THERMAL AND CATALYTIC CRACKING, AROMATISATION AND HYDROGENATION OF HIGH BOILING PARAFFINIC PETROLEUM HYDROCARBONS UNDER PRESSURE

By M. Ramacharyulu, S. Sourirajan and S. S. Ghosh
(Department of Chemical Technology and Chemical Engineering,
Indian Institute of Science, Bangalore-3)

Received December 7, 1957

INTRODUCTION

Thermal and catalytic cracking processes form the most important developments in the modern refining of petroleum. The processes are concerned mainly with the production of gasolines of high anti-knock quality from high boiling petroleum fractions, and are carried out either at atmospheric or at high pressures.

The application of pressure in cracking of hydrocarbons dates back to 1865 when Young[1] subjected hydrocarbon oils to cracking under a pressure of 20 p.s.i.g. Benton *et al.*[2] also employed the same pressure range to effect decomposition of oils. The application of really high pressures of the order of 200–500 atmospheres was made by Ipatief[5] and Bergius[3] for high pressure hydrogenation of oils, which paved the way for extensive investigations being carried out subsequently by many other workers. Thus, the pioneering work of Pier, Bergius and Becker was responsible for successful development of the process for producing high quality motor fuels and aviation gasolines by high pressure hydro-cracking of oils. The catalytic pressure hydrogenation was also successfully applied to the desulphurization of mineral oils, thereby enabling the process as a whole to assume considerable technical importance. In this connection, mention may be made also of the work of Waterman *et al.*[4] and Sweeny *et al.*[6]

It is now fairly wellknown that gasolines produced by high pressure hydrogenation of oils are practically devoid of aromatic ingredients responsible for high anti-knock properties. Hence, the process of catalytic reformation combined with desulphurization of gasolines and naphthas, carried under the influence of slight hydrogen pressures, is the one which assumed importance during the Second World War. This process, known as ‘ hydroforming ’, was originally developed in Germany by the I. G. Farben Industrie and its basic patents were held by them.

Due to its immense technical importance the experimental data on cracking-hydrogenation-aromatisation of hydrocarbon oils under pressure are mostly covered by patents. As such, the knowledge obtainable from published literature regarding relationship between the different process variables and their bearing on the nature of feed-stock, nature of products, etc., are far from adequate. Moreover, the diverse character of petroleum obtained from different natural sources presents a problem which does not permit postulation of any single method for application to all types of feed-stocks. Hence, in each individual case, it is necessary to carry out initial laboratory investigations with a feed-stock of known composition with special reference to the presence of a distinct hydrocarbon class in the same. With this end in view, the present investigation was taken up by the authors. A hydrocarbon feed-stock of distinctly paraffinic composition, boiling in the middle oil range, was employed with a view to making a study of the effect of high pressure on the cracking-hydrogenation-aromatisation of the same.

THERMODYNAMIC CONSIDERATIONS

The feed-stock employed in this investigation, though distinctly paraffinic, is somewhat complex in nature. However, it is possible to predict the effect of variables like temperature, pressure, residence period, catalyst, etc., on cracking, hydrogenation and aromatisation of the predominating hydrocarbon of the feed-stock for its maximum conversion into ingredients of gasoline boiling range and of high anti-knock value. From a comprehensive analysis of the feed-stock it is seen that it corresponds nearly to an average hydrocarbon molecule of the formula $C_{12}H_{26}$. Hence, the thermodynamic considerations of this hydrocarbon for cracking, hydrogenation and aromatisation have been applied here.

Theoretically speaking, a paraffin molecule may decompose in a variety of ways. Splitting of paraffin into a lower olefin and a lower paraffin, decomposition into elemental carbon and hydrogen, dehydrogenation to olefin, dehydrocyclisation to naphthenes and aromatics, disproportionation, etc., are some of the many possible reactions that are likely to take place at temperatures normally employed in the cracking of higher paraffins. These primary reactions may be followed by secondary ones if the products of primary decomposition enter into subsequent secondary reactions, either with the original hydrocarbon molecule or with one another. As the object of this investigation is to effect maximum possible conversion of the feed-stock into products of gasolinic boiling range it is necessary that the experimental conditions should be controlled as effectively as possible. As an example, taking the case of the following splitting reaction of $C_{12}H_{26}$ hydrocarbon,

$$C_{12}H_{26}\,(g) \rightleftharpoons C_5H_{12}\,(g) + C_7H_{14}\,(g),$$

from a knowledge of heat of reaction as well as free energy of reaction at different temperatures (calculated from heats and free energies of formation of each constituent), it can be concluded that the cracking reaction is endothermic, and that quantitative yields of products can be obtained under suitable experimental conditions, *i.e.*, the equilibrium yields of gasolinic fractions should increase at higher temperatures.

Besides the consideration of effect of temperature on the cracking of higher paraffins, a non-catalytic type of cracking may be assumed to be a monomolecular reaction. In catalytic cracking, however, the rate is governed by the concentration of the reactants on the catalyst surface, and in this case the velocity constant of a simple first-order reaction is only approximately applicable. Further, in the catalytic cracking of paraffinic hydrocarbons, in addition to simple splitting reactions, secondary reactions like polymerisation, alkylation, aromatisation, hydrogen transfer and coke formation are also involved. As these secondary reactions are not uni-molecular, the theoretical calculation of yields of gasoline in catalytic cracking is not a simple proposition.

Since the cracking of a hydrocarbon molecule results in an increase in volume, theoretically speaking, application of high pressures will not favour the same. An idea of the extent to which pressure alone might influence the reaction can be had by calculating the values of K_p at different pressures. In such calculations the use of activity coefficient charts[16] is made to obtain the fugacities of hydrocarbons by following the method of Dodge.[7] Hence for such calculations, it is first of all necessary to have the values of critical constants (from Critical Table) of the respective components of the reacting mixture. By referring the values of critical constants and their reduced variables to the activity coefficient charts,[loc. cit.] the activity coefficients of the respective components are found out. Thus, in the case of the above reaction, the activity coefficient at 700° K. of the respective components, as found out by the above method, are

$$^{\gamma}C_{12}H_{26} = 0{\cdot}375$$
$$^{\gamma}C_{5}H_{12} = 0{\cdot}900$$
$$^{\gamma}C_{7}H_{14} = 0{\cdot}780$$

and

$$K_{\gamma} = \frac{^{\gamma}C_{5}H_{12} \times {}^{\gamma}C_{7}H_{14}}{^{\gamma}C_{12}H_{26}}$$

$$= \frac{0{\cdot}90 \times 0{\cdot}78}{0{\cdot}375} = 1{\cdot}872.$$

The values of K_p can then be calculated as

$$K_p \text{ at any pressure} = \frac{K_p \text{ at 1 atm.}}{K_{\gamma}},$$

and for the above reaction

$$K_p \text{ at } 700^{\circ}\text{ K. and 50 atms.} = \frac{7{\cdot}67 \times 10}{1{\cdot}872} = 4{\cdot}10 \times 10.$$

The values of equilibrium constant for the above reaction, thus calculated, for 700° K. and various pressures up to 200 atms. are shown in Table I.

TABLE I

K_p values at 700° K. and various pressures for the reaction,
$C_{12}H_{26}(g) \rightleftarrows C_5H_{12}(g) + C_7H_{14}(g)$

Pressure	K_p value
1 atm.	$7\cdot67\times10$
50 atms.	$4\cdot10\times10$
100 atms.	$3\cdot65\times10$
200 atms.	$3\cdot05\times10$

By comparing the above values one can easily understand how pressure influences the equilibrium yield of products. In general, a reduced yield of gasolinic ingredients will be expected with increased pressure. It has, however, been stated already that the products of the primary cracking reactions, produced in whatever amounts under the reaction conditions, may subsequently enter into secondary reactions of olefin hydrogenation (in presence of high pressure hydrogen), olefin polymerisation, alkylation, etc. As these secondary reactions lead to a reduction in volume they will be favoured by increasing the pressure. By following the method of Dodge*loc. cit.* as stated above, the K_p values of such reactions at different pressures can be similarly calculated, and the values will be found to stand in favour of application of high pressure for obtaining higher equilibrium yields of products. It will, however, be necessary to see the extent to which such secondary reactions are influenced by temperature at constant pressure, since in accordance with our previous discussion high temperature conditions are necessary for producing from the feed-stock the cracked products to serve as reactants for the secondary reactions. For this purpose, one may consider the reactions,—(1) hydrogenation of pentene, (2) polymerisation of butene, and (3) alkylation of isobutane and isobutene, as these hydrocarbons are expected to be present, among others, in the reaction mixture as the products of primary decomposition of the feed-stock. The equilibrium constant of these reactions have been calculated for a pressure of one atmosphere and various temperatures up to 1000° K. and are shown in Table II.

TABLE II

Reaction	300° K.	400° K.	500° K.	600° K.	700° K.	800° K.	900° K.	1000°
Hydrogenation of olefin $C_5H_{10}+H_2 \rightleftarrows C_5H_{12}$	$1\cdot8\times10^{15}$	$3\cdot64\times10^{9}$	$1\cdot62\times10^{6}$	9×10^{3}	$2\cdot1\times10^{2}$	$1\cdot3\times10$	$1\cdot41$	$0\cdot24$
Polymerisation of olefin $2C_4H_8 \rightleftarrows C_8H_{16}$	$7\cdot9\times10^{6}$	$1\cdot6\times10^{3}$	$1\cdot01\times10$	$0\cdot36$	$3\cdot4\times10^{-2}$	$1\cdot5\times10^{-3}$	$1\cdot5\times10^{-3}$	$5\cdot4\times1$
Alkylation iso-butane+iso-butene $\rightleftarrows$ 2, 2, 4-tri-methyl pentane	$1\cdot4\times10^{5}$	$6\cdot41\times10$	0 62	$2\cdot7\times10^{-2}$	3×10^{-3}	$0\cdot65\times10^{-4}$	$2\cdot1\times10^{-4}$	$8\cdot5\times1$

From the above values it is seen that hydrogenation of olefins is thermodynamically possible at all temperatures under atmospheric pressure. However, polymerisation and alkylation reactions are possible to any significant extent only below 600° K.

For the above reactions to take place, the cracking of $C_{12}H_{26}$ into suitable hydrocarbon fragments is an important prerequisite. Thermodynamically, the primary cracking reaction is possible only above 600° K., under which condition the secondary reactions may get suppressed. Under such circumstances, therefore, it is imperative to use high pressures at appropriate temperature conditions for obtaining maximum yield of gasolinic ingredients from the feed-stock.

CATALYSTS EMPLOYED

The catalysts employed in this investigation include synthetically prepared silica, alumina, magnesia and chromia and Indian kieselguhr. Composite catalysts made of silica-alumina, silica-magnesia, alumina-magnesia, kieselguhr-alumina and kieselguhr-magnesia have also been tried in this investigation.

The methods of catalysts preparation are briefly outlined below:

Silica (SiO_2).—By making its hydro-gel from pure grade water-glass in acid (HNO_3) medium.

Alumina (Al_2O_3).—By dissolving pure aluminium foil in potassium hydroxide, acidifying with HNO_3, and precipitating $Al(OH)_3$ from the acidified solution by passing CO_2.

Magnesia (MgO).—By precipitating from a hot dilute magnesium nitrate solution with an excess of KOH.

Chromia (Cr_2O_3).—By precipitating from an alcoholated solution of chromic acid and by boiling under reflux.

Indian kieselguhr.—By boiling raw kieselguhr of appropriate mesh size with HNO_3, filtering and washing.

Silica-Alumina ($SiO_2 : Al_2O_3$).—From a solution of potassium aluminate of known Al_2O_3 content having a sodium-free silica hydro-gel in suspension, and passing CO_2 through the solution.

Silica-Magnesia ($SiO_2 : MgO$).—From a hot solution of magnesium nitrate of known MgO content having a sodium-free silica hydro-gel in suspension, and precipitating magnesium hydroxide on the hydro-gel by means of hot dilute KOH.

Alumina-Magnesia ($Al_2O_3 : MgO$).—From a suspension of magnesium hydroxide in potassium aluminate solution, by precipitating aluminum hydroxide with CO_2.

Kieselguhr-Alumina.—From a suspension of acid-treated kieselguhr in potassium aluminate solution by precipitating aluminium hydroxide with CO_2.

Kieselguhr-Magnesia.—From a suspension of acid treated kieselguhr in magnesium nitrate solution by precipitating magnesium hydroxide with hot dilute KOH.

The catalysts, after precipitation, are filtered, washed and dried at 110° C. Before use, the catalysts are heated to 400° C. for final calcination. In case of chromia catalyst which appears black in the oxidised state and dark green in the reduced state, before use the same is reduced *in situ* in a current of hydrogen for an hour at the reaction temperature.

EXPERIMENTAL

Apparatus:

The investigation has been carried out in a static system of apparatus which consists of a high pressure reaction bomb having connection to a gas compression system and provided with pressure gauges, high pressure valves and cylinders. The flow diagram of the apparatus is shown in Fig. 1.

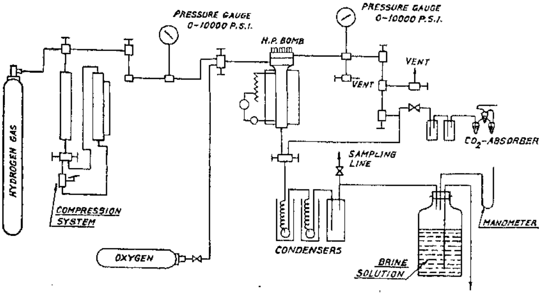


FIG. 1. Flow Diagram of the Apparatus.

The reaction bomb is fabricated out of special alloy-steel of nickel-molybdenum-chromium composition conforming with the B.S. 4 S 11. En. 110 specification. The sectional diagram of the bomb is shown in Fig. 2. The studs, nuts, thermocouple sheath, etc., are made of austenitic steel of D.T.D. 176 A specification. The bomb has a liquid volume of about 200 cm.^{3} A stainless steel tube holding a perforated copper grid at its lower end serves as the catalyst chamber, through which passes a tight-fitting thermocouple sheath, both being supported by the bomb cover by means of pressure tight joints. 25 cm.^{3} of catalyst of -5 to $+10$ mesh is filled into the free space of the catalyst chamber. The bomb is provided with external electric heating arrangement, the reaction temperature being regulated at any desired level by means of a sunvic energy regulator as shown in Fig. 1. The gas compression unit is connected to the reaction bomb through suitable high pressure control valves, and consists of a small hand-operated hydraulic oil pump capable of compressing gases from usual pressures of commercial gas cylinders to the required experimental high pressure.

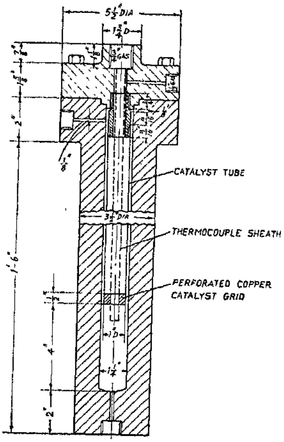


FIG. 2. Reaction Bomb.

Experimental Procedure:

A known volume of feed-stock is introduced into the reaction chamber. Hydrogen, or any other gas as the case may be, is compressed and filled in at the laboratory temperature to the required gauge pressure. The bomb is heated slowly and brought to the reaction temperature in about 2 to 3 hours. The pressure of the system rises with temperature, the reaction setting in simultaneously. The reaction is over when the pressure of the system indicates a steady condition. The time of residence of the oil in the reaction zone is one of the operating variables. In so far as the degree of conversion to gasoline is concerned, the same has been found to reach a maximum value within two hours after which there is no further increase. Hence a residence period of two hours has been maintained throughout this investigation.

On the completion of the reaction, the pressure of the system is released at the reaction temperature and the products are led through a condensing system consisting of a glass trap immersed in ice-cooled water followed by another in dry-ice and acetone. The non-condensable gases are collected in a gas holder. The liquid and the gaseous products of reaction are analysed as described below. The carbon deposited on the catalyst during an experiment is burnt out in a current of air or oxygen and is estimated by absorbing the carbon dioxide in a caustic potash bulb. The catalyst is thus regenerated and the system made ready for the next experiment.

Analysis of Products:

Total liquid product.—This is determined by weighing the liquid collecting in the trap immersed in ice-cooled water.

Gasolinic fraction.—The yield of gasoline is determined by distilling 15 to 25 cm.[3] of the liquid product. The distillation is carried out in accordance with the standard A.S.T.M. method,[8] and the fraction distilling between 45°–175° C. is taken as the gasoline.

Degree of unsaturation of the liquid product.—This is determined from the Bromine Number in accordance with the A.S.T.M. Standard method D_{275}–46 T[9].

Olefines and aromatics.—The degree of olefinicity or aromaticity is found out by determining the Aniline Point of the product. The volumetric percentage of olefines and aromatics taken together is determined by treating a known volume of the liquid product with P_2O_5 and H_2SO_4 absorption mixture.[10] The aromatics content of the product is determined by fractional adsorption through activated silica gel.[11]

Paraffins, iso-paraffins and cyclo-paraffins.—In a mixture of these three classes of hydrocarbons, free from olefins and aromatics, the cyclo-paraffins are determined from the values of N_D^{20}, D^{20} and the refractivity intercept by employing Thomson's Nomogram.[12] The determination of iso-paraffins is carried out by the antimony pentachloride method.[13]

Liquefied and non-condensable gases.—The product collecting in the dry ice-acetone trap usually consists of C_3 and C_4 hydrocarbons. This is brought to the gaseous state by carefully vapourising the contents of the trap, and then analysed by the conventional method of gas analysis for saturates and unsaturates. Combining the results with the average carbon number, as found by fractional combustion of a fresh sample, propane, propylene, butane, and butylene contents of the liquefied gaseous products are found out. The non-condensable gases collected in the gas holder are analysed similarly and their C_1 and C_2 hydrocarbon contents, both saturated and unsaturated, are found out.

Conversion calculations.—The 'actual' and 'process' conversion of the feed-stock into gasolines, olefines and aromatics are calculated as follows:

Actual conversion = Percent. conversion based on the volume of liquid products of reaction.

$$\text{Percent. Process conversion} = \text{Actual conversion} \times \frac{\text{Vol. of liquid products}}{\text{Vol. of reactant (feed-stock)}}$$

RESULTS AND DISCUSSION

1. . *Effect of autogenous pressure of the feed-stock at different temperatures.*—It is seen from the results given in Table III and represented graphically in Fig. 3 that there is practically no reaction at least up to 325° C., and the same is noticeable only above 325° C. At still higher temperatures the yield of gaseous

TABLE III

Effect of autogenous pressure of the feed-stock on the yield of various products at different temperatures

Catalyst: Nil, Feed-stock Vol.: 20 cm.^{3}, Residence period: 2 hours.

Reaction Temperature ° C.	300	325	350	375	400
Maximum pressure attained (p.s.i.g.)	..	..	40	100	500
Reactants:					
Feed-stock in gm.	15·280	15·280	15·280	15·280	15·280
Products:					
Hydrocarbon oil in gm. ..	15·200	15·120	15·000	13·085	8·120
Total gas in litres at 25° C. ..	..	..	0·150	2·050	6·000
Hydrogen in litres at 25° C. ..	..	..	..	0·020	0·030
Paraffins:					
C_1 and C_2 gases in litres at 25° C.	..	..	0·120	1·860	5·000
Average C-number	..	..	1·4	1·4	1·4
C_3 and C_4 gases in litres at 25° C.	..	..	..	0·010	0·100
Average C-number	..	..	..	3·2	3·2
Olefins:					
Ethylene gas in litres at 25° C. ..	..	..	0·030	0·120	0·470
C_3 and C_4 gases in litres at 25° C.	..	..	..	0·040	0·400
Average C-number	..	..	..	3·4	3·4
Total material accounted ..	99·5%	99·0%	98·6%	95·0%	90·0%

products goes on increasing rapidly. The 'total material' accounted for at temperatures of 350° C. and above shows a regular decrease in value at higher temperature, the reason for which may be attributed to the increased carbon deposition. It is evident from Fig. 3 that although up to 350° C. there is no sign of aromatisation of the feed-stock, the same is found to have definitely taken place at 375° and 400° C. This is perhaps due to the secondary reactions of polymerisation and condensation of the gaseous olefinic products of the primary reaction. The higher yields of gasoline at elevated temperatures are likewise explained as due to such secondary reactions, involving also alkylation, of the gaseous products of initial breakdown of higher paraffinic hydrocarbons in the feed-stock.

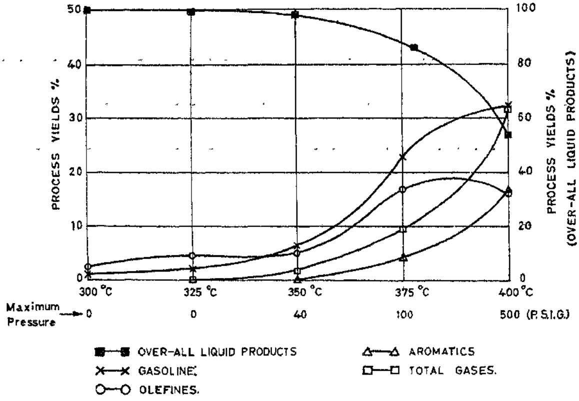


FIG. 3. Effect of Autogenous Pressure of the Feed-Stock on its Cracking under Pressure.

2. *Effect of initial hydrogen pressures at different temperatures.*—In the absence of catalysts, the effect of initial hydrogen pressure has been studied in a set of experiments carried out with a cold hydrogen pressure of 250 p.s.i.g. The maximum pressures developed in the system at different temperatures with the corresponding yields of various products are shown in Fig. 4. In so far as the overall liquid and gaseous products are concerned, it is seen that their yields are almost comparable to those obtained in cracking experiments conducted under the autogenous pressure of the feed stock (*vide* Table III and Fig. 3). A similar set of experiments conducted at the reaction temperatures of 300°, 325°, 350°, 375° and 400° C. with different initial hydrogen pressures ranging from 250 to 3700 p.s.i.g. bring out an interesting relationship between the gasoline formation and the maximum pressure developed in the system (reaction pressure). From these experiments; the optimum conditions for the maximum formation of gasoline with minimum of cracked gases are found to be 350° C. and a maximum reaction pressure

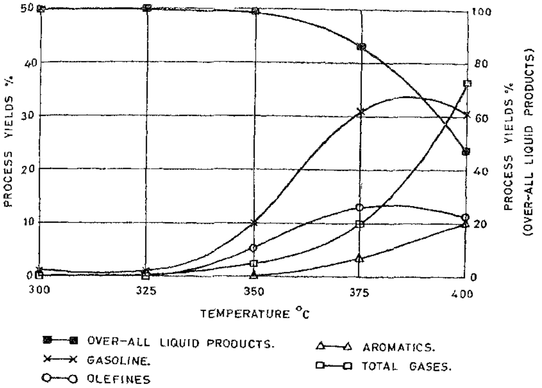


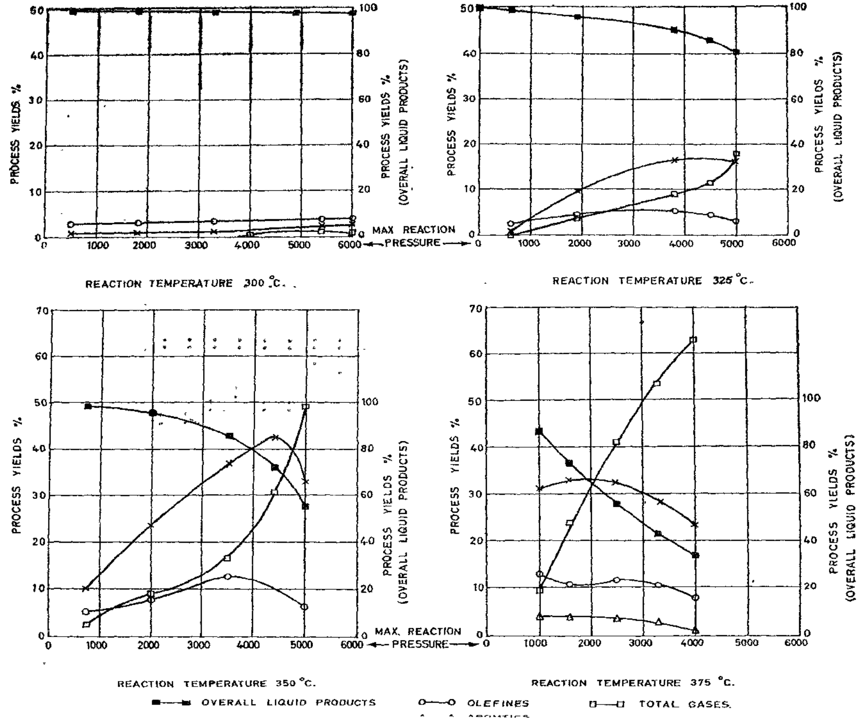
FIG. 4. Effect of Initial Hydrogen Pressure of 250 P.S.I.G. on the Pressure Cracking of the Feed-Stock.

TABLE IV

Effect of a hydrogen pressure of 3500 p.s.i.g. at 350° C. on the properties and composition of gasoline

Boiling range	30°–175° C.
Specific gravity at 20° C.	0·7230
Refractive index at 20° C.	1·4070
Bromine Number	18·0
Olefines (Vol. %)	12·9
Cycloparaffins (Vol. %)	6·0
Iso-paraffins (Vol. %)	47·2
n-Paraffins (Vol. %)	46·8
Aromatics (Vol. %)	Nil

of about 3500 p.s.i.g. (Fig. 5). The analysis of the gasoline obtained under the above optimum conditions are given in Table IV, from which it can be concluded that, in general, under such hydrogenating-cracking conditions, the application of initial hydrogen pressure favours the formation of gasoline, particularly at 350° C. and above. This apparently contradicts the theoretical considerations discussed earlier, and can be explained as due to the destructive hydrogenation of the higher paraffinic hydrocarbons of the feed-stock. Under such conditions the olefine contents of the products are also reduced, thereby increasing correspondingly the yield of saturates.


PROCESS YIELDS %
PROCESS YIELDS %
(OVERALL LIQUID PRODUCTS)
MAX. REACTION
PRESSURE
0
1000
2000
3000
4000
5000
6000
0
10
20
30
40
50
60
70
0
20
40
60
80
100
REACTION TEMPERATURE 300 °C.
REACTION TEMPERATURE 325 °C.
REACTION TEMPERATURE 350 °C.
REACTION TEMPERATURE 375 °C.
■—■ OVERALL LIQUID PRODUCTS
○—○ OLEFINES
□—□ TOTAL GASES.

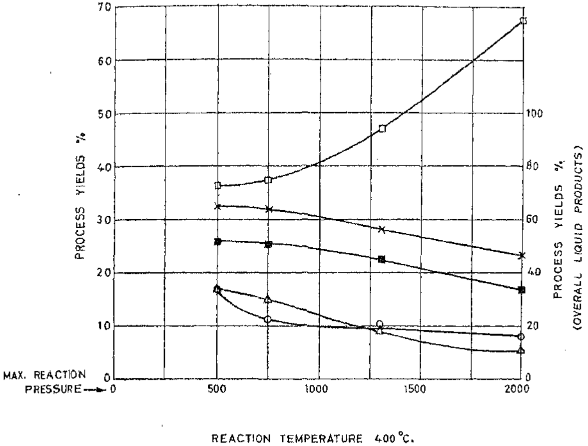


FIG. 5. Effect of Pressure on the Yield of Products Obtained by Cracking-Hydrogenation at Various Initial Hydrogen Pressures and Reaction Temperatures.

From the results of gas analysis given in Table V, it can be inferred that initial hydrogen pressure brings about more of methanization, and at higher temperatures the gas becomes highly paraffinic in nature having more of C_3 and C_4 saturated hydrocarbons. At about 400° C., however, the formation of saturates is considerably suppressed due to the velocity of cracking reactions greatly overtaking the velocities of hydrogenation of olefines which usually takes place at higher temperatures.

The effect of initial hydrogen pressure is very marked on the aromatisation of the feed-stock. From Fig. 5, it can be seen that there is practically no formation of aromatics at least up to 350° C., and that the same appears in the product only at about 375° C. The absence of aromatics at lower temperatures supports the view held by Waterman, *et. al.*,[loc. cit.] according to whom the ring formation in the cracking of paraffins is substantially prevented in the presence of high hydrogen pressures. The presence of increased amounts of aromatics in the gasoline fraction at higher temperatures can likewise be explained as due to the cyclisation reaction more prominently coming into play following the initial cracking reactions with a velocity considerably higher than that of the hydrogenation of olefines. In so far as the composition of gasoline obtained under optimum conditions of pressure and temperature, as mentioned above, is concerned, it is seen from Table IV that there are no aromatics present in the same. Nevertheless, the gasolines are still sufficiently rich in other anti-knock ingredients, such as iso- and cyclo-paraffins.

TABLE V

Effect of initial hydrogen pressure at different temperatures on the gas composition

Reaction Temperature °C.	300	325	350	375	400
Initial hydrogen pressure (p.s.i.g.) ..	3700	3000	2600	2000	500
Gas Composition:					
Paraffins:					
C_1 and C_2 gases in litres at 25° C.	0·150	4·500	6·000	9·500	10·000
Average C-number	1·2	1·2	1·2	1·2	1·4
C_3 and C_4 gases in litres at 25° C.	..	..	1·800	2·050	0·450
Average C-number	..	..	3·4	3·4	3·3
Olefines:					
Ethylene gas in litres at 25° C. ..	..	..	..	..	..
C_3 and C_4 gases in litres at 25° C.	..	..	0·20	0·15	0·60
Average C-number	..	..	3·2	3·4	3·5
Total material accounted	97·8%	97·2%	98·8%	98·2%	94·0%

3. *Influence of gas medium on Cracking-Hydrogenation-Aromatisation of the feed-stock.*—Besides hydrogen, other gases such as carbon dioxide, carbon monoxide, nitrogen, methane, steam, etc., have also been employed from time to time as the pressurizing media to examine their influence on the cracking of hydrocarbons under pressure, but the research data of such investigations are covered by patents. From the results of the previous experiments conducted with hydrogen as the pressurizing medium, it is seen that substantial conversion of the feed stock to gasoline takes place even at 325° C. Whether this is due to the effect of pressure alone or a part is also played by the gas medium has been studied here by conducting some experiments in presence of inert gases, such as carbon dioxide and nitrogen, as pressurizing media, the results of which are given in Table VI.

It is seen from the results that the degree of methanization is most pronounced in case of hydrogen. It is further seen that the differential effect of gas media on the olefines content of the products is almost negligible. However, the nature of the gas has got profound influence on the degree of conversion into gasolinic fractions, the yield of which is highest in case of hydrogen, being followed by nitrogen and carbon dioxide in the order. Ellis and Haslam[14] made a similar observation. The variation in the degree of conversion to gasolines under the influence of different gas media has been explained by Schanen[15] as due to some specific catalytic effect of the gases. That gases like nitrogen and carbon dioxide will have any catalytic effect in such conversion processes, however, appears unlikely. On

TABLE VI

Influence of different gas media on the Cracking-Hydrogenation-Aromatisation of the feed-stock

Catalyst: Nil — Residence period: 2 hours
Feed-stock volume: 20 cm.^{3} — Reaction Temperature: 350° C.

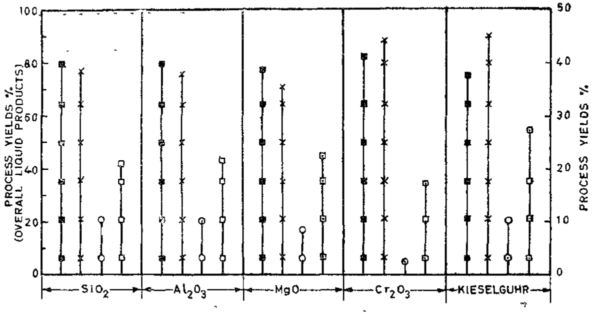
Gas medium	Nil	CO_2	N_2	H_2
Maximum Reaction Pressure (p.s.i.g.)	40	3300	3500	3500
Paraffins:				
C_1 and C_2 gases in litres at 25° C.	0·12	0·60	1·50	3·50
Average C-number	1·35	1·20	1·20	1·20
C_3 and C_4 gases in litres at 25° C.	..	..	0·05	0·19
Average C-number	..	..	3·2	3·2
Olefines:				
Ethylene gas in litres at 25° C.	0·03	..	..	..
C_3 and C_4 gases in litres at 25° C.	..	..	0·05	0·01
Average C-number	..	..	3·10	3·10
Gasoline Process Conversion %	5·9	14·0	21·0	33·9
Aromatics ,, ,,	..	..	..	..
Olefines ,, ,,	5·2	13·6	14·8	12·7
Total gases ,, ,,	0·70	2·45	6·77	16·42

the other hand, the increased gasoline formation might be explained as due to some 'wall effect' of the gases which prevents the combination of the carbonium ions produced from the hydrocarbon feed-stock at elevated temperatures. In presence of additional hydrogen in the pressurizing medium, the carbonium ion is quickly hydrogenated resulting in still higher yields of gasolines.

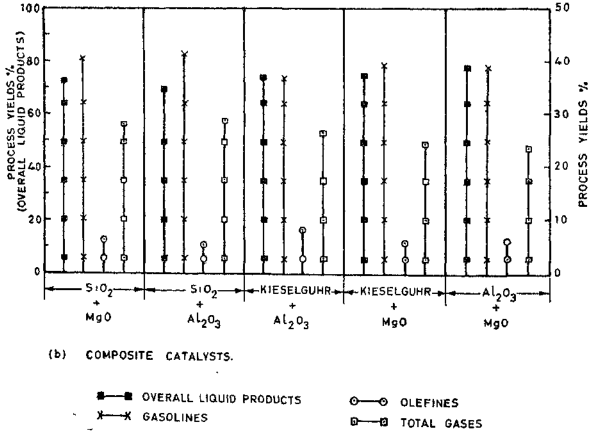
4. *Influence of Catalysts.*—In the experiments conducted in presence of initial hydrogen pressures, under purely thermal conditions the optimum temperature and reaction pressure for maximum conversion of the feed-stock to gasolinic fractions with as low yield as possible of cracked gases have been found to be 350° C. and 3500 p.s.i.g. respectively. The influence of catalysts on the characteristics of cracking, hydrogenation, aromatisation, etc., of the feed-stock have been studied in the first instance in a set of experiments conducted under similar conditions by employing pure single component catalysts, such as silica, alumina, magnesia, chromia and Indian kieselguhr, the results of which are shown in Fig. 6 (*a*). It is seen from the results that, although the effects of silica and alumina are almost similar to those of thermal ones, at least chromia and Indian kieselguhr exhibit a

marked superiority over others in respect of gasolinic yields. However, complete absence of the effect of aromatisation is noticed with all the catalysts. Morevoer, with chromia the olefinic products are almost negligible which can be attributed to the high hydrogenating activity of this catalyst.

On comparing the above results with those obtained by employing, under similar conditions, composite catalysts like silica-alumina, silica-magnesia, alumina-



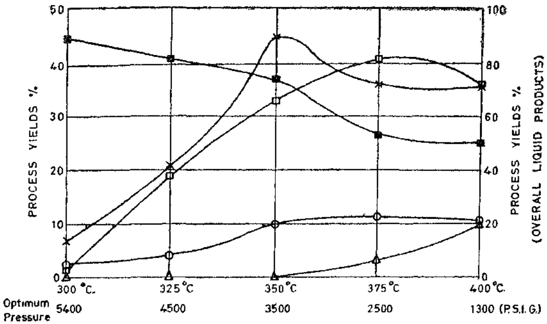
(a) PURE SINGLE COMPONENT CATALYSTS AND INDIAN KIESELGUHR



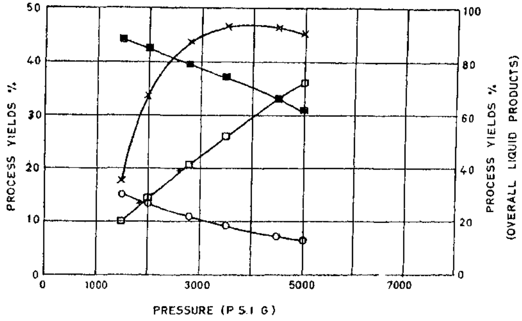
(b) COMPOSITE CATALYSTS.

FIG. 6. Influence of Various Catalysts on the Yields of Products.

magnesia, kieselguhr-alumina and kieselguhr-magnesia of 50: 50 compositions [(Fig. 6 (*b*)], one would clearly see their superior effects over those of the pure thermal bed experiments. However, these particular compositions do not show any marked superiority over single component catalysts. Only in case of silica-



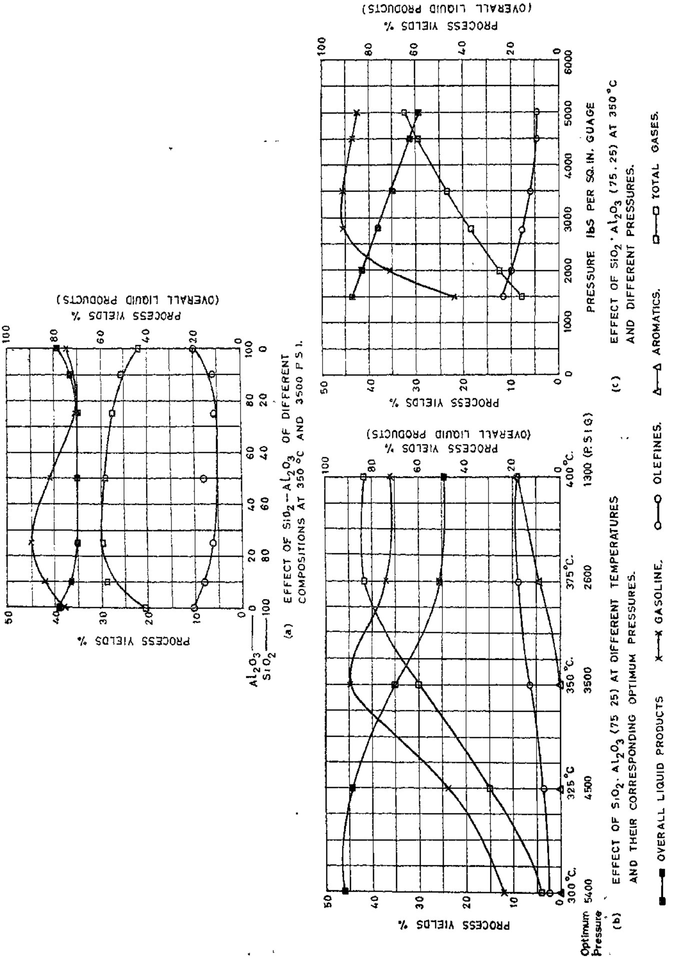
(a) AT DIFFERENT TEMPERATURES AND CORRESPONDING OPTIMUM PRESSURES.



(b) AT 350 °C AND VARIOUS PRESSURES.

■—■ OVERALL LIQUID PRODUCTS. ○—○ OLEFINES. □—□ TOTAL GASES.
×—× GASOLINE. △—△ AROMATICS.

Fig. 7. Influence of Indian Kieselguhr as a Cracking and Hydrogenating Catalyst on the Yields of Various Products.



(a) EFFECT OF $SiO_2-Al_2O_3$ OF DIFFERENT COMPOSITIONS AT 350 °C AND 3500 P.S.I.

(b) EFFECT OF $SiO_2 \cdot Al_2O_3$ (75 : 25) AT DIFFERENT TEMPERATURES AND THEIR CORRESPONDING OPTIMUM PRESSURES.

(c) EFFECT OF $SiO_2 \cdot Al_2O_3$ (75 : 25) AT 350 °C AND DIFFERENT PRESSURES.

■—■ OVERALL LIQUID PRODUCTS ×—× GASOLINE. ○—○ OLEFINES. △—△ AROMATICS. □—□ TOTAL GASES.

FIG. 8. Influence of Varying the Composition of SiO_2-Al_2O_3 as a Composite Cracking and Hydrogenating Catalyst on the Yields of Various Products.

alumina, and to some extent silica-magnesia compositions, the yield of gasoline is found to be a little more than with either of the single component catalysts, but there are also more of gaseous products of decomposition. Here, too, it is observed that there is absolutely no sign of aromatisation with any of the combinations. As the silica-alumina composition is found to act as the best, a more detailed investigation with the same has been carried out, the results of which are discussed below.

As stated above, Indian kieselguhr has been found to act as a good cracking catalyst, also possessing sufficient activity for destructive hydrogenation of the feed-stock. In Fig. 7 (*a*) are shown the results of further experiments with this catalyst conducted at different temperatures between 300° and 400° C., and in each case employing such initial hydrogen pressure as to develop a maximum reaction pressure corresponding to the optimum. Here again it is seen that 350° C. is the best temperature condition for the maximum yield of gasoline. Studying the effect of the same catalyst at 350° C. and various reaction pressures up to 5000 p.s.i.g. [*vide* Fig. 7 (*b*)], it is found that appreciable conversion of the feed-stock to gasoline takes place at pressures even lower than those employed in case of thermally conducted cracking and hydrogenation experiments (*cf.* Fig. 5). There is, however, considerable increase in the yield of gaseous products with Indian kieselguhr being employed as a catalyst.

The effect of varying the composition of silica-alumina composite catalyst has been studied in detail, the results of which are represented graphically in Fig. 8. In Fig. 8 (*a*) are shown the results obtained with different silica-alumina compositions, the experiments being conducted at 350° C. and 3500 p.s.i.g., from which it is clearly seen that silica (75%) and alumina (25%) is the best one for gasoline formation. .This composition is also seen to behave even better that Indian kieselguhr as it effects the same degree of conversion at still lower pressures [*vide* Fig. 8 (*c*)]. However, neither Indian kieselguhr nor silica-alumina (75: 25) has any activity for aromatisation under the prevailing hydrogenating conditions at least up to 350° C. The effect of varying temperatures with the corresponding optimum hydrogen pressures on the yield and composition of gasoline is shown in Fig. 8 (*b*). It can be concluded from the results of investigation with catalysts that, although possessing no aromatising activity, silica-alumina combination having the composition 75: 25 is the best catalyst at least for cracking and destructive hydrogenation of the feed-stock for the maximum formation of gasolines with the minimum of cracked gases.

SUMMARY AND CONCLUSION

1. An investigation on cracking-hydrogenation-aromatisation of a paraffinic feed-stock has been carried out at high pressures to examine the possibility of achieving maximum conversion of the same into fractions of gasoline boiling range with high anti-knock qualities.

2. The thermodynamic considerations of such conversion processes, based on the predominating hydrocarbon ($C_{12}H_{26}$) present in the feed-stock, indicate that at high pressures maintenance of substantially high temperature conditions is necessary for initial breakdown of the hydrocarbon molecule, which is a prerequisite for secondary reactions of hydrogenation, polymerisation, alkylation, etc., for the formation of ultimate gasolines,—the latter reactions being favoured at high pressures.

3. Experiments carried out under the autogenous pressure of the feed-stock have shown high gasoline formation only above 375° C. With initial hydrogen pressure, however, the same degree of conversion takes place at lower temperatures.

4. An important relationship between the initially employed pressure of hydrogen and the reaction temperature has been found to exist. The optimum conditions for maximum possible conversion of the feed-stock into gasolines with minimum of cracked gases have been found to be 350° C. as the temperature and 3500 p.s.i.g. as the maximum reaction pressure.

5. In the presence of initial hydrogen pressure more of methanization takes place, and the hydrogenation of primarily produced olefines increases the yield of saturates in the liquid and gaseous products.

6. The effect of aromatisation is not much noticeable below 375° C. which is further suppressed by application of initial hydrogen pressure.

7. Under pressure conditions, conventional cracking catalysts like silica, alumina, magnesia, Indian kieselguhr, etc., function also as cracking-hydrogenation-catalysts, but invariably all of them are found unsuitable for aromatisation.

8. A composite catalyst made of silica (75%) and alumina (25%) has been found to act as the best for maximum gasoline formation with the minimum of cracked gases.

9. The gasolines produced from the feed-stock under the conditions of cracking-hydrogenation are low in aromatics content. However, the presence of iso- and cyclo-paraffins enhance the anti-knock properties of the final gasolines.

10. In conclusion, it can be said that by employing the method of such hydrocarbon conversion under pressure more favourable conditions of heat transfer can be established, thereby eliminating local overheating and ultimate degradation of the hydrocarbon molecules into carbon and hydrogen. Considerable improvement in the yield and quality of gasolines is expected to be achieved by introducing the recycling operation, while in the present investigation a static system of apparatus has been used.

ACKNOWLEDGMENT

The authors express their sincere thanks to Prof. E. Weingaertner for his inspiring and critical survey and helpful suggestions during this investigation. Thanks are also due to Dr. M. R. Aswathanarayana Rao for his keen interest and

encouragement and to Prof. K. R. Krishnaswami for providing facilities to conduct this investigation in the High Pressure Laboratories of the General Chemistry Department.

REFERENCES

1. Young, J. .. British Patent, 1865, 3345.
2. Benton, *et al.* .. U.S. Patent, 1890, 342564.
3. Bergius, F. .. *The Historical Development of Hydrogenation* (*Science of Petroleum*), Vol. III, p. 2130.
4. Waterman, H. I., *et al.* .. *J. Inst. Pet. Tech.*, 1927, 413; 1929, 369.
   Trans. Far. Soc., 1939, **35**, 985.
   Petroleum Times, 1925, 259.
5. Ipatief, V. N. .. *Natural Patroleum News*, 1931, **49**.
6. Sweeney, W. J., *et al.* .. *Ind. Eng. Chem.*, 1934, **26**, 195.
7. Dodge, B. F. .. *Chemical Engineering Thermodynamics* (McGraw Hill), 1944, p. 494.
8. *A.S.T.M. Standards on Petroleum Products and Lubricants*, Nov. 1949, p. 692.
9. ——————— .. *Ibid.*, 1949, p. 1037.
10. Kurtz, S. S., *et al.* .. *Ind. Eng. Chem.*, 1947, 175.
11. Mair, B. J., *et al.* .. *Jour. Res. Nat. Bur. Standards*, 1940, **24**, 395; 1935, **15**, 51
12. Thomson, G.W., *et al.* .. *Ind. Eng. Chem.* (An. Ed.), 1949, **21**, 644.
13. Wolfgang Leithe .. *Ibid.*, 1951, **23**, 493.
14. Ellis, C., *et al.* .. U.S. Patent, 1938, 2, 137, 275.
15. Sachanen, A. N. .. *Conversion af Petroleum* (Reinhold Publishing Corporation), 1940, p. 157.
16. Newton, R. H. .. *Ind. Eng. Chem.*, 1935, **27**, 302.