A PROCESS STUDY OF THE PREPARATION OF 2,3-HYDROXYNAPHTHOIC ACID (BON ACID) FROM 2-NAPHTHOL

A THESIS
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BY

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(P.G.Phadtare)

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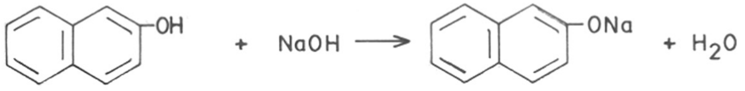
INTRODUCTION

General

2-Oxynaphthoic acid, commercially known as 'BON' acid, is a valuable intermediate in the dyestuff industry. The arylamides of BON acid (Naphthol AS series) have vastly extended the scope of azoic colors. The dyes produced on cotton fibre by these naphthols are comparable to anthraquinonoid vat dyes for their deep brilliant shades and all round fastness properties.

BON acid is prepared by the action of dry CO_2 on dry alkali naphtholate. The process is usually referred to as the Kolbe synthesis after its discoverer. Later Schmitt improved the process by carrying out the carbonation under pressure and at elevated temperatures. The method consists of the following stages : preparation of anhydrous sodium 2-naphtholate from 2-naphthol and aqueous caustic soda by vacuum dehydration; carbonation of the anhydrous salt with CO_2 under pressure at 230-270°; recovery of 2-naphthol; and purification of the final product. The scheme of reactions may be represented as follows :



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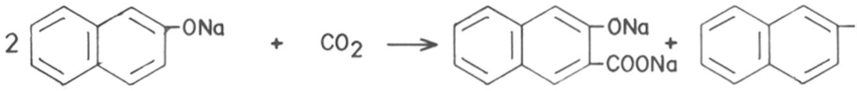

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Broadly speaking there are two methods of carrying out the reaction. The so-called dry method, which is extensively used in industry, employs a series of distillations to remove 2-naphthol as the reaction progresses, in order to facilitate an increased yield of the product. The principal difficulty in this process is mechanical; nevertheless it has been successfully used in industry.

Several workers have suggested modifications to the Kolbe-Schmitt reaction to overcome some of the difficulties encountered in the dry process. Among these may be mentioned :

1. The use of a liquid medium, both for dehydration and carbonation, e.g. 2-naphthol, dioxane, pyridine, toluene and xylene.
2. The use of sodium hydride along with anhydrous alkali naphtholate during carbonation.
3. The elimination of the dehydration step by using anhydrous K_2CO_3 directly with 2-naphthol for carrying out the carbonation at high temperature and pressure (Marasse method).

4. Preparation of 2-hydroxy-1-naphthoic acid and its subsequent conversion to 2-hydroxy 3-naphthoic acid (BON acid).

Of all these methods the one employing a liquid dispersent appears to have several advantages which include reduction in mechanical load and improvement in mass transfer.

Much has been published on the chemistry and general technology of the Kolbe-Schmitt reaction, but there is surprisingly little information on the process kinetics of this reaction (with particular reference to the preparation of BON acid). On the solvent dispersion method the literature is particularly scanty. The normal yields obtained in industry by the dry process are of the order of 86 per cent with a theoretical conversion of about 35 per cent. The principal reason for the low yield is the loss of 2-naphthol as undesirable tar. In the only reports available on the industrial application of the liquid dispersent process, the conversions are stated to be 32 per cent and the yields of the order of 60 per cent.

Object and summary of present work

Both the dry and solvent methods are apparently capable of improvement. In view of the relatively little information available on the solvent process and its reported advantages, it was decided to examine this method in a systematic manner. Thus the present investigation was undertaken with the object of studying the effect of several process variables on the conversion of 2-naphthol to BON acid using a medium of kerosene oil for dehydration as well as carbonation.

The dehydration step was first studied in considerable detail. A significant improvement has been introduced in this step by incorporating trace quantities of an additive which cuts down the dehydration time from 24 hours to about 8 hours and also ensures total dehydration, a necessary pre-condition for high selectivity during carbonation.

Over 100 runs were organised to study the carbonation step, and it was found that under optimum conditions a conversion of about 33 per cent could be obtained with a selectivity of about 59 per cent (yield : 77 per cent). It was also found that the high pressures normally used in industry are not necessary and that pressures of 50-70 psig give the most favourable results. Higher pressures in fact tend to be detrimental to the desired reaction.

A probable mechanism based on mass transfer has been proposed for the Kolbe-Schmitt reaction, and an equation for predicting the overall reaction rate as a function of reaction time has been developed.

Chapter-II

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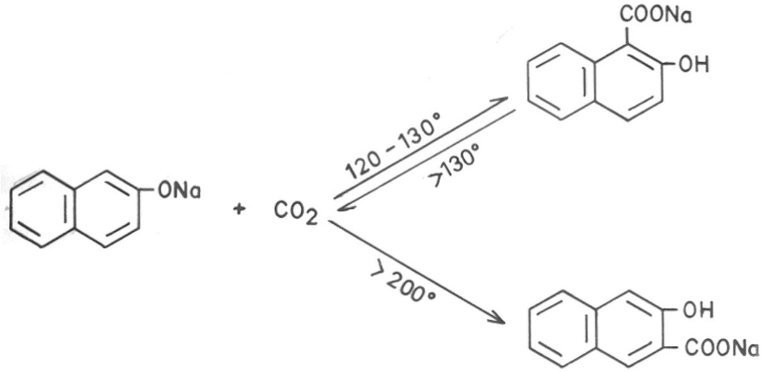
LITERATURE SURVEY

CHEMISTRY

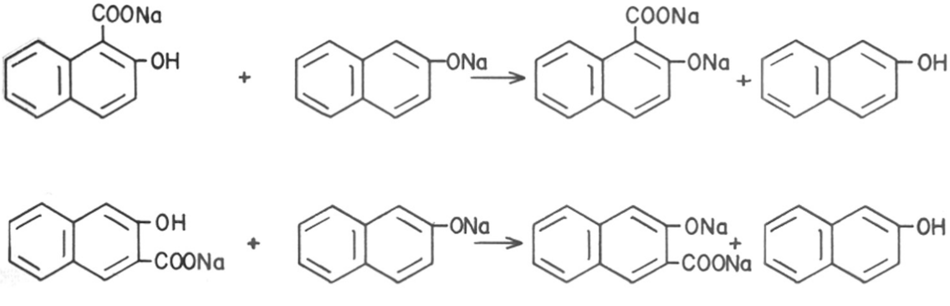
The action of CO_2 on dry sodium 2-naphtholate gives two isomeric acids[56]. The salt of the valuable 2-hydroxy 3-naphthoic acid forms at temperatures above 200°, preferably in the range 230-270°, while the salt of 2-hydroxy 1-naphthoic acid forms between 120 and 130° and starts decomposing above 130°.



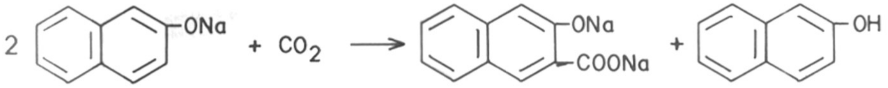
(I)

(II)

Isomers I and II undergo further reaction with sodium 2-naphtholate to give the corresponding disodium salts[54].

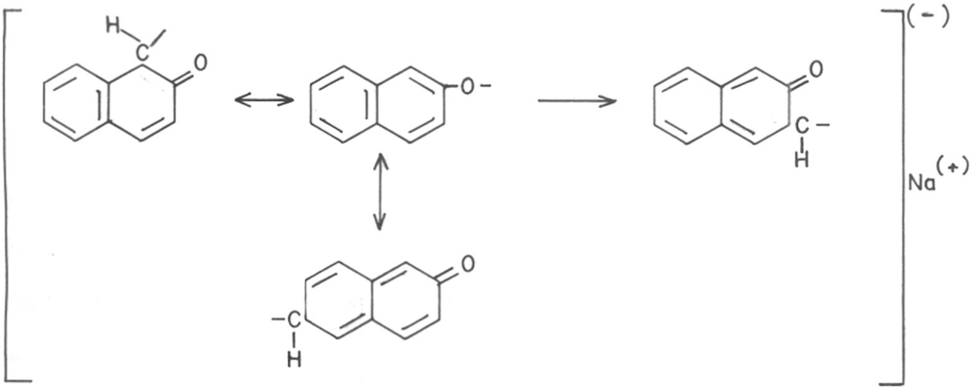


The overall reaction for 2-hydroxy 3-naphthoic acid may then be represented as



The maximum theoretical conversion possible is thus only 50 per cent.

Tijmastra[42,46], Schwenk[43,55], Reimer Tiemann[49], Siedel, Wolf and Kranse[54,56] and other workers have postulated theories for the mechanism of the carboxylation of sodium 2-naphtholate by CO_2 (Kolbe-Schmitt reaction in general). But the theory put forward by Karpuchin and Chussid[44,45,54] seems to be the most acceptable. They pointed out that the products obtained by carboxylation at different temperatures exist in tautomeric forms. Thus it has to be considered as a Mesomeric system.



Depending on the temperature, the arrangement of CO_2 may occur to give an alkali salt, 2-hydroxy 1-naphthoic acid or 2-hydroxy-3-naphthoic acid.

TECHNOLOGY

(1) Kolbe-Schmitt process (dry)

Kolbe and Schmitt[2] prepared 2-hydroxy 1-carboxy-naphthalene (m.p. 154°) by treating dry sodium 2-naphtholate with CO_2 at 120-145° at atmospheric pressure. The sodium salt of hydroxycarboxylic acid formed was dissolved in water and acidified to give hydroxycarboxylic acid, but the acid was unstable and decomposed easily to 2-naphthol and CO_2.

Later Schmitt[4] obtained 2-hydroxy-3-carboxynaphthalene, a stable yellow compound (m.p. 216°), by carrying out the carbonation of dry sodium-2-naphtholate at 200-250° under pressure. This method of manufacturing BON acid has since remained standard in the chemical industry. The manufacturing process as given in BIOS[37] is briefly described below.

Caustic soda as 50 per cent liquor and 2-naphthol (in the molar ratio 1:1) are charged into a cast steel vessel heated by a coil using steam at 450 psi and provided with a fredreking type stirrer through an adjustable gear box. The sodium 2-naphtholate formed is completely dehydrated under vacuum, first at 190° under 40 mm vacuum and finally at 220-230° under 15 mm vacuum. The dehydration takes about 24 hours.

The dry sodium-2-naphtholate is then carbonated in three steps starting at a temperature of 220-230° and finishing at 260° with a final pressure of 4.5 atm. After each step (lasting for 5-6 hours) the free 2-naphthol formed is distilled at about 220-230° under 15 mm vacuum. The total free 2-naphthol distilled in three distillations is nearly 42 per cent of the charge, and the total time for carbonation and distillation is 28 to 30 hours.

After the third distillation, water is introduced into the kettle and the reaction mass brought to about 145°. The solution is then dumped in a neutralisation tank. Free 2-naphthol is precipitated at a pH of 6.8 and BON acid at a pH of 2. The following yields of BON acid are normally obtained.

72.6 per cent on 2-naphthol consumed (selectivity
35.6 per cent on 2-naphthol charged

(See page 32 for definitions of yield and conversion)

Other methods described in the patent literature[3,4,6,12,14,17,23,29] on the dry process do not deviate significantly from the process described above.

(2) Marasse method

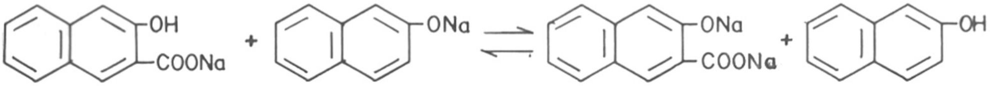
Marasse[56] in 1893 proposed a simple modification to the Kolbe-Schmitt reaction in order to overcome the difficult and time consuming preparation of the hygroscopic naphtholate. The procedure involves heating 2-naphthol with an excess of anhydrous K_2CO_3 at 230° under a high CO_2 pressure (1200-2000 psi) to give the K-salt of 2-oxynaphthoic acid. Acidification releases the free acid in good yield, but there is also a likelihood of the formation of the isomer, 2-hydroxy-6-carboxynaphthalene.

This modification has been applied to approximately one hundred phenols[50,51,53] and has given good results in many cases. The excess of potassium carbonate acts as an extender and prevents the fusion of the mixture. Industrially this procedure is expensive since only potassium, rubidium and cesium carbonates have been found suitable.

(3) Use of liquids

(a) Solvents

In some patents[7,9,10,16,32,35] 2-naphthol has been exploited as a solvent. Since 2-naphthol dissolves its sodium salt, carboxylation would be advantageous from a technical standpoint. The reaction



leading to the formation of the disodium salt may be suppressed to some extent by using excess of 2-naphthol (as solvent). Thus it should be possible under ideal conditions to obtain conversions of over 50 per cent. The theoretical conversion is usually restricted to 50 per cent in view of the above reaction going to completion. But the reported observations[22] are not promising. 2-Naphthol was not found to be inert in the Kolbe-Schmitt reaction, and as a result large quantities of tar are formed under certain conditions.

Organic liquids, which have a solvent action on 2-naphthol and alkali 2-naphtholate but do not dissolve the alkali salt of 2-naphtholcarboxylic acids and which are stable and chemically inert, may be used as solvents. Dioxane, pyridine, their homologues and acid soluble coal tar fractions fulfil these conditions and have been tried; for practical reasons dioxane has received greater consideration than other solvents[18,19,20,21,22,54].

2-Naphthol is allowed to react with an equivalent or excess amount of NaOH in the solvent. Na-2-naphtholate is then dehydrated by azeotropic distillation using fresh dry solvent (for adjustment of volume). If an excess of NaOH is used, the mixture is refluxed for some time, and the aqueous layer is then separated and dried over a dehydrating agent, e.g. caustic soda, calcium oxide, barium oxide or calcium carbide.

This procedure leads to efficient dehydration, but is time consuming. To shorten the time of azeotropic distillation, a third solvent (e.g. benzene) which forms a minimum boiling mixture is used[55]. After dehydration, carbonation proceeds smoothly under normal conditions.

The liquid method has a number of advantages. It ensures efficient drying of Na-2-naphtholate. No difficulties are encountered resulting from local overheating or inadequate stirring. It reduces the formation of by-products such as xanthone or tar. As a result hydroxycarboxylic acids can be obtained in higher purity and yields. It makes it possible to carry out carbonation at the optimum temperature of 250° (from the beginning of the reaction) which is not possible in the dry process.

The principal disadvantage of this method is the use of excessively large equipment and the additional investment for handling of solvents and their recovery.

(b) Dispersents

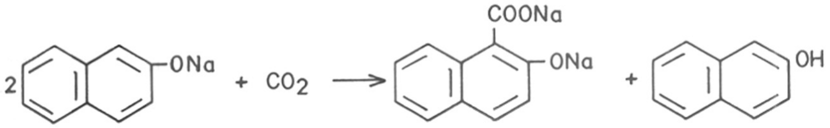
Some organic liquids (e.g. paraffin, toluene, xylene and tetralin) have been suggested[5,23,47] as dispersents (diluents) for carrying out this reaction. These do not dissolve the alkali metal naphtholate and do not react with the starting materials and intermediate or final products. The use of kerosene oil as a dispersent in one of the industrial plants is also known. Such diluents facilitate the preparation of anhydrous naphtholate. However they tend to have an undesirable effect on the carbonation reaction because CO_2 dissolves but sparingly in the diluent (hydrocarbon) and the contact of CO_2 with the suspended and coated naphtholate particles might not be efficient.

It is therefore necessary to use as little of the diluent as possible and also to get the naphtholate in a finely divided state for the carbonation to proceed smoothly and with the required reaction rate.

(4) Other methods

(a) Conversion of alkali salt of 2,1-hydroxynaphthoic acid to BON acid

Dry sodium 2-naphtholate is subjected to the action of CO_2 at a temperature of 40-60° (or in some cases at 120-130°) with or without a liquid medium under atmospheric pressure[11,15,27,28,30,44,54,55]. The product is obtained as a disodium salt of 2,1-hydroxy-naphthoic acid. It is then processed in the usual manner.



The conversion of 2,1-hydroxy-naphthoic acid is practically quantitative, i.e. 50 per cent on the 2-naphthol charged. This can be increased to 100 per cent of the naphtholate charged if an equivalent amount of metallic sodium is used.

This reaction is best carried out in an indifferent liquid, or preferably in a liquid which is a solvent for both naphthol and naphtholate.

The disodium salt of 2,1-hydroxy-naphthoic acid, substantially free from naphthol and other materials containing free hydroxyl groups, is heated to 220-360° in a chemically indifferent solvent under N_2 or CO_2 atmosphere till the tautomerisation is complete. The conversion to BON acid is substantially quantitative. It is claimed[13,36] that this method can be made continuous.

In another process[34] the disodium salt of 2,1-hydroxynaphthoic acid is heated to 235-45° under a CO_2 pressure of 4.5 atm. with intermittent addition of 2-naphthol. After the tautomerisation the free 2-naphthol is distilled out in vacuo and the product is separated in 65-70 per cent yield.

These processes involve the additional cost of preparing 2,1-hydroxy-naphthoic acid, and if a liquid medium is used the cost of solvent handling and recovery is also added up. Further there is no improvement in the conversion and yield as compared with the direct methods.

(b) Use of sodium hydride

A patent[33] has described the preparation of dry Na-naphtholate by using NaOH or NaH in a nitrogen atmosphere. The dry salt is treated with CO_2 at a pressure of 5 atm. at 230-250°, preferably with the addition of more NaH. Higher yields are claimed by a further reaction of the carboxylation product with CO_2 and additional NaH.

Chapter--III

Chapter-III

EXPERIMENTAL

The experimental assembly for this investigation was set up with the object of studying the effect of process variables on the Kolbe-Schmitt reaction leading to the formation of BON acid in the presence of kerosene oil as a dispersent. The principal features of the experimental technique are briefly described under the heads : (1) equipment, (2) principal raw materials, and (3) operation.

1. EQUIPMENT

All the experiments in the course of this investigation were carried out in two reactor assemblies. Reactor A, in which the earlier part of the investigation was carried out, was the smaller of the two and was not provided with a sampling device. The latter part of the investigation was carried out in reactor B which was not only larger but was also provided with an arrangement for sampling.

Reactor A

A diagrammatic sketch of the reactor and accessories is shown in Fig. (1), and a photograph of the unit appears in Fig. (2). This consisted essentially of a stainless steel reactor, 8 cm diameter x 19 cm height, with a volumetric capacity of 860 ml. The reactor was provided with an anchor type stirrer which could be driven at 160 rpm by a $\frac{1}{8}$ H.P. motor through a suitable pulley arrangement. The stirrer stuffing box was provided with a jacket (for the portion inside the reactor) for water cooling. In the flanged lid of the reactor were openings for charging, vapour outlet (used during distillation of the solvent) and CO_2 inlet. A thermowell of appropriate length was also provided. The reactor was heated by electrical resistance wire wound over its outer surface, and the heat input was controlled through a variac and an ammeter. The entire reaction assembly was tested for a pressure of 300 psig at 350^o and was found to be leak-proof.

The assembly also had provision for adequate drying of CO_2 and for condensing the mixture of kerosene oil and water during dehydration.

Reactor B

This assembly is shown diagramatically in Figs. (3 and 4). The reactor (stainless steel), 20 cm diameter x 20 cm height, had a volumetric capacity of about 6 litres and was flanged at the top as in reactor A. In addition to the features already described under reactor A, this reactor was provided with a bottom discharge fitted with a ½ inch stainless steel gate valve. A stainless steel pressure tube, approximately 20 ml in capacity and closed at one end, was fitted to the gate valve at its open end. Whenever it was desired to collect a sample, it was only necessary to fill the tube by opening the valve, close the valve again and then remove the tube from the reactor assembly. An arrangement was provided in this assembly for recording the temperature continuously through a Cambridge circular recorder. A photograph of the assembly appears in Fig. (5).

2. PRINCIPAL RAW MATERIALS

In the course of this investigation the following chemicals of specifications stated against them were used :

(i)	2-Naphthol	-	Technical grade; brown grains; purity 96-97 per cent.
(ii)	Sodium hydroxide	-	Commercial grade; flakes; purity 93-94 per cent.
(iii)	Carbon dioxide	-	Commercial grade; dry CO_2 from cylinder.
(iv)	Kerosene oil	-	Superior Burmah Shell grade kerosene oil; boiling range 160-265°; 60 per cent distilled below 200°.

3. OPERATION

The operation of the reactor assembly was essentially according to a pre-determined procedure. Several factors were varied in the process, such as kerosene oil to 2-naphthol ratio, temperature, pressure and time. A brief description is given below of the essential features of the operation under the heads : charging, dehydration, carbonation, working up of reactor mass, and analysis of products. The exact procedure, which would include details of time, temperature and pressure, will vary from run to run.

Charging

Kerosene oil and 2-naphthol were charged in the reactor in a pre-determined ratio. Stirring was then started and NaOH was added as 50 per cent liquor. Heating was commenced and the temperature brought to about 60° in ½ hour. An accurately weighed quantity of an additive was then added to the reaction mass.

Dehydration

An air condenser and a water condenser (along with a separating funnel as receiver) were connected in series with the distillation arm of the reactor. The feed hole of the reactor was connected to a graduated reservoir of fresh kerosene oil. Heating was then increased and the temperature raised to 90° in another ½ hour. At this temperature a mixture of kerosene oil and water started to distill over. In order to ensure a constant ratio of kerosene oil to 2-naphthol in the reactor, kerosene oil was introduced into the reactor through the graduated reservoir at the same rate at which it distilled over from the reactor. In order also to ensure that moisture was not introduced along with the kerosene oil, carefully dried kerosene oil was used. (In the later part of the investigation it was found unnecessary to dry the kerosene oil before use since the water content of the oil was found to be negligible as determined by Karl Fischer reagent.)

By this distillation almost all the water (water added with caustic soda plus water formed during the reaction) could be removed in the first two to three hours. The last traces of moisture came out in the form of droplets in the distilling kerosene oil. The quantitative removal of water was ascertained in each run by measuring the water removed. Dehydration was considered to be complete only when the water removed was equal to the water added and that formed during the reaction. In order to make sure that the last traces of moisture have been completely removed, distillation and addition of kerosene oil were continued till there were three complete change-overs of kerosene oil from the reactor. This meant the addition of 6 litres of kerosene oil to the reactor during distillation.

The next step in the dehydration cycle was the adjustment of 2-naphthol to kerosene oil ratio in the reactor to a pre-determined value, either by adding or removing kerosene oil. At the end of this adjustment, the temperature in the reactor reached a stable value of 230 to 235° in the majority of runs. The total time of dehydration was then defined as the time required to reach this stage.

Considerable care was exercised during dehydration since even traces of moisture are known to interfere seriously with the carbonation of Na-2-naphtholate to BON acid.

Carbonation

The condensers and feeding line were disconnected and these openings in the reactor were plugged. The needle valve fixed to the reactor was then connected to the CO_2 cylinder through a trap filled with silica gel.

CO_2 was introduced inside the reactor at a slow, regulated rate at the desired temperature. The pressure and temperature were then varied according to a pre-determined plan. It was found that at the beginning of carbonation the control of the reaction temperature was difficult. Also an appreciable absorption of CO_2 was noticed in the first two to three hours, after which there was practically no absorption till the end of the reaction. The reaction was stopped after the desired time interval, and the products of reaction were worked up.

Working up

After carbonation the heating was cut off and the reactor mass was allowed to cool down under stirring. When the temperature came down to 90°, the residual gas was released slowly. Water was then added and the mass heated to about 125° to ensure complete dissolution of the product. The solution was cooled to about 90° and was discharged through the bottom valve. This solution varied from dark brown to dark red in colour. 150 to 200 ml. of a 20 per cent solution of NaOH was then added and the solution was further diluted by water to 8.6 to 10.2 Tw.

The diluted solution was heated to 70-80° by steam for 15 minutes, after which steam was stopped but stirring was continued for one hour and then allowed to settle for ½ hour. This procedure helped to separate the tar efficiently.

The tar was removed by filtration. The filtrate consisted of two layers, the aqueous layer containing BON acid and 2-naphthol and the organic layer containing kerosene oil plus dissolved tar. The kerosene layer was removed, and the aqueous layer was worked up for the isolation of 2-naphthol and BON acid in the following manner.

The aqueous layer was heated to 65-70° and the pH brought down to 6.8 by 50 per cent sulfuric acid when 2-naphthol was precipitated out. The complete precipitation of 2-naphthol was ensured by the following test : a sample filtered through a dry filter should remain clear with further dilution with water. The precipitated 2-naphthol was then filtered and the filtrate worked up for BON acid. 2-Naphthol cake was washed with a little carbonate solution and then with water to neutral pH. The crude wet cake was dried in a vacuum dryer at 40-50° and its purity estimated. In a few test cases, the wet cake was distilled under high vacuum in a specially constructed distillation unit and the purity of the cake determined directly.

The filtrate was heated to 70-80° and the pH brought down to 2 with 50 per cent sulfuric acid when BON acid precipitated out. The slurry was then cooled to 50°, filtered, and the BON acid washed free of acid. This was dried in a vacuum dryer at 40-50°.

ANALYSIS

Primary aromatic amine salts are quantitatively diazotised by nitrous acid at low temperature ($0-5^{o}$). The resulting diazonium salts are very soluble in water, and couple rapidly and quantitatively with naphthols in alkaline solution. This forms the basis for the estimation of naphthols.

The iodometric method was tried for the estimation of naphthols under different titrating conditions [37,63,62,64] but this did not give consistent result under any of the conditions.

Preparation of standard diazo solution

Sodium nitrite solution (0.5N) was prepared, and its exact strength was determined by sulfanilic acid and oxidation with potassium permagnate [60,58,63,64]. This standardised sodium nitrite solution was used in finding out the content of p-chloroaniline in a prepared solution (0.25N, in excess HCl). A known strength of p-chloroaniline solution (50 ml) was taken in an ambered colored volumetric flask (250 ml capacity) and was diazotized at $0-5^{o}$ with sodium nitrite solution; a little amount of potassium bromide was used for stabilizing the diazo solution. This standard diazo solution was used in the estimation of naphthols as given below.

Preparation of naphthol solutions

2-Naphthol

1.44 gm 2-naphthol was dissolved in 10 ml of 2N NaOH and 400 ml water, and then made up to 500 ml.

BON acid

1.88 gm of BON acid was dissolved in 10 ml of 2N NaOH and 400 ml water and then made up to 500 ml.

Estimation by standard diazo solution[37,60]

2-Naphthol

50 ml of 2-naphthol solution was transferred to a beaker, containing 20 ml of 2N Na_2CO_3 (buffer) plus some ice pieces and cold water (total volume about 200 ml). The standard diazo solution from the jacketed burette (cooled by ice cold water circulation) was added to the naphthol solution in stages of 0.5 ml each with efficient stirring. Each time a drop of the mixture was spotted on a clean filter paper. The clear outer ring was tested by spotting with diazo solution and with a fast coupling (H-acid or J-acid) solution. In the beginning the clear outer ring gave a colored rim with diazo solution which became faint and then vanished with further addition of diazo solution indicating exhaustion of 2-naphthol in the titrating mixture. At this stage the clear outer ring was tested by spotting with H-acid solution indicating the presence of excess diazo solution in the titration mixture. The end point was taken as the mean of the last spot with diazo and the first spot with the H-acid solution.

BON acid

The estimation of BON acid was carried out by a similar procedure.

Estimation of 2-Naphthol in BON acid[37]

18.8 gm of BON acid was creamed with 50 ml water and dissolved in the cold with 110 ml N/1 NaOH solution. This solution was treated with 5 gm pure ammonium sulfate. The separated free 2-naphthol was then extracted with ether three times taking 25 ml ether for each extraction. The total ether extract was filtered and evaporated. The residue was dissolved in the minimum amount of N/1 NaOH and water, the volume was made up to 100 ml. 25 ml of this solution was then titrated with standard diazo solution for determining the total amount of 2-naphthol.

Sodium hydroxide[58,63,64]

Commercial grade sodium hydroxide (flakes) was analysed by titrating against standard potassium hydrogen phthalate solution and was found to be 93 to 94 per cent.

Tar

The tar obtained in each run was dried and weighed as such.

Chapter-IV

Chapter-IV

RESULTS AND DISCUSSIONS

In this chapter the results obtained will be discussed under the following broad classifications : dehydration, and carbonation.

Details of experimental procedure and working up of reaction products have been described in chapter III, and unless specifically stated it may be assumed that this procedure has been adopted in obtaining the data presented and discussed in this chapter.

DEHYDRATION

In the experiments designed to study dehydration, the conditions of carbonation were fixed on the basis of the data reported in the literature. It was thus ensured that any variation in conversion was due to changes in dehydration conditions only.

(a) Preliminary experiments

A few preliminary runs were carried out in reactor A maintaining the reaction conditions generally as described in the literature. The conditions used were as follows.

Charge :

Chemical	Amount	Specification
2-Naphthol	149 gms	97 per cent
Caustic soda	42.5 gms	94 per cent

Chemical	Amount	Specification
Water	92 ml	Distilled water
Kerosene oil	450 ml	180-210° range

Dehydration :

4.0 litres of kerosene oil were continuously added during distillation in order to maintain a ratio of 1:3 (2-naphthol to kerosene) over the entire dehydration period.

Dehydration time = 24 hours

Total water recoverable = Water added (92 ml) plus reaction water (18 ml)

= 110 ml

Carbonation :

2-Naphthol to kerosene ratio = 1:1.3

Temperature = 230°-250°

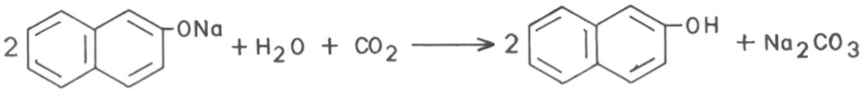
Pressure = 0-150 psig

Time = 24 hours

CO_2 was introduced at 230°, and the pressure and temperature were raised gradually to 150 psig and 250°, respectively, in the course of five hours.

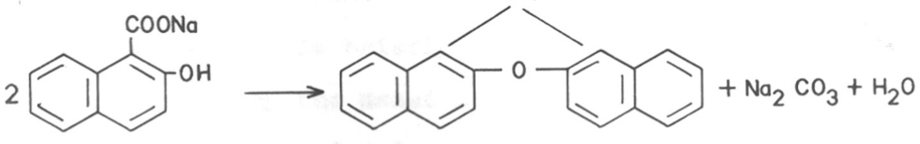
Several runs were made under these conditions, and they are recorded in Table-1. In all these runs the conversion to BON acid was found to be poor, varying generally from 5 to 10 per cent, against the theoretical conversion of 50 per cent. The total water recovered was never 100 per cent and, as can be seen from the table, it varied from 90 to 95.5 per cent even though the final temperature attained during dehydration was 200°.

The complete removal of water before carbonation is essential since it inhibits carbonation and leads to side reactions resulting in the loss of 2-naphtholate. Water forms strong chelation with sodium 2-naphtholate, thus preventing the addition of CO_2 to give BON acid. The hydrolysis of this complex gives free 2-naphthol and sodium hydroxide; introduction of CO_2 then leads to the formation of sodium bicarbonate which decomposes to sodium carbonate and water again. The total reaction is given by



~~The water formed in this reaction is again free to prevent more of the sodium naphtholate from going to BON acid. Thus the consumption of sodium naphtholate in the side reaction is continuous but in the diminishing order.~~ The free 2-naphthol does not form sodium naphtholate again, since in its fused form it is inert to alkali.

In another side reaction one mole of water is formed per mole of xanthone (the main constituent of by-product tar).



Hence it is essential to ensure the absence of moisture during the reaction and also to avoid the side reactions which result in the formation of water.

(b) Effect of temperature

In all the runs discussed earlier, the water recovery was poor. It is likely that under the distillation conditions used the water present in physical combination with the naphtholate may not have been removed. It was therefore thought that the last traces of water could be removed by heating the naphtholate to a high temperature (270-320°) in the final stages of dehydration. Temperatures above 307° might be more effective as sodium naphtholate melts at that temperature, thus facilitating the removal of bound water.

The experiments carried out for investigating the effect of temperature were divided into four groups : (1) experiments at 200°; (2) at 230°; (3) at 280°; and (4) at 320°. The experimental technique involved in group (1) where the temperature did not exceed 220° (which is within the boiling range of kerosene) was in accordance with the procedure described earlier. For groups (2), (3) and (4), where the final dehydration temperatures were 230°, 280° and 320° respectively, this procedure could not be followed since it would not be possible to obtain these temperatures by the open distillation method adopted at the lower temperature. The procedure used is briefly described below. Distillation was carried out by the usual method up to 200°, at which stage the reactor was closed and heating continued. The water (along with kerosene) from the reactor was then discharged intermittently by opening the valves. It was observed that after three such discharges there were no visible droplets of water in the kerosene discharge.

The results of these experiments are summarised in Tables-2 and 3. The runs recorded in Table-2 were carried to completion, while the runs recorded in Table-3 were stopped after dehydration in order to observe the physical state of the naphtholate. It will be observed that in the first two groups the recovery of water was of the order of 95 per cent. This recovery figure is in consonance with the values recorded in Table-1 for the preliminary experiments which were also carried out under similar conditions. Observations about the physical state of the sodium 2-naphtholate showed that it was in the form of finely divided grains well suspended in kerosene.

Contrary to expectations, the conversions to BON acid obtained in groups (3) and (4) were lower than at the lower dehydration temperatures. It will be observed from Tables-2 and 3 that in both these cases the recovery of water was over 98 per cent, which is higher than the recovery at the lower temperatures. The physical form of sodium naphtholate provides a possible clue for the low conversions in spite of superior water recovery. At both these temperatures (280° and 320°), the sodium naphtholate was observed to be in the form of lumps which were not probably accessible to carbonation to the same extent as finely divided grains.

The obvious conclusion follows that although increasing the temperature of dehydration enhances the recovery of water, a necessary pre-condition for efficient carbonation, the conversion to BON acid is still poor in view of the unfavourable physical state of the sodium naphtholate.

(c) Use of additives

An alternative method, for the complete removal of moisture, is the use of a suitable additive along with the normal charge. Chemicals normally used for dehydration were tried and screened for this purpose. The chemicals investigated were NaOH, KOH, $CaCO_3$, $CaCl_2$, silica gel, bauxite and kieselguhr. Dehydration runs were carried out using these chemicals (independently) to the extent of 1 to 5 per cent (on 2-naphthol charged). The principal object of this study was to examine the effect of these chemicals on water recovery and also on the physical state of the naphtholate. The data on dehydration alone are summerised in Table-4.

The results show that $CaCl_2$, bauxite, NaOH, and KOH give a water recovery of 99 to 100 per cent when used along with the normal charge (to the extent of 1 to 2 per cent on 2-naphthol) without affecting the fine grain structure of the naphtholate. In other cases the recovery of water is not satisfactory.

Using these additives ($CaCl_2$, bauxite, NaOH, KOH) both dehydration and carbonation were then carried out in order to observe the effect of these additives on the conversion of 2-naphthol to BON acid under experimental conditions described on page 24.

The results obtained are summarised in Table-5. It will be observed that in the case of $CaCl_2$, recovery of water as well as conversion to BON acid are superior to the results obtained with the other chemicals. In the case of bauxite the 2-naphthol recovered was greenish in colour.

From Table-4 it may be observed that the use of about 2 per cent $CaCl_2$ (on 2-naphthol charged) is adequate to ensure quantitative removal of water. In all the runs discussed so far, a dehydration time of 12 hours was arbitrarily fixed using 2 per cent $CaCl_2$.

Another series of runs was organised in which the amount of water removed was determined as a function of time. This was done in the following way. During distillation the separable water removed with kerosene was measured, and the water content of kerosene was also determined by the Karl Fischer reagent.[61] Separable water ceased to come out after three hours. In Fig. (6) the water content of kerosene is plotted as a function of time. It will be seen that the water content levels off after about 6 hours at a value of 83 mg of water for 50 ml of kerosene oil, which corresponds to the normal solubility of water in the oil. The higher proportion of water in kerosene at lower dehydration times is due to the physically bound moisture in the oil as evidenced by the turbid nature of the oil. Although the separable water is removed within 3 hours, it is evidently necessary to continue the dehydration to about 6 hours in order to ensure the removal of moisture physically held by naphtholate.

In summary, the results of experiments carried out on the dehydration of sodium 2-naphtholate show that, with 2 per cent $CaCl_2$ (on 2-naphthol charged) and a dehydration time of about 6 hours, quantitative removal of water is possible.

CARBONATION

The principal object of the studies on carbonation was to optimise the conditions for conversion and yield with respect to the three significant process variables : pressure, temperature and carbonation time. The ranges of these variables within which the conditions were sought to be optimised were determined from the reported literature data.

In the dry process as practised in industry, the reaction is not carried out at any particular temperature or pressure, but both are varied during a batch according to a pre-determined pattern and the reaction mass is held at the final temperature and pressure for a specified period. In the dispersent method used in the present study, it was found possible to obtain the final temperature and pressure within a very short time, and the reaction could therefore be carried out at any specified temperature and pressure. Due to the presence of a dispersent it should be possible to obtain similar conditions in a larger unit.

It has been pointed out earlier that the 2;1 isomer predominates at carbonation temperature below 200°, and this acid shows a strong tendency for side reactions leading to the formation of tar. At the outset, therefore, it was decided to use temperatures above 220° in the present investigation.

Definition of terms

A reference to reactions (1) and (2) shows that, under ideal conditions assuming full conversion to BON acid, half the quantity of 2-naphthol charged should be recovered. The maximum conversion based on 2-naphthol charged cannot therefore exceed 50 per cent. Since 2-naphthol (produced during reaction), BON acid and 2-naphtholate all tend to form tar, in industrial practice the yield of the reaction is defined in terms of the two useful products recovered, namely BON acid and 2-naphthol. Conversion and yield are therefore defined as :

$$\text{Conversion} = \frac{b}{a}$$

$$\text{Yield} = \frac{b+c}{a}$$

where

a = total moles of 2-naphthol charged,
b = moles of BON acid formed,
and c = moles of 2-naphthol recovered.

In defining the conditions for the maximum utilisation of 2-naphthol for the production of BON acid, it is convenient to define another term which will be a direct measure of this factor. This term which may be called selectivity will be expressed as

$$\text{Selectivity} = \frac{b}{a-c}$$

The results obtained will now be discussed in terms of conversion, yield and selectivity. A high selectivity with too low a conversion may not be economical, while at the same time high conversion with low selectivity will certainly be wasteful.

Variables and their ranges

The variables whose effects were studied together with the ranges of these variables are listed below.

Temperature : 230-270°
Pressure : 20-150 psig
Carbonation time : 4 to 16 hr (5 to 120 minutes in the kinetic runs)
2-Naphthol to kerosene oil ratio : 1:1 to 1:2

2-Naphthol to kerosene oil ratio

In addition to the three important variables listed above (temperature, pressure and carbonation time), the ratio of 2-naphthol to kerosene oil is also likely to influence the rate of the reaction. The major role of kerosene oil (or any dispersent) is that it dissolves the CO_2, and the reaction between sodium naphtholate and CO_2 then proceeds by the transfer of CO_2 across a film of the dispersent surrounding the solid particles of naphtholate. Details of the mass transfer mechanism associated with the reaction will be discussed in a separate section.

From the practical point of view, it was considered desirable to vary the ratio of 2-naphthol to kerosene oil from 1:1 to 1:2 and to see if any systematic trends could be observed. Experiments were carried out in reactor A under the following conditions :

Charge :

Chemical		Amount
2-Naphthol	..	149 gm
Caustic soda	..	42.5 gm
Water	..	92 ml
Kerosene oil	..	450 ml
Calcium chloride	..	3 gm

Dehydration :

Additional kerosene oil (used during distillation)	..	4 L
Average time	..	6 hr
Final temperature	..	200-205°
Total water recovery	..	100 per cent

Carbonation :

Carried out at different 2-naphthol to kerosene oil ratios (1:0.6, 1:1, 1:1.5) and pressures (20,50,100, 150 psig) keeping temperature (250°) and time (14 hr) fixed.

The results of this investigation are summarised in Table-6. It will be observed that there is a general tendency for the conversion to increase with decrease in the ratio of 2-naphthol to kerosene oil. In other words, the lesser the quantity of the dispersent used the higher is the conversion. The experimental values for the ratio 1:0.6 at 100 and 150 psig are not reproduced in the table as there is some doubt about their accuracy. With respect to yield and selectivity, no particular trend is observable from the data.

A further series of runs was carried out in reactor B at a pressure of 70 psig, temperature of 250° and carbonation time of 4 hr. These runs were carried out after the effect of temperature, pressure and carbonation time was evaluated, in order to determine the influence of this ratio under the optimum conditions of pressure, temperature and time. The experimental conditions employed were :

Charge :

Chemical		Amount
2-Naphthol	..	760 gm
Caustic soda	..	212 gm
Water	..	460 ml
Kerosene oil	..	2000 ml
Calcium chloride	..	15 gm

Dehydration :

Additional kerosene oil (used during dehydration)	..	6 L
Average time	..	8 hr
Final temperature	..	230-250°
Total water recovery	..	100 per cent

Carbonation :

Carried out under different 2-naphthol to kerosene oil ratios (1:1, 1:1.3, 1:1.5, 1:2) keeping temperature (250°), pressure (70 psig), and time (4 hr) fixed.

The results obtained are summarised in Table-7. It will be observed that, as in the case of runs carried out in reactor A, the conversion shows a definite tendency to decrease with increase in the kerosene oil content. The results are plotted in Fig. (7). There is no observable trend in yield and selectivity.

Effect of temperature and pressure

The effect of temperature and pressure was studied (1) in reactor A at a fixed carbonation time of 14 hours, and (2) in reactor B at different carbonation times. In both these cases conditions of dehydration were maintained as described under dehydration. In the present section the results of runs carried out in reactor A will be described, while the results of runs carried out in reactor B will be discussed in the next section.

The experimental conditions used were the same as those described on page 34 with this difference that the ratio was maintained at 1:1 but the temperature was varied from 230 to 270°.

It is evident from the results summarised in Table-8 that higher pressures and temperatures are detrimental to the reaction. The data obtained show a systematic trend in conversion at 250°, while at other temperatures maximum values of conversion, yield and selectivity are discernable.

The reaction involved being very complex, it is not possible to derive a generalised conclusion from these results.

Effect of carbonation time (temperature and pressure)

These runs were carried out in reactor B as it was provided with a bottom discharge (chapter III). While it was possible to operate this arrangement satisfactorily, it was considered desirable to discharge the entire mass after a specified carbonation time rather than analyse the reaction products by sampling through the bottom discharge. A few test runs showed that the analysis of a sample at a particular carbonation time was some what different from that of the entire reaction mass when it was discharged at that carbonation time. The results discussed below are based on runs for which analyses were carried out by discharging the entire mass.

Table-9 summarises the results at 230°; pressure was varied from 20 to 100 psig and carbonation time from 4 to 16 hours. Tables-10 and 11 summarise the results at 250° and 270°, respectively, for the same ranges of pressure and carbonation time. As the reaction leading to the formation of BON acid is one of several competing reactions possible, generalised conclusions about the trends in conversion, yield and selectivity from these data are not justifiable.

The results however confirm the earlier conclusions (from reactor A data) that higher pressures and temperatures are detrimental to the reaction. A further conclusion can also be drawn : higher carbonation times are also detrimental to the reaction. There is a steep fall in selectivity as carbonation time increases, and it appears that a carbonation time of about 4 hours gives the most favourable results. In Fig. (8) conversion has been plotted as a function of pressure at 230°, 250°, and 270° at a carbonation time of 4 hour. Similar figures for yield and selectivity appear in Figs. (9) and (10), respectively.

From these figures, it is possible to define the optimum conditions for obtaining the best results :

Temperature = 250°
Pressure = 70 psig
Carbonation time = 4 hr

Under these conditions the following results may be expected :

Conversion = 33.5 per cent
Yield = 77 per cent
Selectivity = 59 per cent

Using the optimum conditions summarised above several runs were carried out to see the reproducibility of the results (Table-12). The average derivations were :

Conversion = 3 per cent
Yield = 4.7 per cent
Selectivity = 2.7 per cent

Chapter-V

Chapter-V

MASS AND HEAT TRANSFER APPROACH TO K-S REACTION

Several reactions are possible in the Kolb-Schmitt carbonation of Na-2-naphtholate. Assuming complete reaction of 2-naphthol to the sodium salt during dehydration, the sodium salt can disappear to give BON acid, free naphthol and a variety of other products which together will be called tar. The proportion of these different products will depend on the rates of several possible reactions, including subsequent conversion of BON acid and free naphthol to tar.

The principal overall reaction can however be easily recognised: disappearance of sodium naphtholate by reaction with CO_2. In this chapter a plausible mechanism for this reaction is proposed based on heat and mass transfer considerations.

Reaction model

A diagrammatic sketch of the proposed reaction model is shown in Fig. (11). It will be assumed that the naphtholate particles are in a state of suspension in the reaction mass and that each particle is surrounded by a film of dispersing agent (kerosene oil). It will further be assumed that the reaction takes place by the diffusion of CO_2 across this film to the particle surface and that the particle is spherical in shape.

Fig. (11) shows a sphere (naphtholate) of radius

R on whose surface the reaction takes place by the diffusion of CO_2 (at an initial partial pressure of p°) across an equivalent kerosene film of thickness Z_L. As the reaction progresses, the reaction plane retreats inside the sphere, leaving an outer crust of reaction products and an unreacted sphere of the naphtholate. Thus, at any time θ, let the reaction plane be situated at a distance r from the centre. This unreacted sphere will then be covered by a shell of reaction products (and possibly the dispersant as well) the depth of which will be given by (R-r). The rate of diffusion of CO_2 through this shell will depend on its effective diffusivity. With this model of the reaction, appropriate equations can be derived for the rate of disappearance of sodium naphtholate from considerations of mass transfer as well as heat transfer.

Mass transfer

At any time θ, the rate of diffusion of CO_2 across the product layer is given by

$$r_A = k_L(C-C_r) = \frac{D_e}{Z} \cdot C \qquad \ldots \qquad (1)$$

where

$$k_L = \frac{D_e}{Z} = \frac{D_e}{R-r}$$

The number of moles diffusing per unit time is therefore given by :

$$N_A = \frac{4\pi r R D_e}{R-r} \cdot C \qquad \ldots \qquad (2)$$

where $4\pi rR$ represents the geometric mean of the two surfaces $4\pi R$ and $4\pi r$.

The effective diffusivity De may be written as

$$D_e = ED_m \qquad \ldots \tag{3}$$

where D_m is the diffusion coefficient and E is an empirical constant. Equation (2) may now be re-written as

$$N_A = \frac{k_L 4\pi rREZ_L}{R-r} C \qquad \ldots \tag{4}$$

The rate of diffusion of CO_2 across the equivalent film of kerosene outside the product shell is given by

$$r_A = k_L(C_0 - C)$$

$$\text{or} \quad N_A = k_L 4\pi R^2(C_0 - C) \qquad \ldots \tag{5}$$

From a consideration of mass balance it is clear that the rate of diffusion of CO_2 across the kerosene film should be equal to the rate of diffusion across the product layer. Thus, from equations (4) and (5), equation (6) may be written by appropriate rearrangement:

$$C = \frac{RC_0(R-r)}{EZ_Lr + R(R-r)} \qquad \ldots \tag{6}$$

Substituting equation (6) in (5) and simplifying:

$$N_A = \frac{k_L 4\pi R^2 C_0 E Z_L r}{EZ_Lr + R(R-r)} \qquad \ldots \tag{7}$$

Let $r' = \frac{r}{R}$

and $k_M = \frac{R}{Z_1 E'}$

$$\therefore \quad N_A = \frac{k_L 4\pi R^2 C_0 r'}{\left[r' + k_M(1-r') \right]} \qquad \ldots \qquad (8)$$

For every mole of CO_2, two moles of naphtholate react. Keeping this in mind, the rate of diffusion of CO_2 can be equated to the instantaneous rate of disappearance of the naphtholate:

$$N_A = -2 \rho 4 \pi r^2 \frac{dr}{d\theta} \qquad \ldots \qquad (9)$$

where the right hand side represents the rate of the chemical reaction. Using the parameter r' as defined earlier, equation (9) may be re-written as:

$$N_A = -2 \rho 4 \pi R^2 r'^2 R \frac{dr'}{d\theta} \qquad \ldots \qquad (10)$$

From equations (8) and (10), we may write:

$$-d\theta = \left[\frac{Z_L \rho R}{k_L C_0} \right] \left[\frac{r'^2 \left(r' + k_M(1-r') \right)}{r'} \right] dr' \qquad (11)$$

Now r' represents the fraction of the sphere that has not reacted. Thus, if x is the total conversion of the naphtholate to various products,

$$r' = \frac{r}{R} = (1-x)$$

$$= y(\text{say}) \qquad \ldots \qquad (12)$$

Integrating equation (11) between the limits

$$\theta = 0, \quad r' = 1$$

$$\text{and} \quad \theta = \theta, \quad r' = y$$

we obtain, on simplification,

$$\theta = A_M \left[0.33(1-y^3) + k_M(0.17-0.5y^2 + 0.33y^3) \right] \quad --- \quad (13)$$

$$\text{where} \quad A_M = \frac{Z_L \rho R}{k_L C_0} \qquad \ldots \qquad (14)$$

Remembering that y = 1-x, equation (13) can be used to predict reaction time as a function of overall conversion.

Verification

It is theoretically possible to calculate A_M and k_M from their respective equations. But as there is considerable uncertainty in the composition of the product layer, it is not possible (with available data) to calculate the effective diffusivity or the empirical constant E. Values of Z_L and k_L cannot also be calculated accurately. Thus it is advisable to calculate these constants from experimental conversion data.

A series of experiments was carried out under conditions where tar formation would be minimum so that the overall disappearance of sodium naphtholate can be calculated with reasonable accuracy. The conditions employed were:

2-Naphthol to kerosene ratio - 1:1
Carbonation temperature - 250°
Carbonation pressure - 70 psig
Carbonation time - 5-120 minutes (variable)

The results are summarised in Table-13.

Tar formation during these runs was less than 3 per cent, and was therefore neglected in calculating the overall disappearance of naphtholate. The overall conversion can now be easily calculated from the quantities of 2-naphthol charged and recovered and BON acid produced (Table-13).

From these conversion figures the constants A_M and k_M have been calculated by the method of least squares which gives the following two equations for simultaneous solution:

$$8a + 0.75859b - 202.9 = 0 \qquad .. \qquad (15)$$

$$0.7586a + 0.092052b - 24.734 = 0 \qquad .. \qquad (16)$$

giving $a = 6.0625$ and
$b = 200.8$

where $a = 0.33\ A_M$ and
$b = A_M K_M$

The values of the constants thus become:

$$K_M = 18.39$$

$$A_M = 10.93$$

Fig. (12) shows a plot of θ vs x from the calculated values of K_M and A_M. The experimental values are also plotted.

The average deviation is 15 per cent.

Heat transfer

A similar approach based on heat transfer is possible, but as the mass transfer approach was found to be of more direct use in the present study, equations based on heat transfer have not been presented here.

NOMENCLATURE

C_0 - Concentration of CO_2 in kerosene in equilibrium with its initial partial pressure p^0.

C_r - Concentration of CO_2 on the reaction surface between unreacted naphtholate and the product shell.

C - Concentration of CO_2 on the outer surface of the sphere.

D_m - Diffusion coefficient.

D_e - Effective diffusivity.

E - Empirical constant.

H - Henry's law constant.

k_L - Mass transfer coefficient.

N_A - Diffusion rate of CO_2, moles per unit time.

p^0 - Partial pressure of CO_2.

R - Radius of a sphere of sodium naphtholate.

r - Radius of a sphere of sodium naphtholate after an interval θ.

r_A - Rate of diffusion of CO_2, moles per unit time per unit surface.

Z - Depth of product shell.

Z_L - Thickness of kerosene oil film.

θ - Reaction time.

ρ - Density.

TABLES

Table-1

RESULTS OF PRELIMINARY RUNS ON DEHYDRATION AND CARBONATION

Dehydration time - 24 hr
Expected recovery of water - 110 ml
Carbonation time - 24 hr
2-Naphthol to kerosene ratio :
    During dehydration - 1:3
    During carbonation - 1:1.3

No.	Final temperature °C	Water recovery		Conversion to BON acid %
		ml	%	
1	190	99	90	2
2	190	101	92	2
3	195	103	93.5	8
4	205	103	93.5	4
5	200	103.5	94	4
6	200	104	94.5	6
7	200	103	93.5	8
8	195	102	92.5	negligible
9	200	105	95.5	10
10	200	103	93.5	8

Table-2

EFFECT OF DEHYDRATION TEMPERATURE ON CARBONATION

Dehydration time - 24 hr
Expected recovery of water - 110 ml
Carbonation time - 24 hr
2-Naphthol to kerosene ratio :
    During dehydration - 1:3
    During carbonation - 1:1.3

No.	Final temperature °C	Water recovery ml	Water recovery %	Conversion %
1	200	103	93.5	8
2	200	104	95.0	11
3	230	103.5	94.0	9
4	230	104	95.0	13
5	280	107	97.5	3
6	280	108	98	3.5
7	320	108	98	1
8	320	107.5	98	negligible

Table-3

EFFECT OF DEHYDRATION TEMPERATURE ON THE PHYSICAL STATE OF 2-NAPHTHOLATE

Dehydration time - 20 hr
Expected recovery of water - 110 ml
2-Naphthol to kerosene ratio - 1:3

No.	Final temperature °C	Water recovery ml	Water recovery %	Remarks
1	200	103	93.5	Finely divided grains.
2	200	103.5	94	-do-
3	230	104	94.5	-do-
4	230	103.5	94	-do-
5	280	108	98	Lumps became very hard on cooling.
6	280	108	98	-do-
7	320	107.5	98	-do-
8	320	108.0	98	-do-

Table-4

DEHYDRATION DATA SHOWING THE EFFECT OF ADDITIVES ON TOTAL WATER RECOVERY

Dehydration time - 12 hr
Final dehydration temperature - 190-200°C
2-Naphthol to kerosene ratio - 1;3

No.	Additive	Amount of additive based on 2-naphthol %	Water recovery		Remarks
			ml	%	
1	2	3	4	5	6
1	Caustic soda	1	108	98	-
2	Caustic soda	2	109.5	100	-
3	Potassium hydroxide	1	108	98	-
4	Potassium hydroxide	2	109	99.5	-
5	Calcium chloride	1	109	99.5	Quick water recovery
6	Calcium chloride	2	110	100	Quick water recovery
7	Calcium chloride	4	110	100	Quick water recovery
8	Calcium chloride	6	110	100	Quick water recovery
9	Bauxite	1	109	99.5	Quick water recovery but distillate turbid

1	2	3	4	5	6
10	Bauxite	2	110	100	Quick water recovery but distillate turbid
11	Bauxite	4	110	100	Quick water recovery but distillate turbid
12	Potassium carbonate	1	103	93.5	0.5 gm 2-naphthol came out
13	Potassium carbonate	2	106	96	Water droplets were recovered over longer period
14	Potassium carbonate	4	104	94.5	Lump formation
15	Calcium carbonate	1	106	96	Water was recovered over longer period
16	Calcium carbonate	4	106	96	Lump formation
17	Silica gel	1	107	97.5	Water was recovered over longer period
18	Silica gel	4	107	97.5	Water was recovered over longer period
19	Kieselguhr	1	104	94.5	Water was recovered over longer period
20	Kieselguhr	4	105	95.5	Water was recovered over longer period

Table-5

DATA SHOWING THE EFFECT OF DIFFERENT ADDITIVES ON CARBONATION

Dehydration time - 12 hr
Expected water recovery - 110 ml
Final temperature of dehydration - 200°C
Carbonation time - 14 hr
2-Naphthol to kerosene ratio :
    During dehydration - 1:3
    During carbonation - 1:1.3

No.	Additive	Amount of additive based on 2-naphthol	Water recovery		Conversion	Remarks
		%	ml	%	%	
1	Sodium hydroxide	1	109	99.5	24	-
2	Sodium hydroxide	2	109.5	100	23	-
3	Potassium hydroxide	1	109	99.5	22	-
4	Potassium hydroxide	2	109	99.5	22.5	-
5	Calcium chloride	1	110	100	27	Water recovery was rapid
6	Calcium chloride	2	110	100	28.5	Water recovery was rapid
7	Bauxite	1	110	100	22	Recovered 2-naphthol was greenish
8	Bauxite	2	110	100	21	Recovered 2-naphthol was

Table-6

Effect of 2-naphthol to kerosene oil ratio

2-Naphthol to kerosene oil ratio during dehydration : 1:3
Dehydration time .. .. : 6 hr

Carbonation temperature .. 250°
Carbonation time .. 14 hr
Additive-$CaCl_2$ (on 2-Naphthol) .. 2 per cent

No.	Pressure psig	Ratio →	Conversion, %			Yield, %			Selectivity, %		
			1:0.6	1:1	1:1.5	1:0.6	1:1	1:1.5	1:0.6	1:1	1:1.5
1	20		29.29	19.36	17.86	82.1	76.79	89.82	60.89	56.1	51.59
2	50		32.96	31.95	27.02	74.52	77.56	71.68	55.65	57.81	48.06
3	100			35.02	27.87	77.76	84.53	79.69	58.32	79.28	51.12
4	150			36.31	23.31	62.23	72.23	76.83	41.86	82.21	54.01

Table-7

Effect of 2-naphthol to kerosene oil ratio during carbonation

2-Naphthol to kerosene oil ratio during dehydration : 1:2.5
Dehydration time : 8 hr
Carbonation temperature : 250°
Carbonation pressure : 70 psig
Carbonation time : 4 hr
Additive, $CaCl_2$ (on 2-naphthol charged) : 2 per cent

No.	2-Naphthol/ kerosene oil	Conversion %	Yield %	Selectivity %
1	1:1.0	33.75	73.14	55.71
2	1:1.3	31.09	78.5	59.19
3	1:1.5	25.07	73.6	48.72
4	1:2.0	24.52	79.77	54.80

Table-8

Effect of temperature and pressure

Dehydration time : 6 hr
2-Naphthol to kerosene oil ratio
during dehydration : 1:3
during carbonation : 1:1

Carbonation time : 14 hr

No.	Pressure psig	Temp. °C →	Conversion, %			Yield, %			Selectivity, %		
			230	250	270	230	250	270	230	250	270
1	20		11.69	19.36	19.01	30.76	76.79	76.33	36.68	56.1	42.66
2	50		24.49	31.95	21.72	90.8	77.56	64.22	70.69	57.81	37.18
3	100		20.41	35.02	28.82	92.47	82.5	67.38	70.86	79.28	46.06
4	150		15.31	36.31	-	74.8	72.23	-	36.9	82.21	-

Table-9

Effect of carbonation time

2-Naphthol to kerosene oil ratio
during dehydration .. : 1:2.5
during carbonation .. : 1:1
CaCl$_2$ (on 2-naphthol charged) .. : 2 per cent

Dehydration time .. 8 hr
Carbonation temperature .. 230°

No.	Time of carbonation hr	Pressure psig →	Conversion, %			Yield, %			Selectivity, %		
			20	50	100	20	50	100	20	50	100
1	4		25.1	29.86	26.79	80.85	76.58	71.08	56.67	56.03	48.07
2	8		30.88	31.81	29.35	73.89	72.44	68.17	54.34	53.08	47.97
3	12		31.19	27.92	33.64	70.91	69.13	72.09	51.77	47.47	54.67
4	16		31.19	27.71	30.47	69	64.12	66.88	50.19	43.57	47.9

Table-10

Effect of carbonation time

2-Naphthol to kerosene oil ratio
during dehydration .. : 1:2.5
during carbonation .. : 1:1
$CaCl_2$ (on 2-naphthol charged) .. : 2 per cent

Dehydration time .. 8 hr
Carbonation temperature .. 250°

No.	Time of carbonation hr	Pressure psig →	Conversion, %			Yield, %			Selectivity, %		
			20	50	100	20	50	100	20	50	100
1	4		24.34	33.94	34.36	77.11	77.27	76.83	57.52	59.88	59.9
2	8		22.09	33.03	29.35	71.99	71.94	63.66	44.28	54.05	44.68
3	12		-	30.16	28.32	-	67.17	59.24	-	47.87	41.0
4	16		15.14	21.78	23.31	62.09	56.22	62.73	28.53	33.21	38.48

Table-11

Effect of carbonation time

2-Naphthol to kerosene oil ratio
during dehydration .. : 1:2.5
during carbonation .. : 1:1
$CaCl_2$ (on 2-naphthol charged) .. : 2 per cent

Dehydration time .. 8 hr
Carbonation temperature .. 270°

No.	Time of carbonation hr	Pressure psig →	Conversion, %			Yield, %			Selectivity, %		
			20	50	100	20	50	100	20	50	100
1	4		14.62	28.22	30.4	80.5	71.09	70.13	42.85	49.39	50.49
2	8		12.37	14.32	21.47	67.57	45.86	61.86	27.62	20.91	36.02
3	12		8.181	13.29	8.698	49.55	24.41	43.13	13.94	1.732	13.75
4	16		-	0.8181	-	-	19.27	-	-	1.002	-

Table-12

Reproducibility of optimum results

2-Naphthol to kerosene oil ratio :
during dehydration .. 1:2.5
during carbonation .. 1:1
$CaCl_2$ (on 2-naphthol charged).. 2 per cent

Carbonation time : 4 hr
Carbonation temperature : 250°
Carbonation pressure : 70 psi

No.	Conversion %	Yield %	Selectivity %	Deviation, %		
				Conversion	Yield	Selectivity
1	33.75	73.14	55.71	1.26	6.09	4.03
2	31.39	83.10	59.02	5.54	6.70	1.67
3	34.56	76.40	59.43	4.00	1.90	2.38

Table-13

Results of kinetic runs

2-Naphthol to kerosene ratio
during dehydration : 1:2.5
during carbonation : 1:1

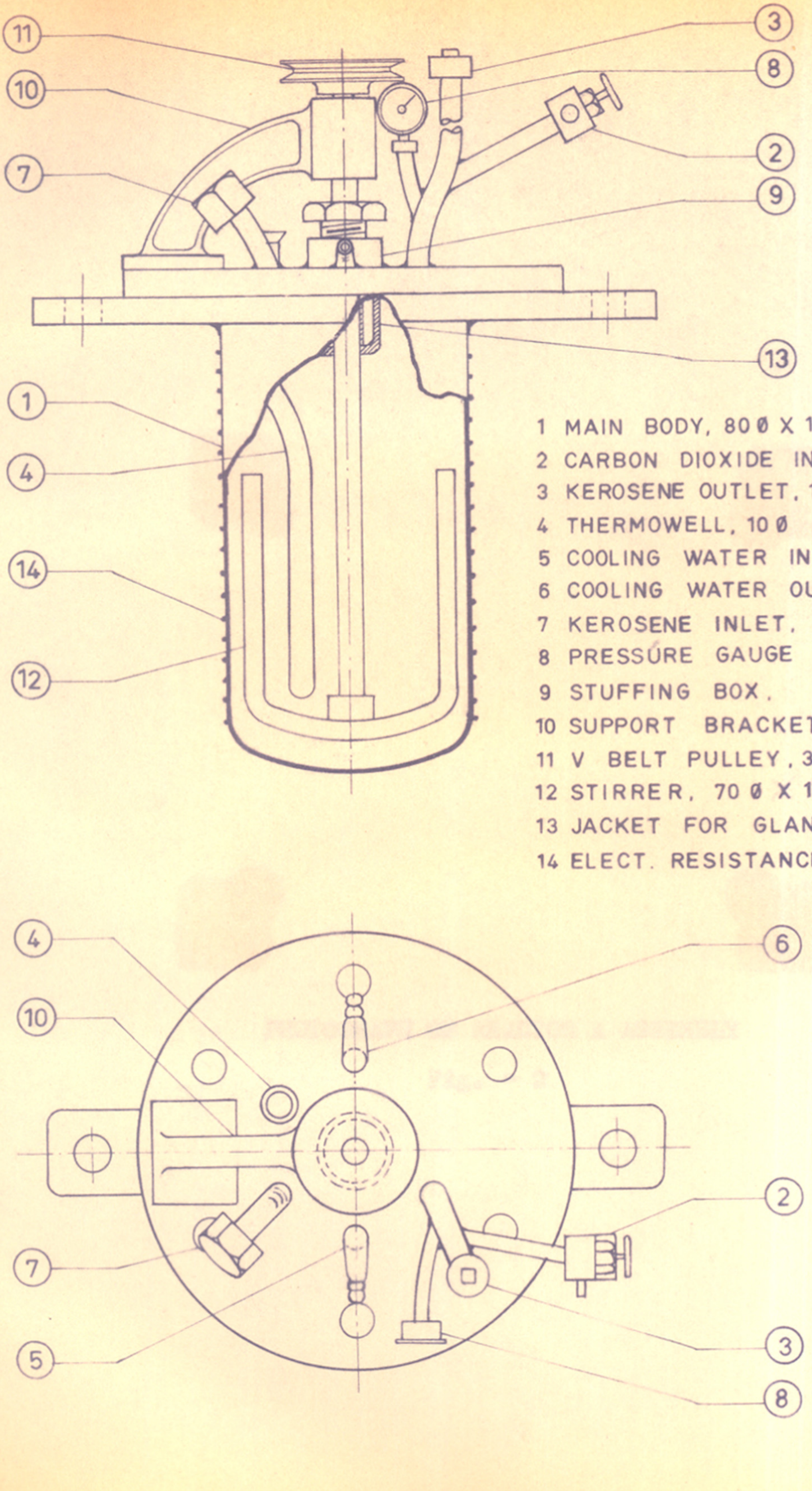
Carbonation temperature : 250°
Carbonation pressure : 70 psig

No.	Reaction time min.	2-Naphthol charged, moles (1)	BON acid formed, moles (2)	2-Naphthol recovered, moles (3)	(3-2) (4)	(1-4) (5)	Total conversion % $\left(\frac{5}{1}\right)$ (6)
1	5	5.15	0.053	3.972	3.919	1.231	23.9
2	15	5.15	0.213	3.918	3.705	1.345	36.3
3	30	5.15	1.237	2.863	1.626	3.524	68.7
4	45	5.15	1.386	2.663	1.277	3.873	75.4
5	60	5.15	1.722	2.037	0.315	4.835	94.0
6	120	5.15	1.853	2.156	0.303	4.847	94.2

FIGURES

PHOTOGRAPH OF REACTOR A ASSEMBLY

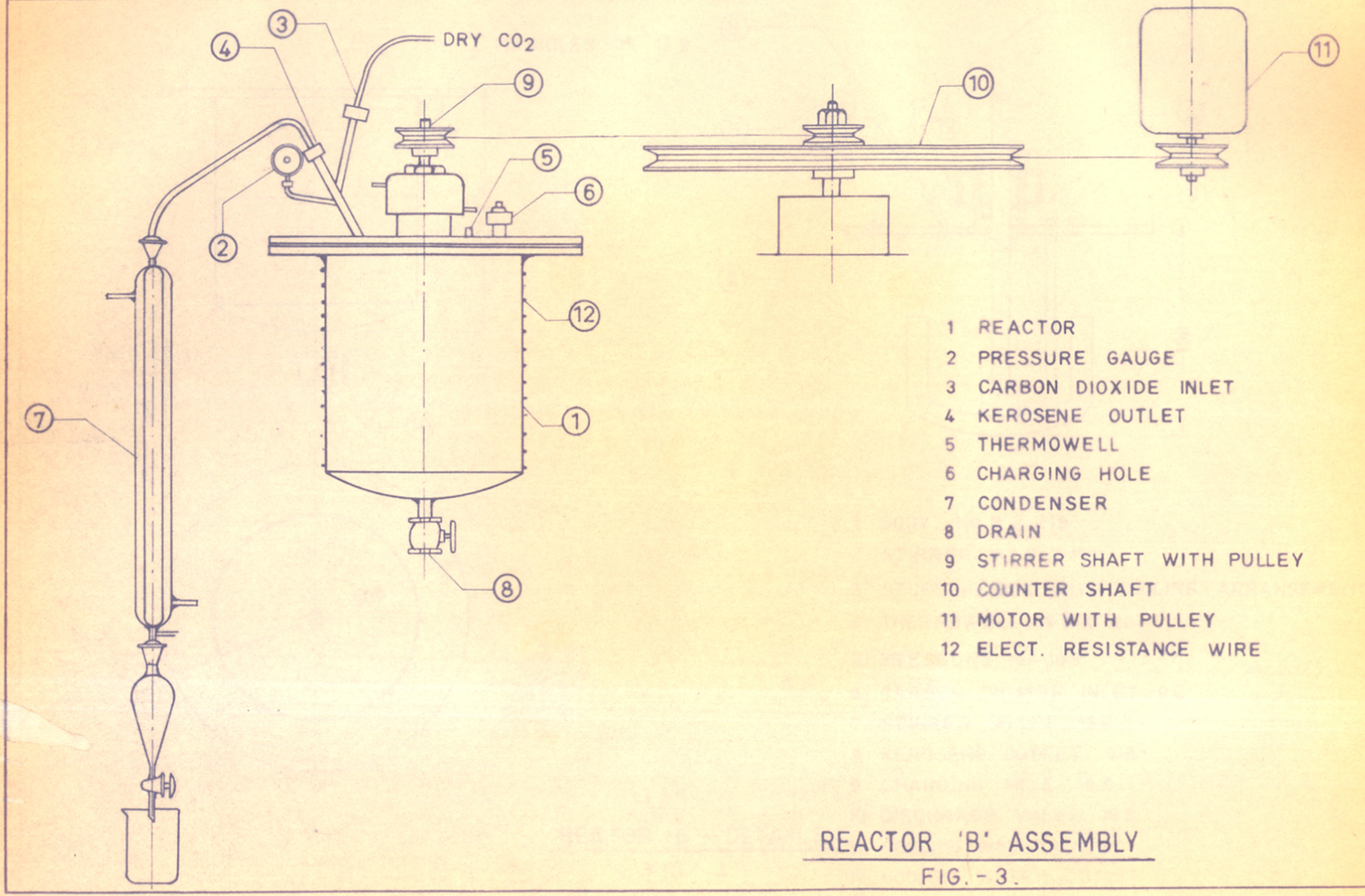
Fig. - 2



1 MAIN BODY, 80 Ø X 190
2 CARBON DIOXIDE INLET, 10 Ø
3 KEROSENE OUTLET, 10 Ø
4 THERMOWELL, 10 Ø
5 COOLING WATER INLET, 6 Ø
6 COOLING WATER OUTLET, 6 Ø
7 KEROSENE INLET, 10 Ø
8 PRESSURE GAUGE
9 STUFFING BOX.
10 SUPPORT BRACKET
11 V BELT PULLEY, 30 Ø
12 STIRRER, 70 Ø X 180
13 JACKET FOR GLAND COOLING
14 ELECT. RESISTANCE WIRE

REACTOR A

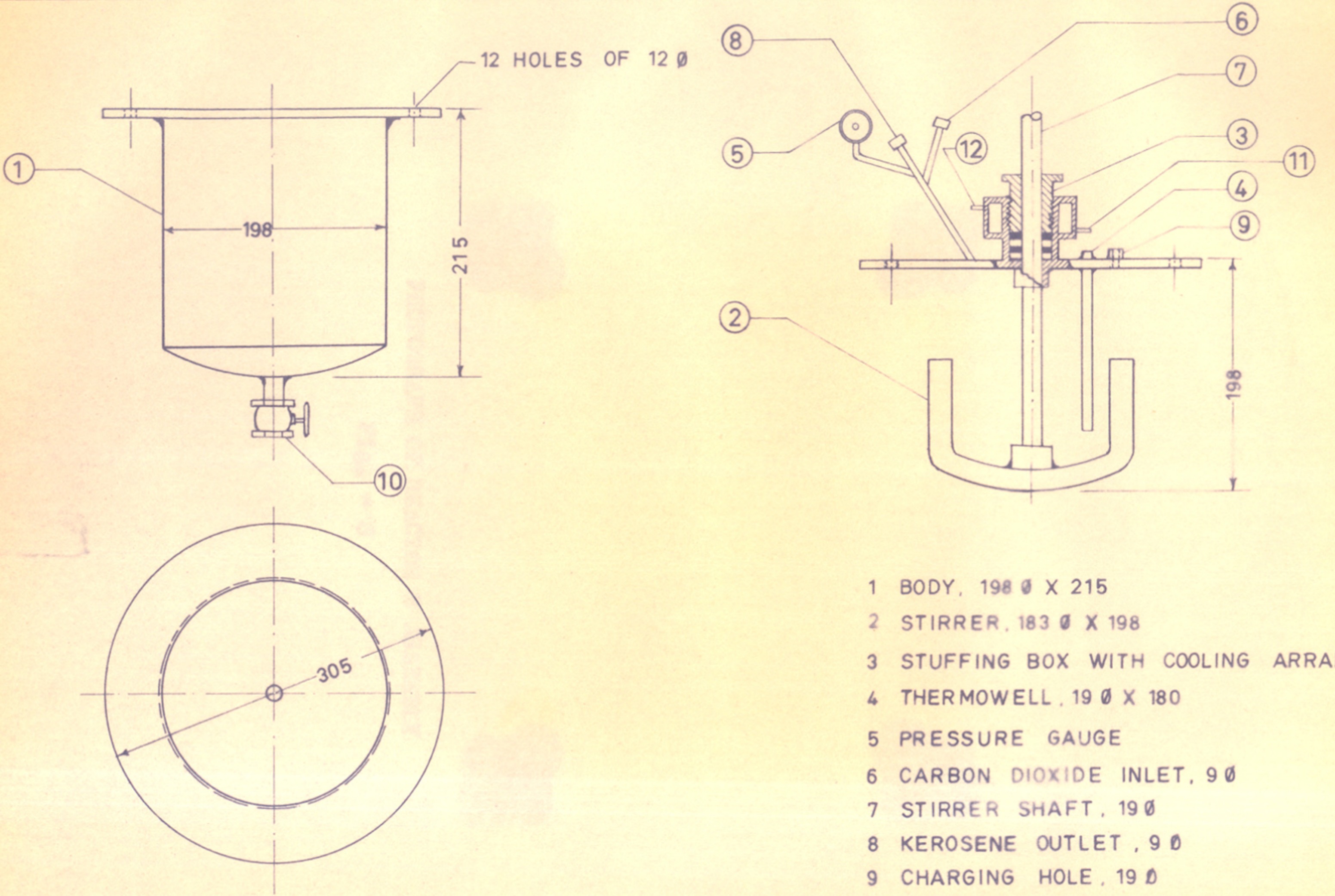
FIG.-1



1 REACTOR
2 PRESSURE GAUGE
3 CARBON DIOXIDE INLET
4 KEROSENE OUTLET
5 THERMOWELL
6 CHARGING HOLE
7 CONDENSER
8 DRAIN
9 STIRRER SHAFT WITH PULLEY
10 COUNTER SHAFT
11 MOTOR WITH PULLEY
12 ELECT. RESISTANCE WIRE

REACTOR 'B' ASSEMBLY

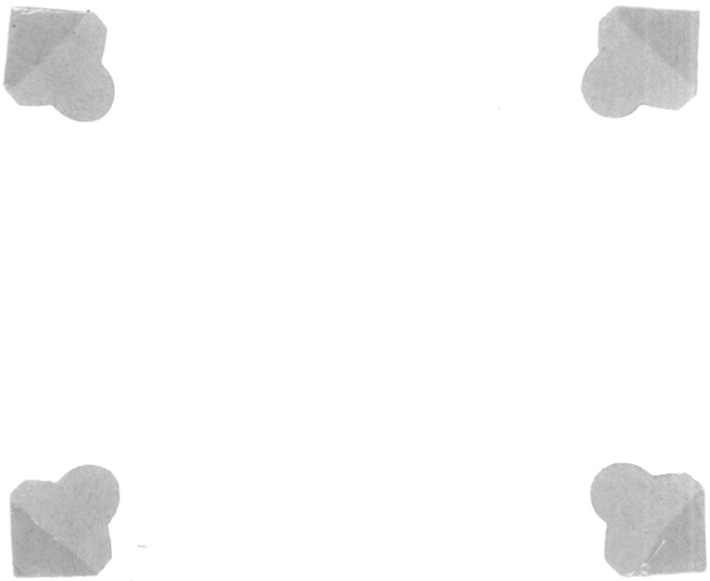
FIG. - 3.



1 BODY, 198 Ø X 215
2 STIRRER, 183 Ø X 198
3 STUFFING BOX WITH COOLING ARRANGEMENT
4 THERMOWELL, 19 Ø X 180
5 PRESSURE GAUGE
6 CARBON DIOXIDE INLET, 9 Ø
7 STIRRER SHAFT, 19 Ø
8 KEROSENE OUTLET, 9 Ø
9 CHARGING HOLE, 19 Ø
10 DISCHARGE VALVE, 19 Ø
11 COOLING WATER INLET
12 COOLING WATER OUTLET

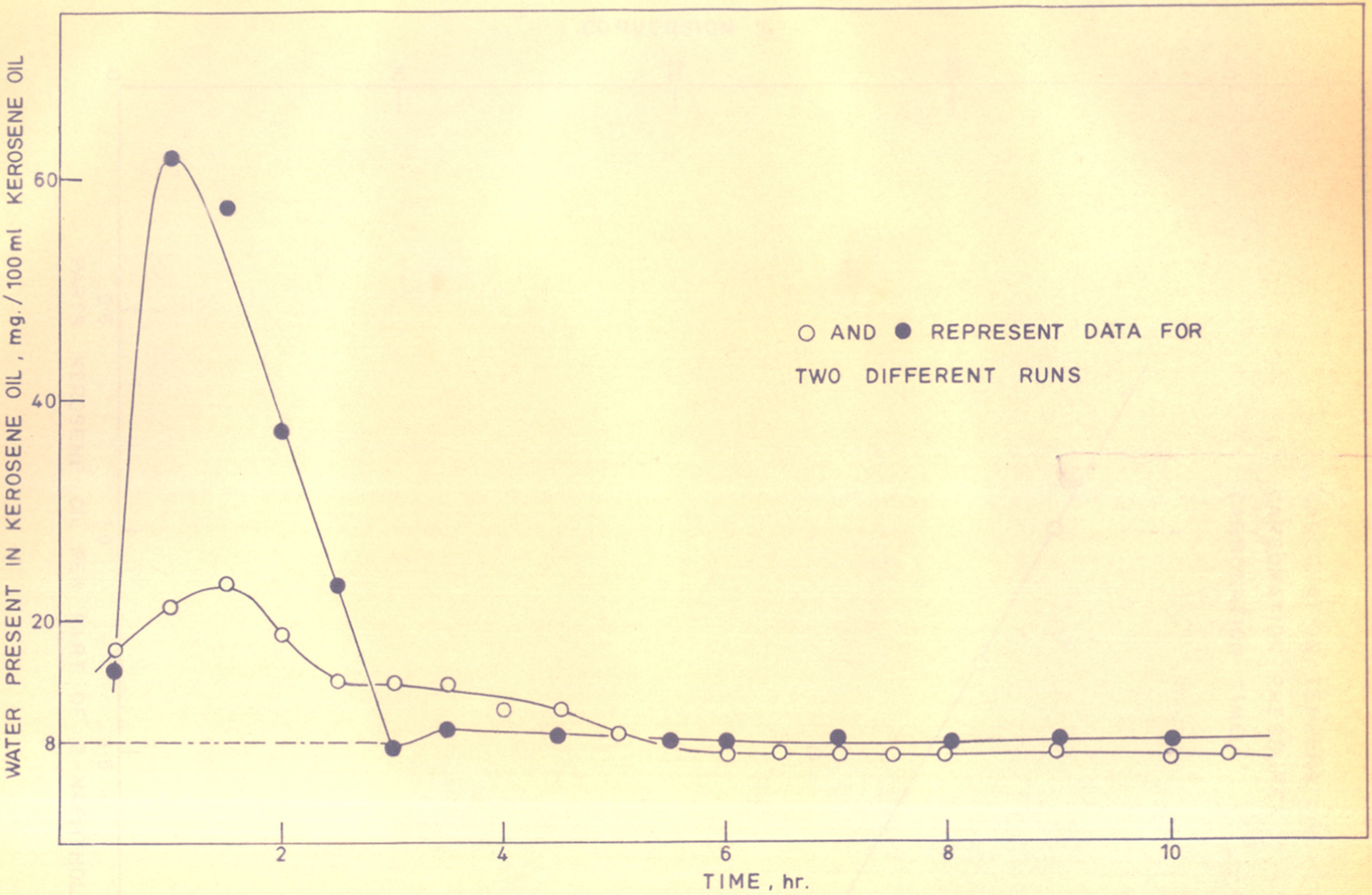
RECTOR B - DETAILS

FIG. - 4



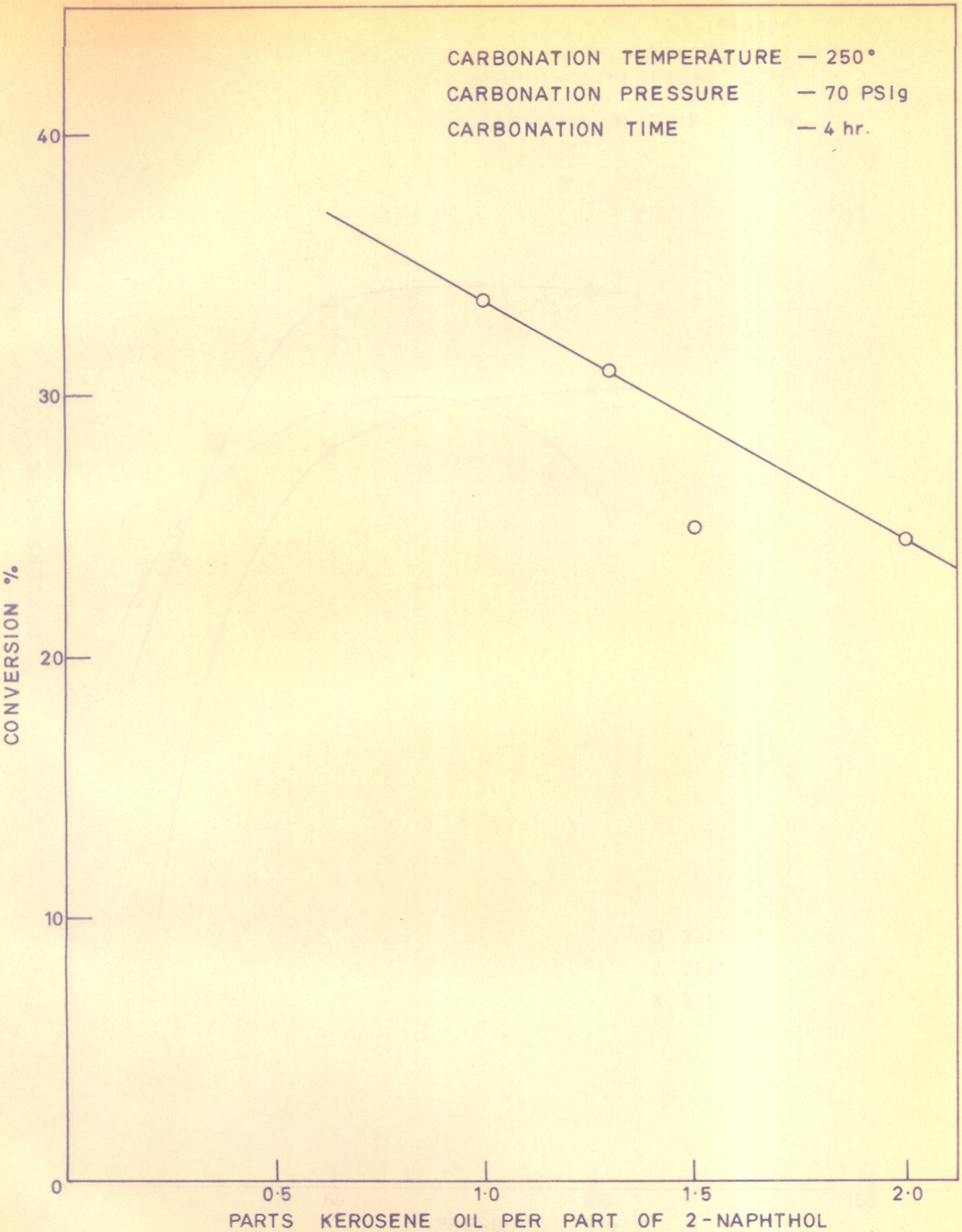
PHOTOGRAPH OF REACTOR B ASSEMBLY

Fig. - 5



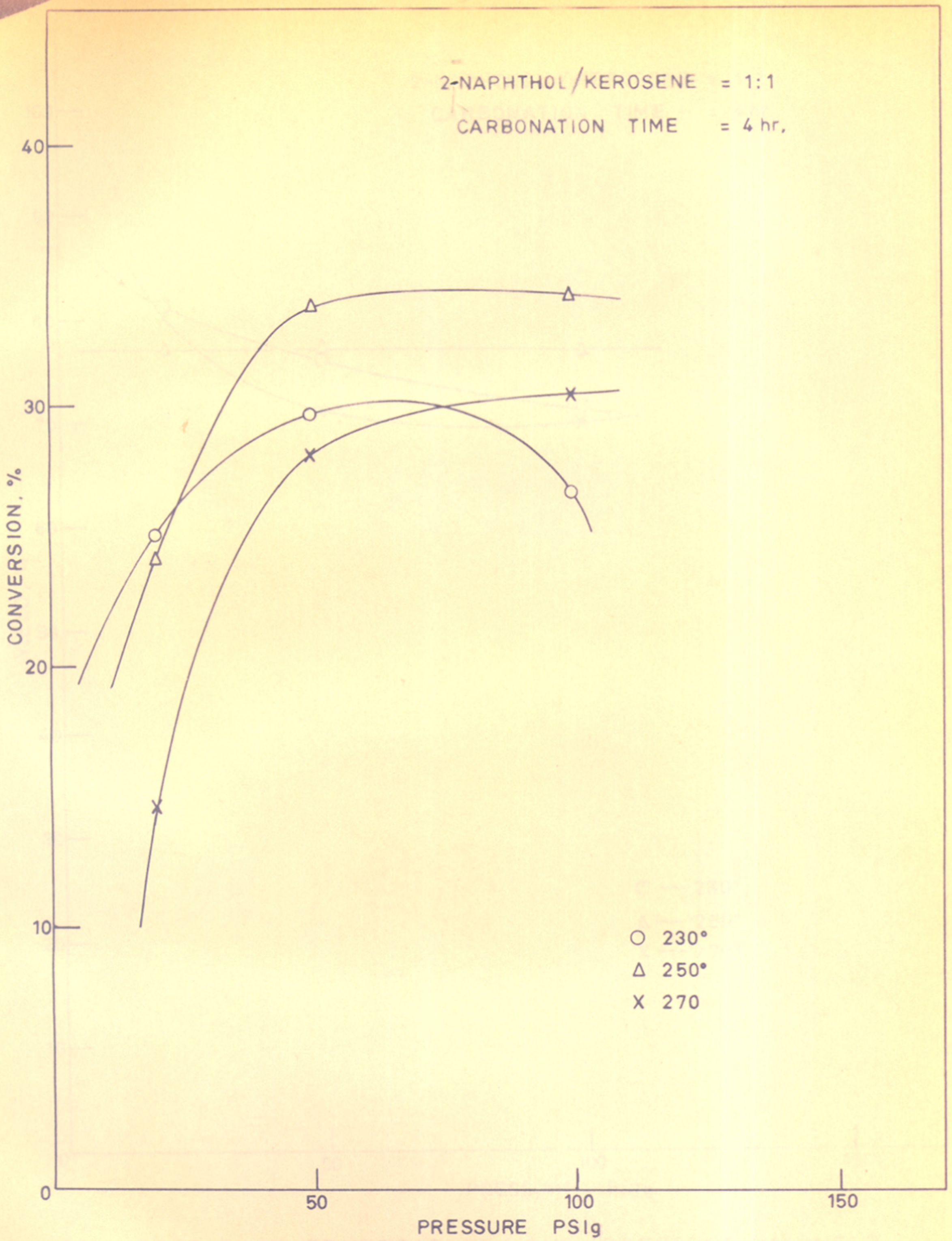
WATER PRESENT IN KEROSENE OIL DURING DISTILLATION

FIG. - 6.



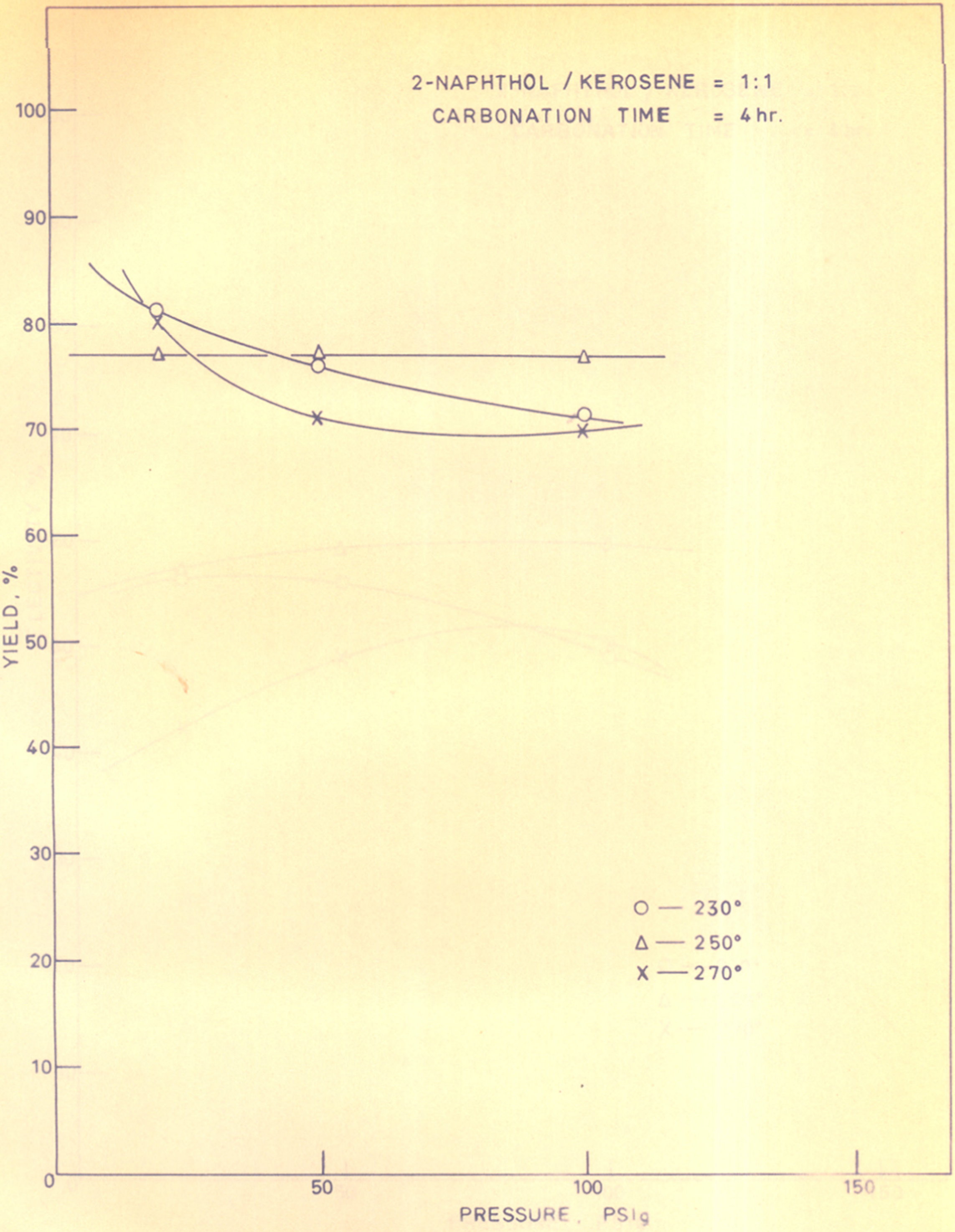
EFFECT OF 2-NAPHTHOL TO KEROSENE OIL RATIO ON CONVERSION

FIG.-7.



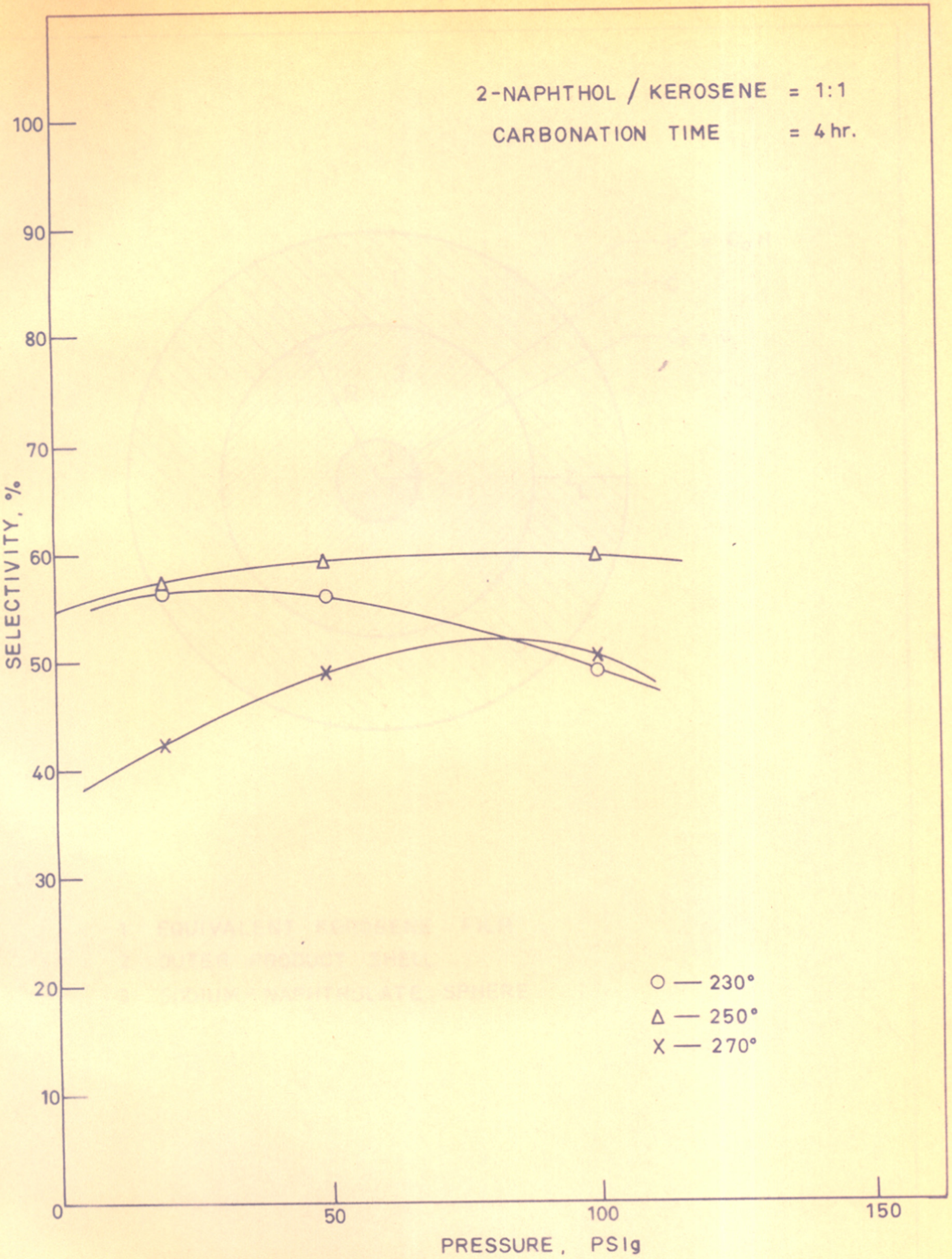
EFFECT OF TEMPERATURE AND PRESSURE ON CONVERSION

FIG. - 8



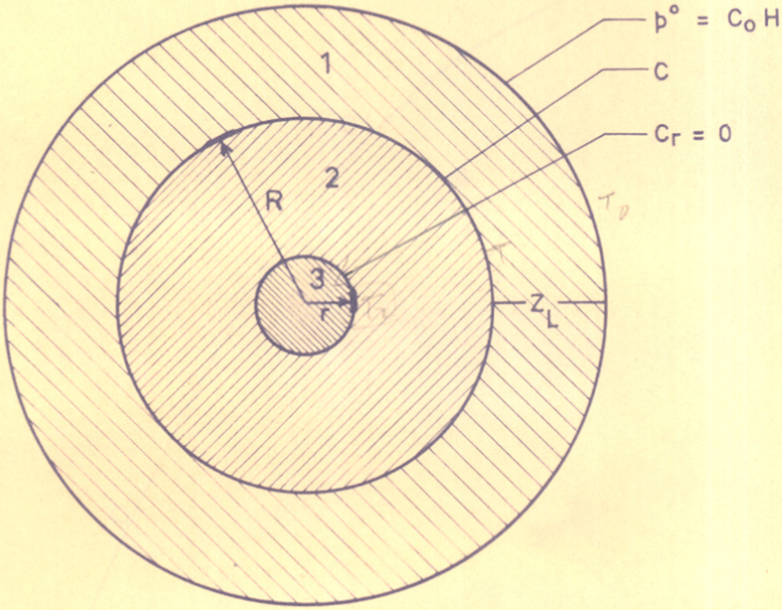
EFFECT OF TEMPERATURE AND PRESSURE ON YIELD

FIG.– 9.



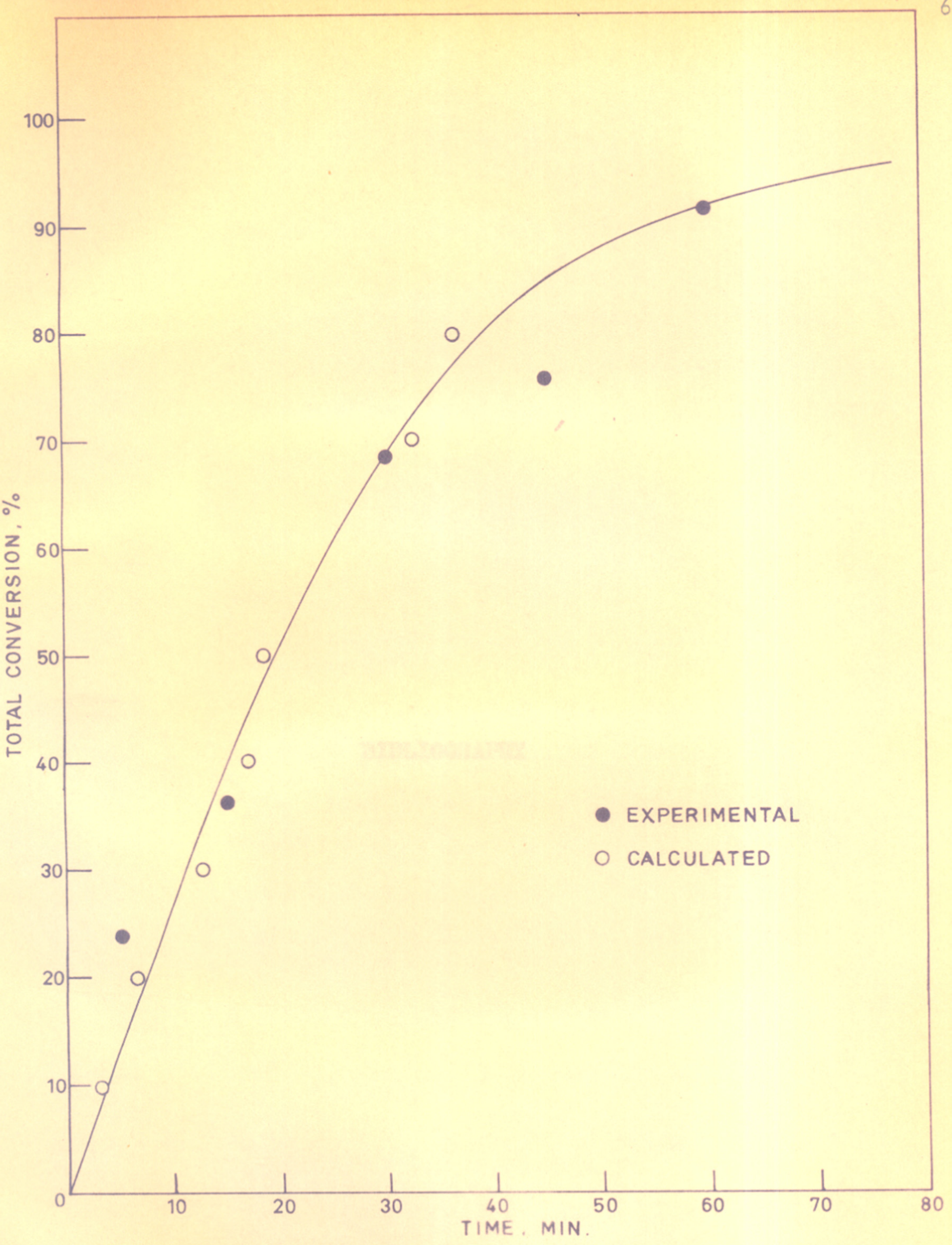
EFFECT OF TEMPERATURE AND PRESSURE ON SELECTIVITY

FIG. – 10.



1 EQUIVALENT KEROSENE FILM
2 OUTER PRODUCT SHELL
3 SODIUM - NAPHTHOLATE SPHERE

FIG. - 11.



EXPERIMENTAL AND CALCULATED VALUES OF TOTAL CONVERSION AS A FUNCTION OF CARBONATION TIME

FIG. - 12.

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BIBLIOGRAPHY

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