveness because of increased compressibility of the medium.

6.3.3 Effect of initial sulfur concentration

The initial sulfur concentrations in crude fractions can be very high, of the order of several thousand ppm as compared to processed fuel fractions such as gasoline or diesel which contain less than 300 ppm for the existing streams, in general. The developed cavitation process is considered as complimentary to the existing refinery operations and hence higher concentration was considered of the order of 300 ppm while lower concentration was considered at ~100 ppm to evaluate the effect of initial sulfur concentration. The results are shown in Figures 6.5 and 6.6. It is evident that the effect of initial sulfur concentration is more significant in diesel as a solvent as compared to other organic solvents. Also, the initial high concentration of 300ppm shows better sulfur removal as compared to 100ppm for all the solvent systems indicating efficacy of hydrodynamic cavitation for satisfactory application, if combined with existing HDS process. The higher removal at the higher initial concentration may be due the increased probability of finding sulfur species for degradation. The overall rate of desulfurization is a function of concentration of S containing species and concentration of hydroxyl radicals. Exact mechanism of oxidative desulfurization occurring with the hydrodynamic cavitation is still not yet fully known. Desulfurization reactions may happen in gas phase (in the collapsing cavity) or in the liquid phase (after hydroxyl radicals diffuse in surrounding liquid from the collapsing cavity). In any of these scenarios, increase in concentration of S containing species will increase the overall rate and therefore overall extent of desulfurization. Again, the highest sulfur removal (~95%) was obtained for n-octanol and lowest for toluene. The intensity of the effect diminishes depending upon the nature of organic phase with the increase in the organic volume. Diesel consists of complex mixtures of aliphatic and aromatic hydrocarbons and the

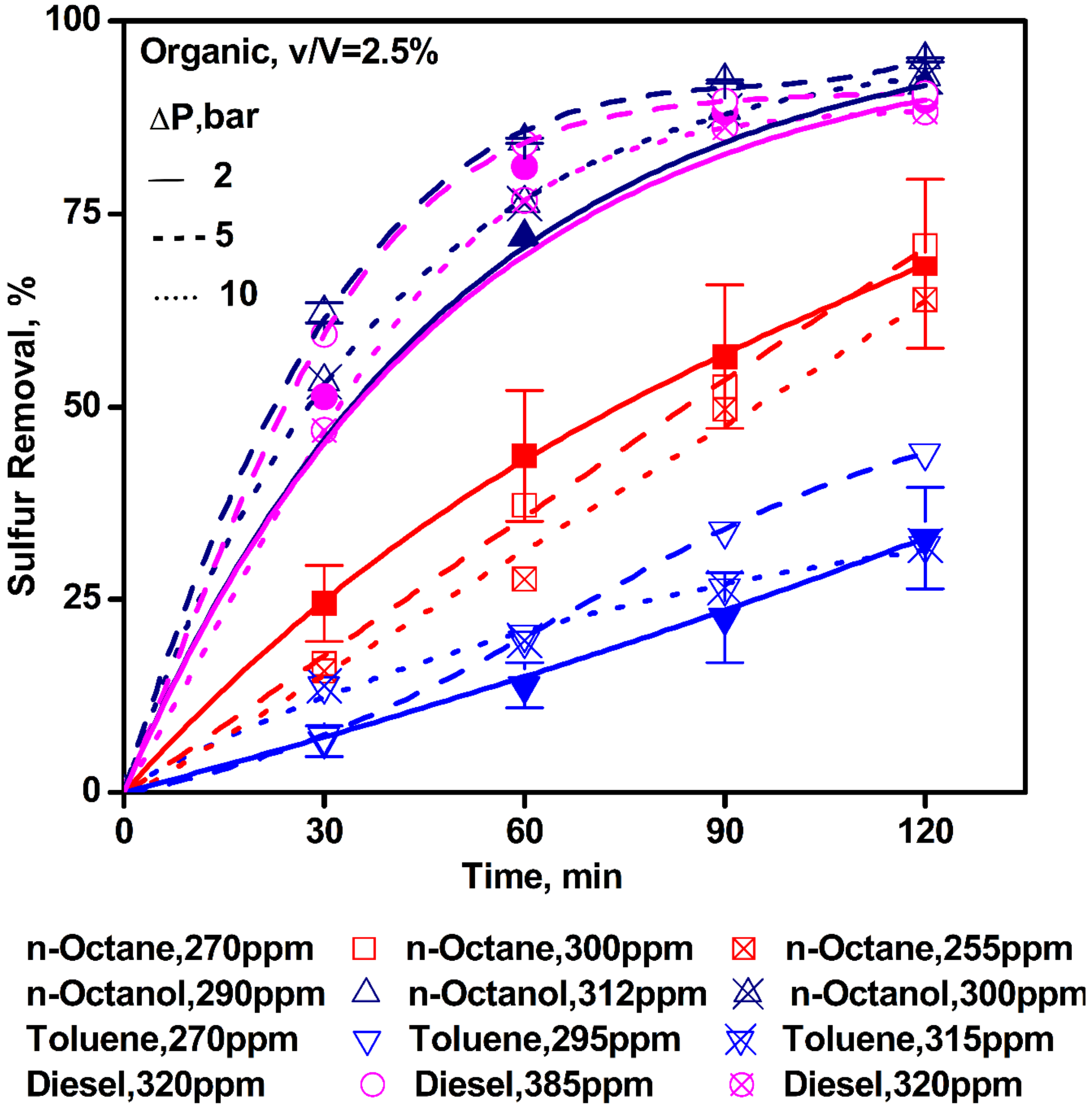

Figure 6.3: Effect of pressure drop at 2.5% organic volume fraction

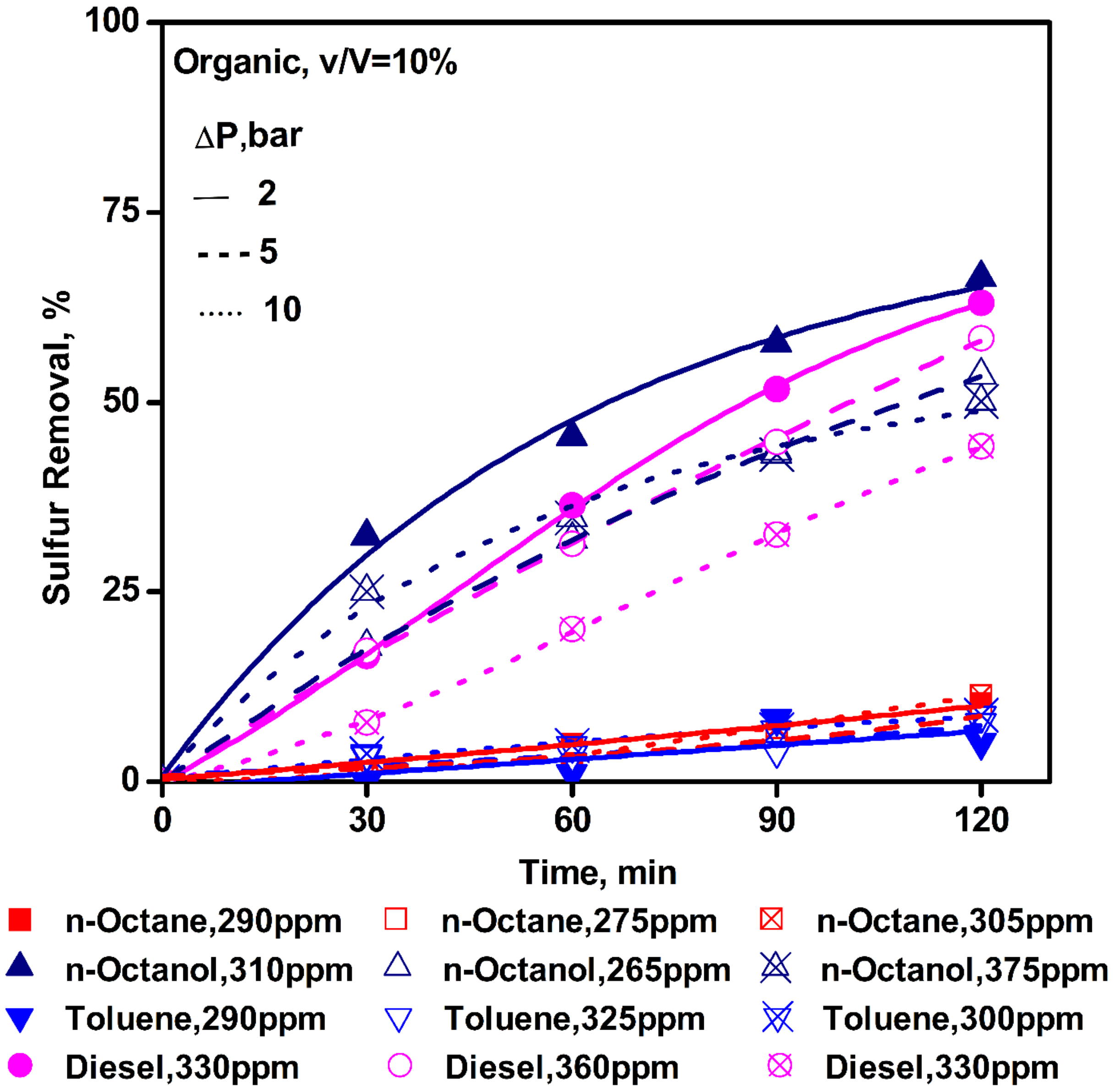

Figure 6.4: Effect of pressure drop at 10% organic volume fraction

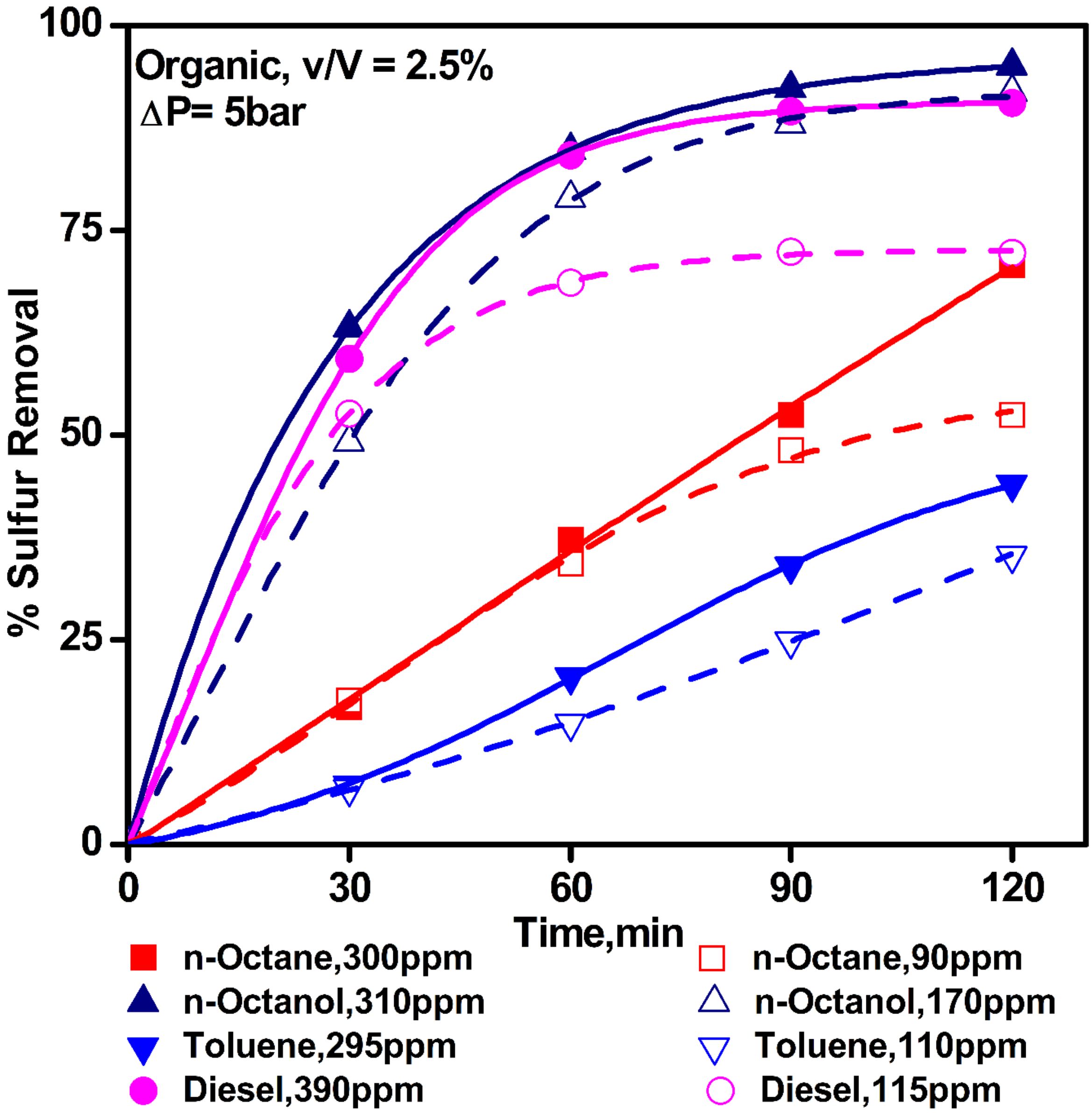

Figure 6.5: Effect of initial concentration at 2.5% organic volume

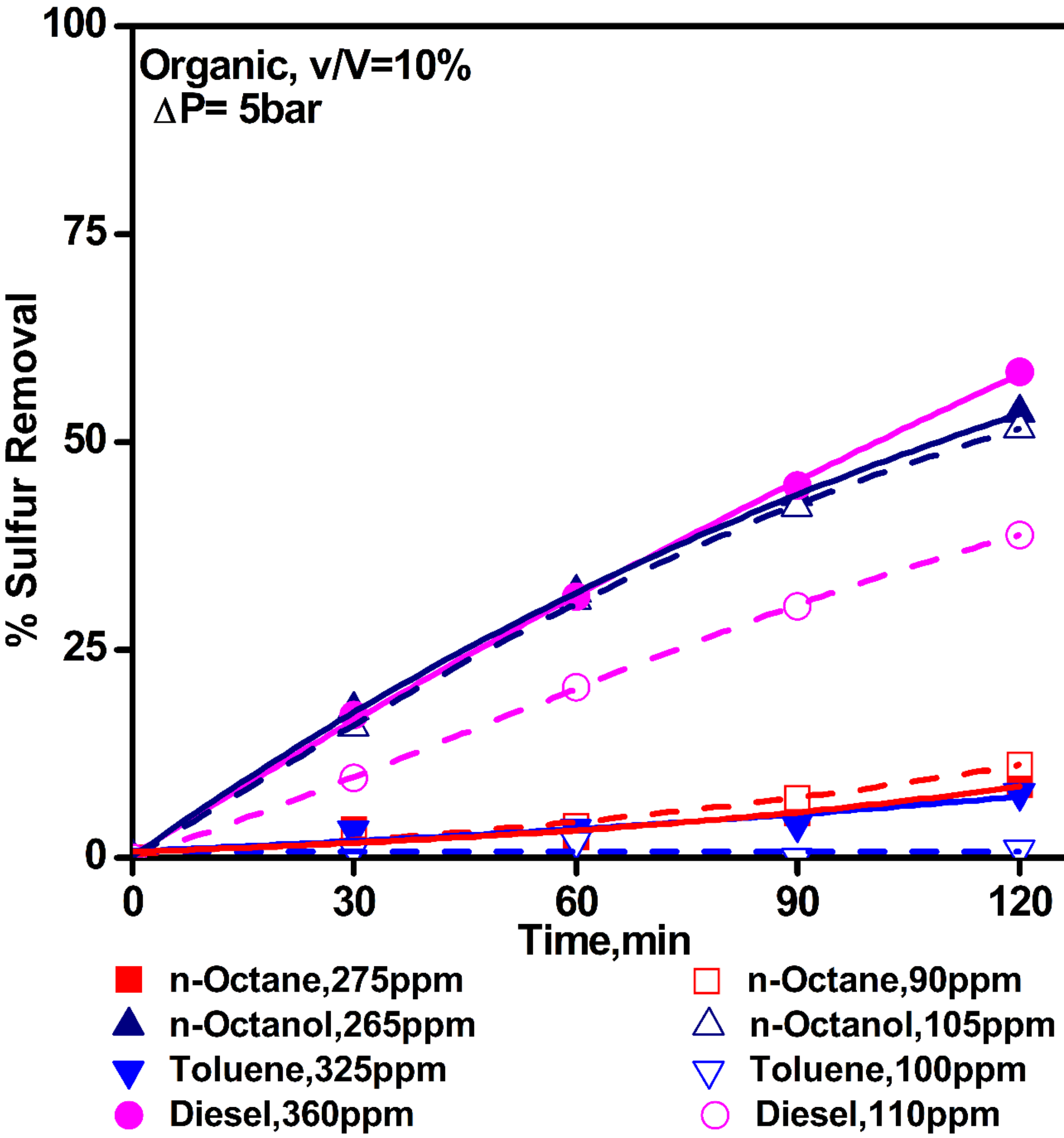

Figure 6.6: Effect of initial concentration at 10% organic volume

aromatic content can be typically in the range of 15–45%. Therefore, the differences due to nature of solvent are believed to be largely due to aliphatic nature of the solvent, while polarity of the solvent could also have some contribution. This is, however, is a complex issue pertaining to the reactivity in different solvents and needs to be investigated in detail. The order of higher impact based on initial sulfur concentration for the organic solvents studied shows the following trend.

Diesel > n-Octanol >n-Octane > Toluene

6.3.4 Effect of solvent phase ratio and nature of solvent

The process scheme developed in this work envisages predefined mixing of the organic and aqueous phases with sulfur present in the organic phase. Thus, it is expected that the ratio of organic to aqueous phase would have a significant bearing on the efficiency of sulfur removal. Figures 6.7 and 6.8 show the results of effect of the organic phase volume in terms of percentage volume of organic phase against the extent of sulfur removal. The two important observations are low organic fraction (2.5%) gives maximum sulfur removal while the nature of organic phase also play important role in deciding sulfur removal efficiency. At 2.5% organic, n-octanol and diesel shows almost equal percentage sulfur removal (~90%) at 300ppm initial concentration at all pressure drop conditions (Figure 6.3 and 6.5). Sulfur removal in the case of 10% n-octanol is higher as compared to 10% diesel for all pressure drop conditions and both initial concentrations. The organic phase ratio indicates high sensitivity for all the solvents, except toluene and lower ratio is favorable at any pressure condition, in general. The order for increase in sulfur removal efficiency for 2.5% organics can be given as:

n-Octane > n-Octanol ≥ Diesel > Toluene

It appears that reducing the organic fraction increase the sulfur removal efficiency significantly, again depending on the nature of the solvent and for the case of initial sulfur concentration of 100 ppm at 2 bar ΔP, the extent of improvement is given in Table 6.1. Toluene, as a solvent, indicated insensitivity in this regard and improvement was less significant even when the organic fraction was reduced from 10% to 2.5%. This clearly indicates that the nature of organic phase has a very high impact on the sulfur removal efficiency.

The results of this work clearly indicate that nature of the organic phase is crucial in determining the efficiency of sulfur removal (n-octanol > diesel > n-octane > toluene), which may be attributed to the aliphatic nature and polarity affecting reactivity during the oxidation reaction as mentioned earlier. Based on the dielectric constants, ε (which is taken as a measure of solvent polarity, higher ε signifying higher polarity), octanol may be considered to exhibit relatively polar character (ε=10) while for toluene, diesel and n-octane, the ε values are 2.4, 2.2 and 1.94 respectively[32,33]. The predominating factor (polarity/aliphatic/aromatic nature) under the extreme conditions of flash shockwaves is difficult to predict. Further, diesel being a complex mixture of hydrocarbons with its varying composition of aliphatic and aromatics, the oxidation chemistry is complex. However, the aliphatic nature of species such as n-octane may facilitate easy degradation while toluene is known to offer inhibition in oxidation due to the presence of π conjugated aromatic system[34]. A postulated mechanism of cavitative degradation of sulfur compounds has the following important steps[27] :

1. Generation, growth and implosion of cavities due to hydrodynamic cavitation

2. Generation of oxidising agents such as hydroxyl radicals and hydrogen peroxide

$$\begin{array}{lcl}
\mathbf{H_2O} & \leftrightarrow & \mathbf{OH^\bullet + H^\bullet} \\
\mathbf{O_2} & \rightarrow & \mathbf{2O^\bullet} \\
\mathbf{O^\bullet + H_2O} & \leftrightarrow & \mathbf{2HO^\bullet} \\
\mathbf{H^\bullet + O_2} & \rightarrow & \mathbf{HOO^\bullet} \\
\mathbf{2HO^\bullet} & \rightarrow & \mathbf{H_2O_2} \\
\mathbf{2HOO^\bullet} & \rightarrow & \mathbf{H_2O_2 + O_2}
\end{array}$$

3. Reaction of thiophene and hydroxyl radicals/oxidising agents and final degradation resulting into formation of water and SO_2

$$\mathbf{Thiophene + 2HO^\bullet \Rightarrow SO_2 + H_2O}$$
$$\mathbf{Thiophene + H_2O_2 \Rightarrow SO_2 + H_2O}$$

The reaction of thiophene and hydroxyl radical resulting into the formation of water, intermediates and SO_2 as suggested in our proposed mechanism are in line with the theoretical analysis of such reactions by Zhang et al.[35]. This conclusion has implications for the treatment of various organics for sulfur removal such as biodiesel and not just different fuel fractions. It is also essential to state that the nature of sulfur compounds is also expected to be critical in determining the process performance.

Table-6.1: Extent of improvement in sulfur removal efficiency ($\Delta P = 2$ bar; Initial sulfur conc. 100 ppm)

Solvent	**% Sulfur removal**	
	10% Organic	**2.5% Organic**
n-Octanol	60	92
Diesel	45	74
n-Octane	19	77
Toluene	0	15

6.3.5 Comparing cavitational yield for orifice and vortex diode

Hydrodynamic cavitation works through the generation of hydroxyl radicals through cleaving of water molecules an active oxidant. The *in situ* generation of oxidising agent participates in the oxidation of organics effecting their removal/degradation[36,37]. Though the mechanism for degradation of pollutants from water using cavitation is well discussed in the literature, there have not been any reports on the two phase/multiphase systems such as the one used in the present study. A plausible mechanism for the removal of sulfur[27] includes cleavage of the sulfur bond from the attack of oxidising agent and release of sulfur dioxide, while the formation of other products such as sulfones was largely unsubstantiated. In view of insolubility of the thiophene in water and the huge difference with respect to the organic solvent, the possibility of physical transfer of the thiophene in the aqueous phase is negligible. Thus, removal of sulfur is believed to be as SO_2 and mineralization of the organic skeleton to final products as carbon dioxide and water. Again, it should also be possible for cavitation to work as a specific form of extractive, but not catalytic, oxidative desulfurization with water as a solvent and without employing any conventional catalyst of the type reported in the literature for ECOD. The other possibilities such as the formation of SO_2, HSO_3, H_2SO_4 etc. or organic species entering into the aqueous phase due to cavitation were not very relevant[27]. However, the formation of acid catalyst can certainly assist oxidative desulfurization[28,29], though, in the absence of an acid catalyst, the contribution of this mechanism may not be significant. Further, the nature and the number of cavities in vortex diode and in orifice could be substantially different and the exact mechanism appears to be much more complex and needs to be investigated in detail. It is believed that the role of solvent may be a facilitator in oxidative interfacial reactions for effecting the transfer of sulfur moiety in cavities housing oxidising species.

Kulkarni et al.[38] reported the velocity and pressure distribution in reverse flow vortex diode suggesting maximum pressure drop in reverse flow as compared to forward flow. Thus, in vortex diode, when the flow enters through the tangential port, a strong vortex flow gets created. As seen from Figure 6.1 and 6.9a, in the vortex flow, tangential velocity increases towards the center and pressure reduces at the center with the color mappings indicating the different pressure/temperature regions. Strongly swirling flow generates a low pressure region at the center of the vortex, extending into the axial port, which leads to cavitation[39] . As pressure is recovered in downstream-axial port then cavity collapse occurs that generates localized high shear, high temperature and pressure conditions and hydroxyl radicals. The orifice used in the present study is a simple single 3 mm diameter constriction which provides increased velocity head at the expense of pressure at the point as shown in Figure.6.1 and Figure 6.9b. The trajectories of cavities and pressure history experienced by cavities in these two cavitation devices are quite different resulting in different distribution of number density and collapse intensity of cavities. It will be instructive to evaluate the performance of vortex diode and orifice for desulfurization of fuels using the definition of cavitational yield which is given by Eq.(1)[40],

$$\boldsymbol{Cavitational\,Yield, Y\ (mg/J) = \frac{R}{\Delta P * Q * t}} \qquad (\mathbf{1})$$

Where R is amount of sulfur removed (mg), ΔP (N/m^2) is the pressure drop across the cavitation device, Q (m^3/s) is flow rate and t (s) is the time required for sulfur removal. Figure 6.9 (a-d) shows the cavitational yield comparison for vortex diode and orifice.

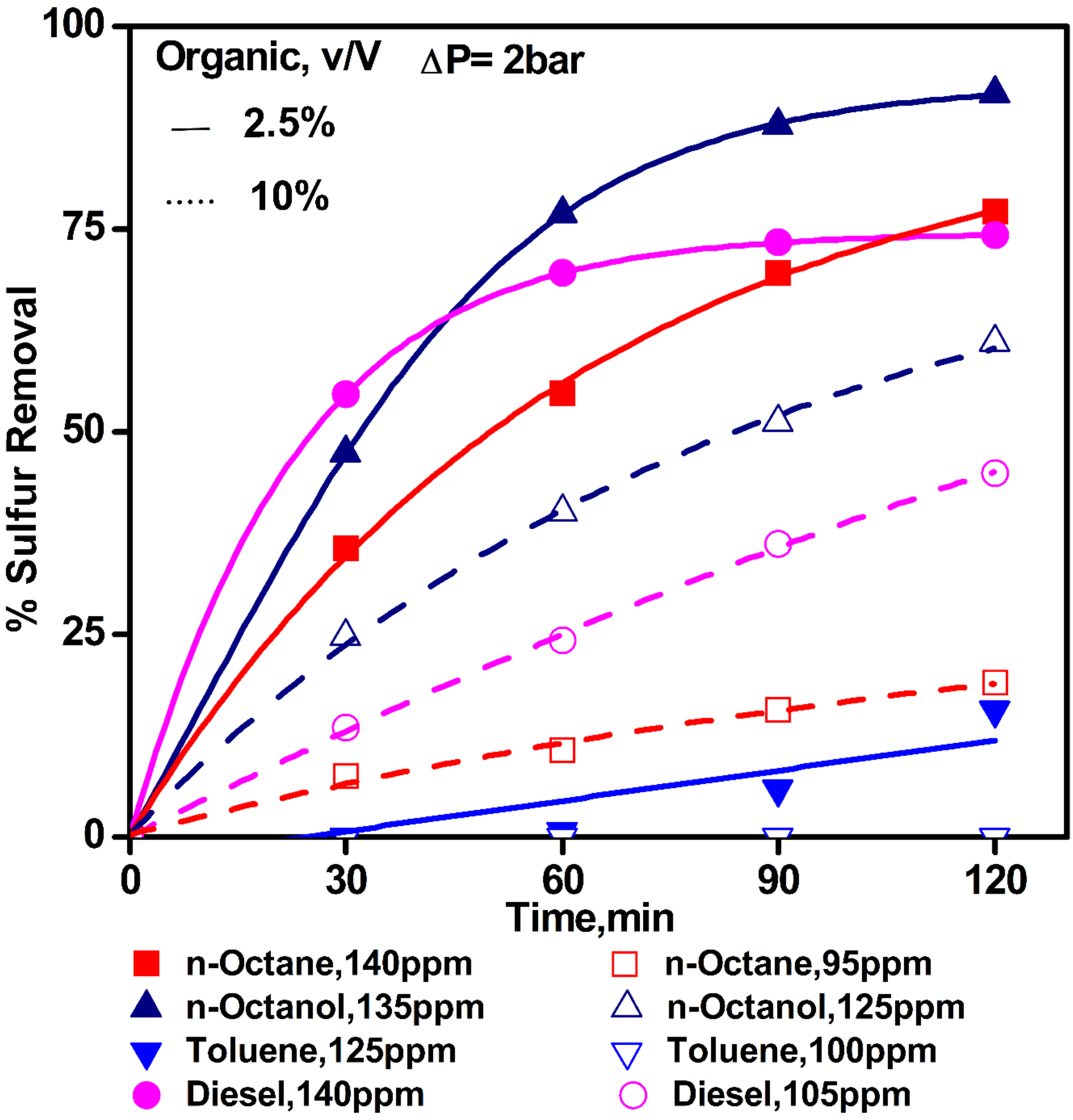

Figure 6.7: Effect of organic phase ratio at pressure drop, 2 bar

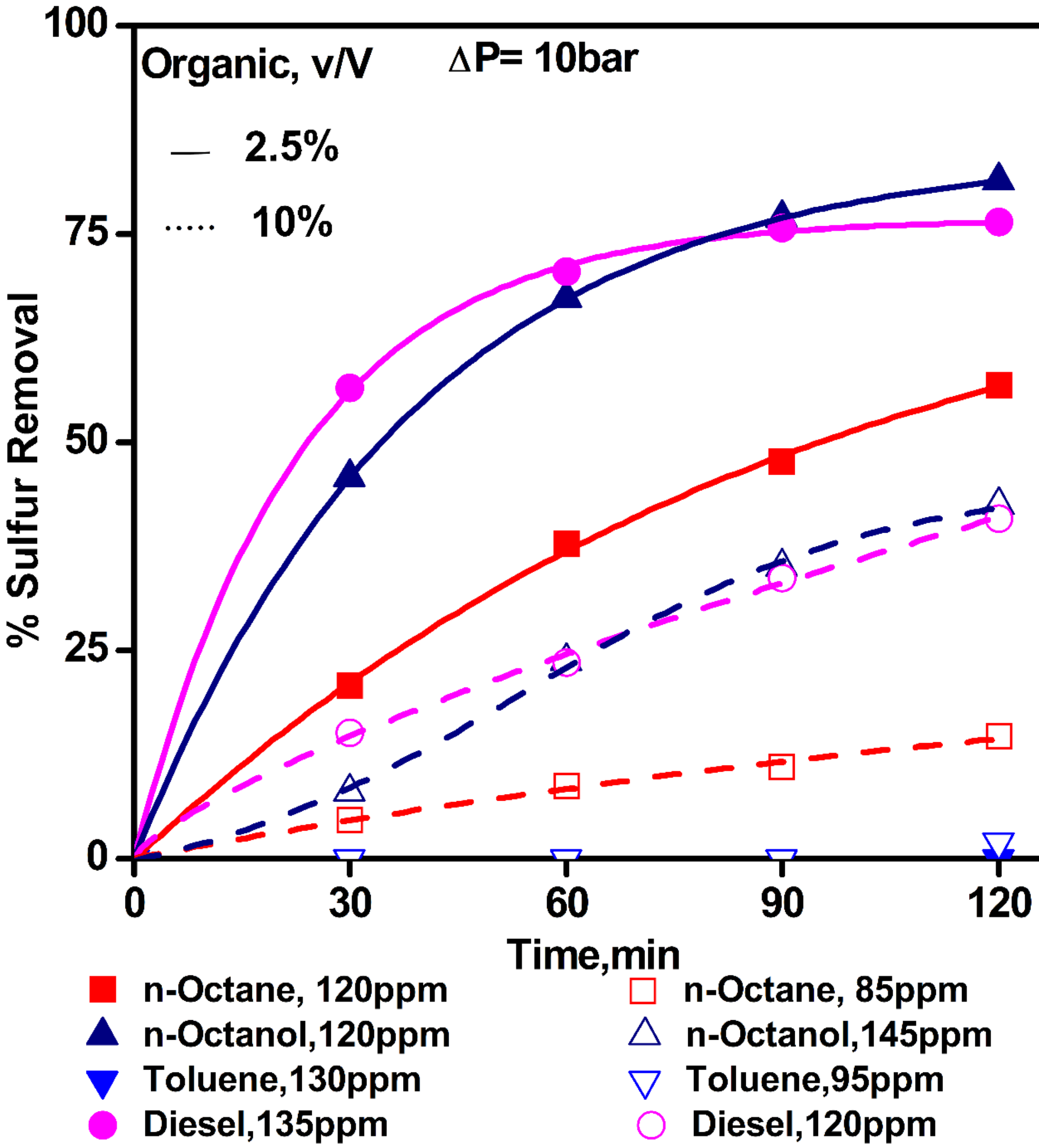

Figure 6.8: Effect of organic phase ratio at pressure drop, 10 bar

It can be seen that there is a huge difference in the cavitational yield depending on the design of the cavitation reactor. As compared to that for orifice, the cavitational yield can be significantly higher for vortex diode and the impact is more prominent at high initial sulfur concentrations (e.g. Y= 8.6×10^{-4}, 1.17×10^{-3}, 3.88×10^{-4} for diode vs. 2.99×10^{-4}, 3.33×10^{-4} and 5.35×10^{-5} for orifice in the case of n-octane, n-octanol, toluene respectively at initial concentration of ~100 ppm at 2.5% organic volume fraction). Similarly, the observed difference indicates 8, 4, 10 and 4 times yield values with vortex diode for initial sulfur concentration of 300ppm and 10% organic volume for n-octane, n-octanol, toluene and diesel respectively. The reason for better cavitational yield in vortex diode can be attributed to the rotational flow in the axial port of vortex diode. The generated cavities and droplets of organic phase remain concentrated in the core of the axial port owing to their lower density compared to the water phase. This realizes significantly enhanced contact among cavities and organic droplets leading to better cavitational yield compared to orifice where no such preferential contact is realized. Although, the sulfur removal is increased at low organic volume fractions of 2.5%, the difference in the cavitation yield here is somewhat less, 4, 3 and 2 times for n-octane, n-octanol, and toluene respectively.

6.3.6 Comparing cost of desulfurization in different cavitating devices

It is instructive to evaluate the cost of hydrodynamic cavitation using different devices from commercial application point of view. The actual cost can be simply obtained by considering cost of 1 electricity unit. Thus, the cost, C (kWh/kg), can be simply related to the cavitational yield ‘Y’ (mg/J) by Eq. (2) as:

$$\mathbf{C} = \frac{\mathbf{1}}{\mathbf{3.6\,\sigma\,Y}} \tag{2}$$

Where, σ is efficiency of the pump. Assuming pump efficiency as 0.6, we get C=0.463/Y, kWh/kg. For example, if Y is 0.001, we get C=463 kWh/kg. In Indian scenario, assuming electricity price of ~Rs 10 / kWh, the cost is less than Rs. 5000/kg of S removed which is quite attractive. A sample calculation of the cost is given below

Step1: Cost calculations using cavitational yield

$$\frac{1}{Y} = Energy\ required\ to\ pump\ for\ desulfurization\ of\ 1mg\ of\ sulfur, \frac{J}{mg}$$

Unit conversion

$$\frac{J}{mg} = \frac{watt.sec}{mg}$$

$$\frac{J}{mg} = \frac{Kilowatt(kW).h}{3.6 \times kg}$$

Step2: Simplified formula for obtaining cost of hydrodynamic cavitation process

$$C = cost\ for\ hydrodynamic\ cavitation, \frac{kWh}{kg} = \frac{1}{3.6 \times Y} \tag{3}$$

Step 3:

$$C = cost\ for\ hydrodynamic\ cavitation, \frac{kWh}{kg} = \frac{1}{3.6 \times \sigma \times Y} \tag{4}$$

Where, σ is centrifugal pump efficiency,
Y is cavitational yield in mg/J and
3.6 is unit conversion factor

Example:

For Vortex diode, 300ppm and 10% n-Octanol (Assume pump efficiency, σ = 60%)
For Y=0.01 mg/J (from Figure 6.10c), the cost is obtained as: **C = 46.30 kWh/kg**

The costs of desulfurization for two different devices and for different organic solvents are given in Figure 6.11 which also indicates effect of concentration and solvent ratio on the cost. It can be seen that the cost is low for many solvents. It should be further noted that even when the efficiency of sulfur removal is lower for higher solvent volume fraction, in general (e.g. 10% compared to 2.5%), the cost of sulfur removal is lower compared to low solvent volume fraction due to the processing of higher volume of organics. Thus, a compromise between sulfur removal efficiency and cost of processing is essential, apart from nature of the solvent. An extraordinarily low cost was obtained for efficient solvent such as n-octanol and also for commercial diesel at 10% volume.

From Figure 6.11, it is seen that the cost of desulfurization is substantially lower in the case of vortex diode as compared to orifice, irrespective of processing parameters. This is also supported by the data of cavitational yields obtained for vortex diode as compared to orifice.

An approximate analysis of the cost comparison with other processes indicates operating cost of conventional hydrodesulfurization process for the removal of sulfur as \$16.84/kgS[41]. Typically, the cost of commercial adsorbent varies in the range of \$0.35/kg-20\$/kg. Considering sulfur selective adsorbent, even if the adsorbent cost is considered on the lower side at ~\$5/kg and capacity is assumed to be 30 mg/g, the cost would be ~\$166/kgS. In this comparison, the cost of hydrodynamic cavitation would be ~\$3/kgS, significantly lower than both hydrodesulfurization and adsorptive desulfurization.

The finding of this work and the comparison between two cavitating devices clearly strengthen the premise stated in our earlier work that the proposed method can be effectively employed to reduce sulfur content of transportation fuels or other organic streams. As an engineering design, the aqueous phase can be recycled by appropriately adjusting the purge and make-up water. Further, the simplicity of the proposed method lies in the use of simple cavitating devices such as orifice or vortex diode, ease of operation, and compact set-up for effective removal of sulfur. Process intensification in the form of aeration or employing homogeneous/heterogeneous catalyst should also be possible. Therefore, the method can be effectively implemented for large scale deep desulfurization operation, not just for fuels, but also for different organics.

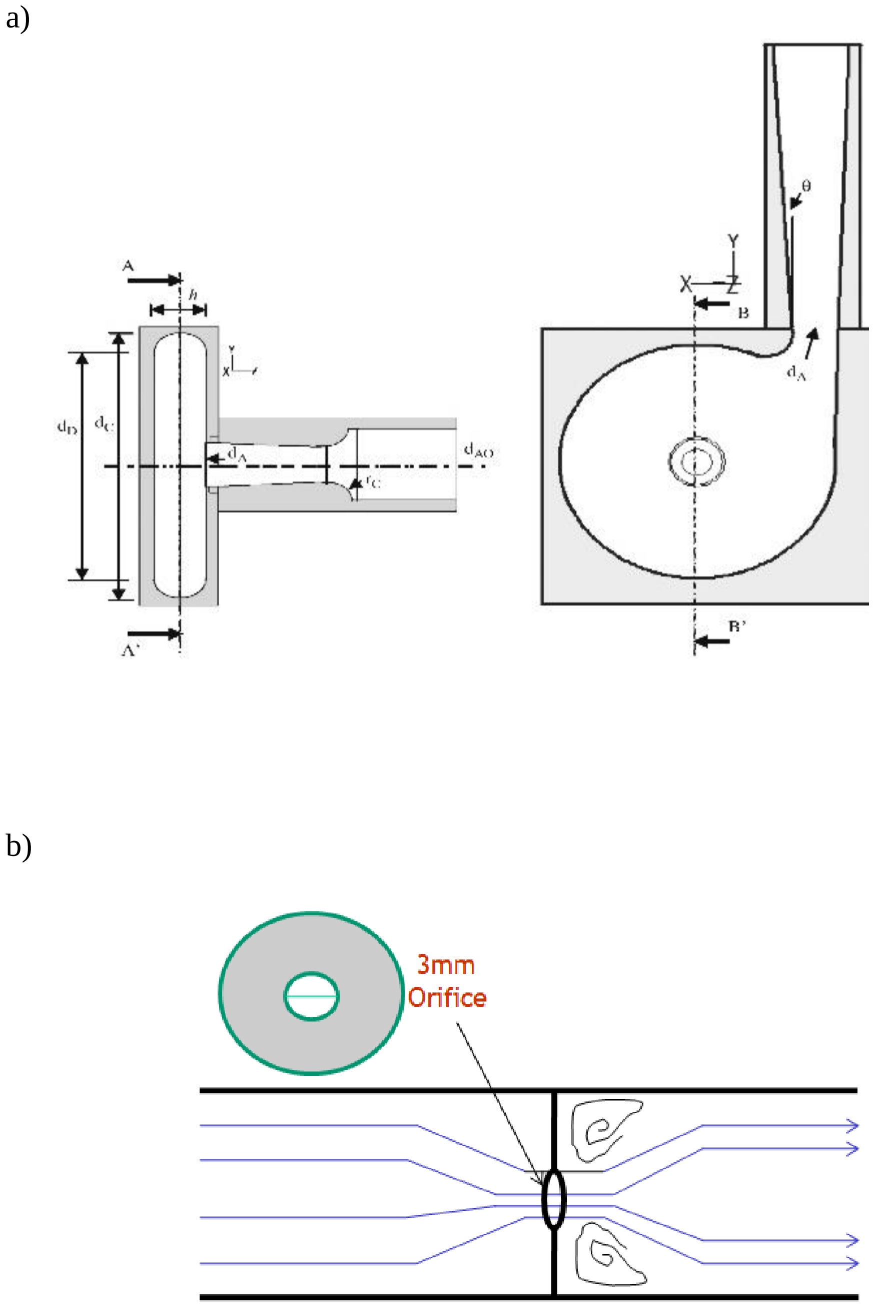

Figure 6.9: Design of (a) Vortex diode[42] (2) Orifice

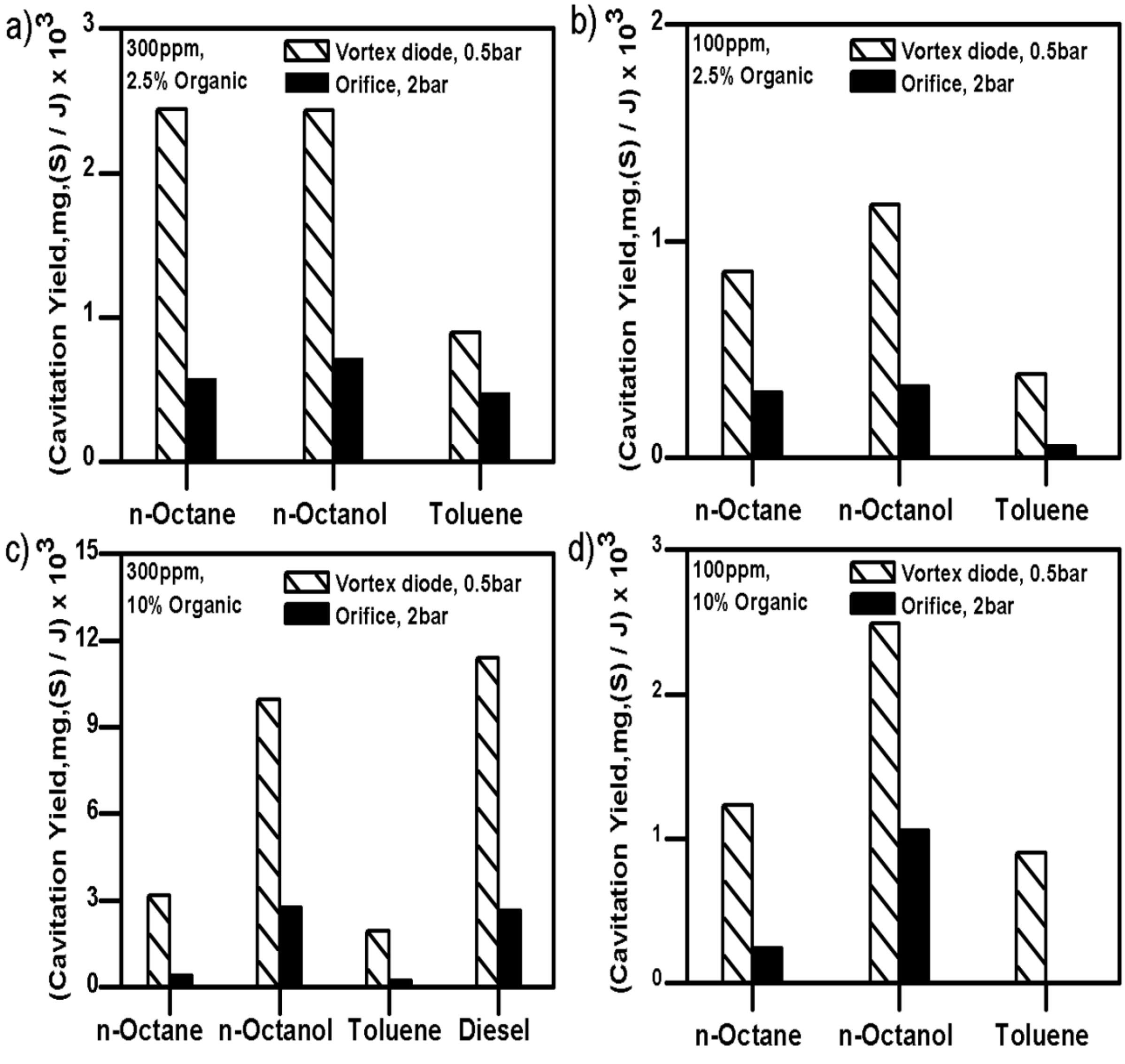

Figure 6.10: Comparison of cavitational yield for vortex diode and orifice

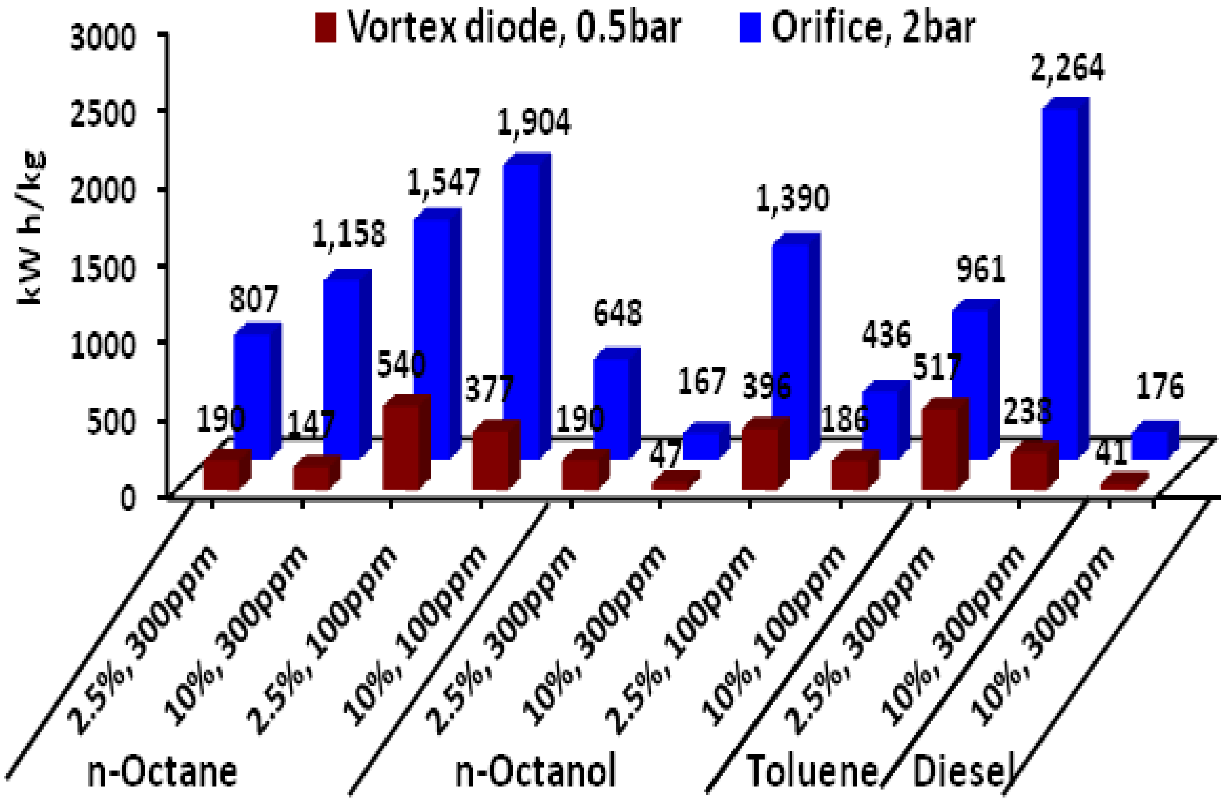

Figure 6.11: Representative cost/energy comparison for desulfurization using hydrodynamic cavitation for orifice and vortex diode

6.4 Conclusions

A multiphase non-catalytic hydrodynamic cavitation process using orifice as a linear flow based cavitating device has been demonstrated for deep desulfurization of fuels or organics and the results have been compared with vortex diode as a vortex flow based cavitating device. The important conclusions can be listed as:

1. The inception of cavitation takes place at a significantly lower pressure drop in the case of vortex diode than that in the orifice. Thus, in vortex diode, the inception was found to occur at a pressure drop of ~0.48 bar as compared to higher pressure drop of ~1.6 bar in the case of orifice.
2. The non-catalytic hydrodynamic cavitation process can efficiently remove sulfur (thiophene) from fuels for the cavitating devices such as orifice and vortex diode.
3. The process offers many advantages, most importantly ease of operation and mild operating conditions for effective sulfur removal.
4. The results on the sulfur removal confirm effect of solvent ratio and the nature of organics apart from pressure drop, and initial concentration of sulfur during the cavitation process.
5. The nature of solvent has high impact on desulfurization and a very high sulfur removal was obtained for n-octanol and commercial diesel as organic phase.
6. The comparison of cavitational yield shows that the yield is nearly an order of magnitude higher in the case of vortex diode as compared to orifice.
7. The cost of desulfurization using hydrodynamic cavitation process was found to be quite low. Further, the operating cost is significantly lower in the case of vortex diode as compared to the orifice.

In view of the efficient sulfur removal from fuels accompanied by the low cost of operation, the proposed method can be considered as techno-economically sustainable alternative and can be effectively implemented for large scale deep desulfurization operations.

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Chapter 7

Chapter 7
Summary

The present study successfully demonstrates the possible technological alternatives to the existing desulfurization processes, especially from the point of view of deep desulfurization of transportation fuels. In the first section, the conventional adsorptive deep desulfurization was investigated in detail using both commercial as well as newer materials for sulfur removal. Further metal modifications were explored in the form of single metal modifications and double metal modification for a number of commercial and newly laboratory synthesized activated carbon materials to gain insight into the possible mechanism of adsorptive sulfur removal and for increasing the adsorption capacity/selectivity for the refractory sulfur compounds. New methodologies were discussed for the synthesis of adsorbents and also for the material modifications and all the materials were thoroughly investigated using different characterization techniques. Four different metals Zn, Co, Ni and Cu were used to modify the surfaces of commercial adsorbents (such as SHIRASAGI TAC and SRCx) and lab synthesized adsorbents (CFP-450), evaluated for deep desulfurization along with process intensification using acoustic cavitation. The important findings of this study include:

1. Sulfur specific adsorbents, commercial Shirasagi TAC, SRCx and laboratory synthesized CFP-450 have high capacity for sulfur removal. A sulfur removal close to 100% can be obtained for refractory sulfur compounds (BT and DBT) for Shirasagi TAC carbon adsorbent.

2. Huge difference in selectivity was observed for the three sulfur compounds, thiophene, benzothiophene and dibenzothiophene, clearly highlighting the dependence on the nature of sulfur compounds. Selectivity for thiophene was lowest and near complete removal of benzothiophene and dibenzothiophene was obtained.

3. Metal modification, in general, increases sulfur removal capacity. Cobalt metal modification of the adsorbent, especially for thiophene removal, was found to be more

effective than Ni, Cu and Zn. Double/multiple metal modification was also effective to a certain extent.

4. A significant increase in thiophene adsorption was observed with single metal modification of CFP-450 by Cu and Ni, which can be further improved by using the double modification.

5. Process intensification using acoustic cavitation could significantly enhance the adsorptive sulfur removal and close to 100% improvement could be obtained for thiophene removal. Modification of carbons and process intensification, combined together, can substantially improve sulfur removal.

6. Thus, tailoring/surface modification of carbon adsorbents along with process intensification appears to be a promising approach in adsorptive deep desulfurization of fuels.

Apart from the conventional approach of adsorptive deep desulfurization, a new approach non-catalytic approach was also developed for deep desulfurization of transportation fuel. The process involves pre-programmed mixing of the organic and aqueous phases, and passing through simple mechanical cavitating devices such as orifice or vortex diode. The effects of process parameters and engineering designs were established for three organic solvents (n-octane, toluene, n-octanol) and commercial diesel for model sulfur compound - thiophene. The important conclusions from this study are:

1. The non-catalytic hydrodynamic cavitation process can efficiently remove sulfur (thiophene) from fuels using the cavitating devices such as orifice and vortex diode.

2. Cavitation inception in vortex diode occurs just before the pressure drop reaches 0.5 bar (~0.48 bar), for orifice the inception of cavitation is at a substantially higher pressure drop and occurs at ~1.25 bar. The major cavitation effect for orifice is however seen at ΔP 1.6 bar or higher.

3. The results on the sulfur removal indicate significant effect of solvent ratio and the nature of organics apart from pressure drop, and initial concentration of sulfur during the cavitation process.

4. Nature of the organic phase is crucial in determining the efficiency of sulfur removal (n- Octanol > Diesel > n-Octane > Toluene), which may be attributed to the aliphatic nature and polarity affecting reactivity during the oxidation reaction.

5. The organic phase ratio indicates high sensitivity for all the solvents, except toluene and a lower ratio is favourable at any pressure condition, in general. The order for the increase/increment in sulfur removal efficiency for 2.5% organics can be given as:
   n-Octane > n-Octanol > Diesel > Toluene

6. The initial concentration of sulfur in the organics and effectiveness of the developed process at low pressure drop have important bearing from the view point of commercial operations. Since conventional hydrodesulfurization process has limitations in bringing down sulfur levels below 300ppm, a process that can take care of sulfur removal from this point can be highly beneficial. The results of this work clearly indicate effectiveness for initial concentrations up to 500ppm. Further, effective deep desulfurization at low pressure drop of just 0.5 bar across vortex diode indicates lower cost of operation and significant ease of operation. Another important aspect of the process is that it is effective without using any catalyst or requiring high temperatures/pressures.

7. The process can completely remove thiophene sulfur from organic streams with considerable ease of operation and under mild operating conditions.

8. The results were also verified using commercial diesel and results indicate a very high removal of sulfur even from the commercial diesel which is a mixture of aliphatic and aromatic organic compounds.

9. Sulfur removal mechanism appears to be much more complex and needs to be investigated in detail. The process essentially exploits in situ generation of oxidising agents such as hydroxyl radicals for oxidative removal of sulfur.

10. Cavitational yield is significantly higher for vortex diode and the impact is more prominent at high initial sulfur concentrations (e.g. Y= 8.6 × 10^{-4}, 1.17 ×10^{-3}, 3.88 × 10^{-4} for diode vs. 2.99 × 10^{-4}, 3.33 × 10^{-4} and 5.35 × 10^{-5} for orifice in the case of n-octane, n-octanol, toluene respectively at initial concentration of ∼100ppm at 2.5% organic volume fraction). Similarly, the observed difference indicates 8, 4, 10 and 4 times yield values with vortex diode for an initial sulfur concentration of 300ppm and 10% organic volume for n-octane, n-octanol, toluene, and diesel respectively.

11. The aqueous phase used in the proposed method can be recycled after removing a purge stream (with corresponding make-up water).

12. Cost of desulfurization is substantially lower in the case of vortex diode as compared to the orifice, irrespective of processing parameters. Estimated operating cost using hydrodynamic cavitation is far lower than the conventional refinery hydrodesulfurization process and adsorptive desulfurization process.

13. The proposed method can be implemented in a compact set-up with effective removal of sulfur. The process may be further intensified using a number of ways e.g. aeration, catalyst etc. Hydrodynamic cavitation usually improves performance with scale-up.

In conclusion, the present study clearly highlights newer developments in the existing deep desulfurization processes such as adsorptive deep desulfurization and also presents a newer technology based on hydrodynamic cavitation for the deep desulfurization of transportation fuels. The analysis provided clearly indicates techno-economic feasibility for the implementation of the developed methodologies.

Chapter 8

Chapter 8
Scope for Future Work

In the present study, we have explored one conventional process of deep desulfurization-adsorptive desulfurization and one new process of hydrodynamic cavitation. Considering the subject of deep desulfurization of fuels that demands sulfur content below 10ppm, adsorptive process appears to be a natural choice. However, the present study while showing improvements using newer materials and material modifications, also highlighted the limitations of the adsorptive processes that require significant research in future:

1. The benefits in terms of high capacity for new or existing commercial adsorbents, material modifications appear to be only incremental and not substantial, limiting the application of adsorbents. Thus, it requires newer developments in terms of new materials and material modifications for commercial application. It is necessary to study effect of multi metal modification on the carbon surface by choosing appropriate metal pairs to enhance the adsorption capacity.

2. The regeneration of conventional as well as new adsorbent materials is far from being satisfactory. Thus, research is required on regeneration of the adsorbents for the adsorptive desulfurization process to be viable.

3. There is limited understanding as far as mechanism of adsorptive deep desulfurization is concerned for different types of adsorbents ranging from zeolites to carbon-based materials apart from the role of metal modification in sulfur removal. This aspect also requires detailed investigation in future to enable tailor made adsorbents for deep desulfurization.

4. The process intensification in the form of acoustic cavitation appears to be attractive and proof of concept has been provided in the present study. This needs to be explored in detail in future.

5. A new process using hydrodynamic cavitation was shown to be very effective in deep desulfurization of fuels. The process needs to be studied in detail for different reactor configurations and for optimization of process parameters such as solvent, recycle of the aqueous stream, energy requirement and so on. Further, systematic research is required for the removal of different sulfur compounds such as benzothiophene and dibenzothiophene.

6. Significant research is required to elucidate exact mechanism of deep desulfurization using hydrodynamic cavitation.

7. Research is required for developing mathematical models for the prediction of sulfur removal behaviour using hydrodynamic cavitation.

8. Research is also needed to explore different process intensification alternatives in desulfurization using hydrodynamic cavitation that may include addition of different oxidising agents or modification of reactor design. The process may also improve by using suitable homogeneous catalyst or heterogeneous catalyst using suitable process modifications. Engineering modifications in this regard may also have to be explored in future.

List of Patents, Publications, Conference Presentations and Achievements

Patent

1. Bhandari V. M., Ranade V. V. and **Suryawanshi N. B**. 2015. *Novel process for desulfurization of fuels and organics*. Patent Filed-20/10/2015 (2015-INV-0092: 0230NF2015)

Publications

1. **Nalinee B. Suryawanshi**, Vinay M. Bhandari, Laxmi Gayatri Sorokhaibam, and Vivek V. Ranade. *Non-catalytic Deep Desulfurization Process using Hydrodynamic Cavitation*. Scientific Reports. 6, 33021 (2016). http://doi.org/10.1038/srep33021

2. **Nalinee B. Suryawanshi**, Vinay M. Bhandari, Gayatri Sorokhaibam and Vivek V. Ranade. *Developing techno-economically sustainable methodologies for deep desulfurization using hydrodynamic cavitation*. Fuel, 210, 482–490 (2017). http://doi.org/10.1016/j.fuel.2017.08.106

3. **Nalinee B. Suryawanshi,** Vinay M. Bhandari, Gayatri Sorokhaibam and Vivek V. Ranade. *Investigating adsorptive deep desulfurization of fuels using metal modified adsorbents and process intensification by acoustic cavitation. Ind. Eng. Chem. Res, 58,18, 7593-7606* *http://doi.org/10.1021/acs.iecr.8b04043* .

Conference presentations

1. **Nalinee B. Suryawanshi**, Vinay M. Bhandari, Laxmi Gayatri Sorokhaibam and Vivek V. Ranade. Evaluating sulfur specific adsorbents, metal modifications and process intensification for enhanced sulfur removal from fuels. *American Chemical society - Asia Pacific International Chapter Conference (ACS-APICC)*, Jeju. Korea, 5-8 Nov, 2017.

2. **Nalinee B. Suryawanshi**, Vinay M. Bhandari, Laxmi Gayatri Sorokhaibam and Vivek V. Ranade.Developing sustainable methodologies for desulfurization of fuels. *Sustainable catalytic technologies*, CSIR-NCL,Pune, 8-9 June, 2017

3. **Nalinee B. Suryawanshi**, Vinay M. Bhandari, Laxmi Gayatri Sorokhaibam and Vivek V. Ranade. Newer developments in desulfurization of transportation fuels. *Recent advancements in chemical, environmental and energy engineering (RACEEE)*, Chennai, 23-24 Feb, 2017

4. **Nalinee B. Suryawanshi**, Vinay M. Bhandari, Laxmi Gayatri Sorokhaibam and Vivek V. Ranade. Air pollution control through deep desulfurization of transportation fuels. *International conference on sustainable development for energy and environment (ICSDEE),* CSIR-NCL, Pune, 16-17 Jan, 2017

5. **Nalinee B. Suryawanshi**, Laxmi Gayatri Sorokhaibam, Monal S. Salvi, Vinay M. Bhandari and Vivek V. Ranade. Newer adsorbents, adsorbent modifications and process intensification for production of ultra-low sulfur diesel. *7th DAE-BRNS symposium on emerging trends in separation science and technology (SESTEC)*, Guwahati, 17-20 May 2016

6. **Nalinee B. Suryawanshi**, Vinay M. Bhandari, Vivek V. Ranade. Newer carbon adsorbents and process intensification methodologies for deep desulfurization of fuels. *National conference on carbon materials (NCCM)*, Delhi, 26-28 Nov. 2015.

Achievements

1. **SRISTI- Gandhian Young Technological Innovation award 2019**. This award is bestowed by Vice President of India on 6th July 2019 at Vigyan Bhavan, Delhi.

2. **SERB-IGCW 2017 award** in knowledge community- Students category for outstanding case studies incorporating the Principles of Green Chemistry and Engineering into Chemistry routes, Chemical designs and Manufacturing Practices; and

steps taken towards pollution prevention while meeting the triple bottom line of People, Profit and Planet. It carries a cash prize of Rs. 50000/- and trophy.

3. **ACS APICC first place oral competition cash award** of $75 for the paper entitled Evaluating sulfur specific adsorbents, metal modifications and process intensification for enhanced sulfur removal from fuels in ACS - Asia Pacific International Chapter Conference, Jeju. Korea

4. **Awarded travel grant** of $450 from ACS-APICC-2017 in ACS- Asia Pacific International Chapter Conference, Korea

5. **Awarded Indian Science and Engineering Research board** (SERB) **grant** to attend the ACS- APICC-2017 conference in Korea

6. **Keerthi Sangoram Memorial Endowment Award of CSIR-NCL for "Best Research Scholar**" **in Engineering Sciences - 2017** for studies in desulfurization of fuels. It carries a cash prize of Rs. 5000/- and citation.

7. **B.D Kulkarni award for Best published research publication in chemical engineering/ Technology with highest impact-2017** for the research publication "Developing techno-economically sustainable methodologies for deep desulfurization using hydrodynamic cavitation". It carries a cash prize of Rs. 5000/- and citation.

8. **B.D Kulkarni award for Best published research publication in chemical engineering/ Technology with highest impact-2016** for the research publication "A Non-Catalytic deep desulfurization process using hydrodynamic cavitation. It carries a cash prize of Rs. 5000/- and citation.

9. **RACEEE 2017- Best Paper award** for the paper entitled Newer Developments in Desulfurization of Transportation Fuels presented in 2nd International Conference on Recent advancements in chemical, Environmental & Energy Engineering held at SSN college of Engineering, Chennai, India, 23-24 Feb 2017