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*AN EVALUATION OF CATALYSTS FOR
THE LIQUID PHASE HYDROGENATION
OF REFINERY VACUUM RESIDUUM*

W.A.O. HERRMANN AND K.W. BOWLES

FUELS RESEARCH CENTRE

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AN EVALUATION OF CATALYSTS FOR THE LIQUID
PHASE HYDROGENATION OF REFINERY VACUUM RESIDUUM

by

W. A. O. Herrmann* and K. W. Bowles**

ABSTRACT

One of the later developments in the catalytic hydrogenation of heavy, asphaltic residual oils to produce gasoline and other petroleum products is the German "Combi" process in which the feed oil is first treated in the liquid phase and then in the vapour phase. Efficient vapour phase catalysts have been developed in Germany and the United States and considerable research work has been carried out on liquid phase catalysts in Germany. However, very little work has been done on this continent to find a satisfactory catalyst for the liquid phase operation. If the Combi hydrogenation process is to be used for the refining of residual oils from Canadian crudes, an efficient and inexpensive liquid phase catalyst must be readily available in Canada.

This report presents the development of an experimental method for the evaluation of a suitable liquid phase catalyst by means of a simple batch, autoclave technique in which the catalyst is added to the oil feed and processed at temperatures of 430 - 470°C and a pressure of 5000 psi. Qualitative tests were made on various catalytic materials of Canadian origin to obtain an initial assessment of their suitability as a liquid phase catalysts. If no coke was produced, the catalyst passed the qualitative test. Finally, some of the catalysts that had successfully passed the qualitative test were tested quantitatively. All these catalysts gave a good reduction of the specific gravity, sulphur content, and pentane insolubles content of the oil product. The efficiency of the catalysts tested was judged by the yield of the oil product. The hematite portion of an iron oxide residue from the Sherritt-Gordon Mines in Alberta with tungsten, chromium, and zinc promoters gave a 70 % yield of oil product. Approximately the same yield was obtained with Bienfait lignite from Saskatchewan which had been depolymerized and impregnated with an iron promoter. From these results, it is considered that the iron oxide residue, with or without promoters, and the Bienfait lignite, with an iron promoter are efficient and inexpensive liquid phase catalysts of Canadian origin.

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EVALUATION DES CATALYSEURS POUR L'HYDROGENATION
EN PHASE LIQUIDE DU RESIDU SOUS VIDE

par

W.A.O. Herrmann* et K.W. Bowles**

RESUME

Une des découvertes les plus récentes dans l'hydrogénation catalytique des huiles résiduelles lourdes et asphaltiques afin d'obtenir de l'essence et autres produits pétroliers est le procédé allemand dit "Combi" dans lequel l'huile d'alimentation est d'abord traitée en phase liquide, puis ensuite en phase vapeur. Les Etats-Unis et l'Allemagne ont mis au point des catalyseurs efficaces en phase vapeur et l'Allemagne a de plus fait des recherches importantes sur les catalyseurs en phase liquide. Cependant, en Amérique, on a fait très peu de recherches en vue de découvrir un catalyseur efficace en phase liquide. Si l'on veut utiliser le procédé d'hydrogénation Combi pour raffiner des huiles résiduelles à partir de bruts canadiens, il nous faut pouvoir disposer au Canada d'un catalyseur efficace et peu coûteux en phase liquide.

L'auteur décrit la mise au point d'un procédé expérimentale d'évaluation d'un catalyseur satisfaisant en phase liquide au moyen d'une méthode simple et discontinue à l'autoclave; le catalyseur est ajouté à l'huile d'alimentation, puis le traitement se fait à des températures de 430-470°C et sous une pression de 5000 l/po². Des essais qualitatifs ont été faits sur divers catalyseurs d'origine canadienne afin qu'il soit possible de passer un premier jugement sur la possibilité de les utiliser en tant que catalyseurs en phase liquide. Si aucun coke n'était produit, le catalyseur était jugé satisfaisant. Finalement, certains catalyseurs

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qui avaient été jugés satisfaisants lors de l'essai qualitatif subissaient ensuite un essai quantitatif. Tous ces catalyseurs ont donné une bonne réduction en ce qui touche la densité, la teneur en soufre et en insolubles (pentane) du produit pétrolier. La portion hématite d'un résidu d'oxyde de fer, provenant de la Sherritt-Gordon Mines en Alberta, additionnée d'agents d'activation (tungstène, chromium et zinc) a permis un rendement de 70% en produit pétrolier.

On a obtenu à peu près le même rendement avec du lignite Bienfait de Saskatchewan; le lignite avait été dépolymérisé et imprégné de fer qui agissait en tant qu'agent d'activation. En fonction de ces résultats, on estime que le résidu d'oxyde de fer, avec ou sans agent d'activation, ainsi que le lignite Bienfait additionné de fer en tant qu'agent d'activation, sont des catalyseurs en phase liquide efficaces et peu coûteux, et d'origine canadienne.

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INTRODUCTION

It was indicated in a previous report (1) that hydrogenation of heavy, asphaltic, high-sulphur crude oil was economically superior to the conventional refinery processing for the production of gasoline and diesel fuel. Furthermore, the thermal yield of the finished products was higher. These conclusions were based on the results of commercial practice in Germany where a specific German catalyst was used in processing this type of feed stock. However, it is necessary to confirm this preliminary assessment by trying Canadian catalyst(s) on Canadian crude oils.

Formerly the hydrogenation process generally consisted of the liquid phase and the vapour phase; both receive a catalytic treatment at an elevated temperature and pressure. The feed for the liquid phase stage is hydrocarbon material which could not vapourize at the reaction temperature and pressure, 435 - 480°C and 700 atmospheres, but the feed for the vapour phase is lighter and, under the operating conditions of 400° - 435°C and 700 atmospheres, the reactions take place in the vapour phase. In the process, the crude oil is first separated by distillation into light, middle, and heavy oils. Then the heavy oil is hydrogenated with a finely-ground dispersed catalyst in the liquid phase while the middle oil is passed over a pelleted catalyst in the vapour state. In the latest development of hydrogenation, the "Combi" process, the liquid and vapour phases are combined; the gaseous product from the liquid phase stage is passed directly to the vapour phase operation, eliminating the intermediate distillation step. At the same time, pumping, storage and other facilities are also dispensed with. Furthermore, the vapour phase feed is not adversely affected by any chemical change taking place in storage. The liquid product from the liquid phase stage is passed to the hot catchpot (receiver) and then recycled.

In Canadian refineries, the crude oil is first subjected to an atmospheric and vacuum distillation to produce light, middle, and heavy oil distillates for further refining to finished products, mainly gasoline, jet fuel, diesel fuel, and fuel oil. The vacuum residuum is used for the production of asphalt, coke, and residual fuel oil. Some Canadian crude oils such as Weyburn, and Lloydminster, and the oil separated from the Athabasca bituminous sands of Northern Alberta are very low-grade petroleums. They are of high specific gravity, contain asphaltic components and up to 5% sulphur. If these oils are processed by cracking in a conventional plant, the gas and coke yields will be excessive. However, the hydrogenation process is particularly suitable for the treatment of these refractory oils.

In the previous report referred to above (1), certain assumptions were made as to the quality and quantity of the products of the liquid phase hydrogenation reaction and on the basis of these, the application of the process in the treatment of refractory residual oils from Canadian crudes appeared to be very promising. In order to confirm this preliminary assessment, it is necessary to carry out experimental work in both the liquid and vapour phase stages and to test the suitability of available catalysts for both processes.

SCOPE OF REPORT

The successful application of the Combi hydrogenation process for the refining of residual oils from Canadian crudes depends to a large extent on the availability of an efficient and inexpensive liquid phase catalyst.

The present report presents a batch autoclave method for testing a liquid phase catalyst and an interpretation of the results. This is followed by qualitative tests on various Canadian catalytic materials to assess them as liquid phase catalysts. Next, some of the materials that passed the qualitative test undergo quantitative tests. Finally, a catalytic material is selected for continuous pilot-plant testing.

BASIC CONSIDERATIONS

The feed stock for the liquid phase reaction comprises a heavy residual oil containing paraffinic, unsaturated, and polynuclear compounds; it contains some sulphur and probably a little nitrogen, as impurities. Therefore, the catalyst must be both a splitting and a hydrogenating catalyst and of sufficient activity to produce a suitable vapour phase feed. The desired reaction should extract the sulphur and nitrogen, reduce the polynuclear compounds, and produce a maximum yield of middle oil that boils in the 200 - 359°C range. At the same time, the gas loss should be low and no coke residue should be formed. If the catalyst is too active, the yield of the gasoline fraction will be excessive and the gas loss may be high. On the other hand, if the activity of the catalyst is low, the oil product will be too heavy, the sulphur extraction will probably be insufficient, and some residual coke may be produced.

REQUIREMENTS OF A LIQUID PHASE CATALYST

The properties of a good liquid phase hydrogenating catalyst are generally considered to be as follows:

- large surface area of at least 150 m²/g;
- a pH value that is slightly alkaline, 7.2 to 7.6;
- low specific gravity or bulk density;
- free of deactivating and inert foreign matter; and
- low cost.

The catalytic substance may be used alone or supported on a suitable material. If a supporter is used, it must possess the above qualifications. If an unsupported concentrated catalyst is used, a small quantity should be required and the cost should be low. On the other hand, it may have a low surface area and it may be too heavy. Furthermore, some inorganic catalysts are so hard as to erode valves and other parts of the equipment. A support for the catalyst may alleviate some disadvantages, but bulk and purchase cost would be greater.

The most effective property of a liquid phase catalyst is the surface area. It is considered that the surface area should be at least $150 \text{ m}^2/\text{g}$. The pH is also important. If the catalyst is acidic, the asphaltenes and other polynuclear compounds tend to be precipitated and to form coke before the reaction temperature is reached. This deleterious reaction may be suppressed by catalysts which possess other counteracting properties. A catalyst which is too alkaline (say pH8) will be less effective than if its pH were between 7.2 and 7.6.

The catalyst used for a liquid phase operation is suspended in that portion of the feed which remains a liquid under the required operating conditions of temperature and pressure. Consequently, the material should be fine in size and relatively light in weight, the former giving a large available surface area and the latter ensuring distribution in the liquid media, agitated by the recirculated hydrogen. Conversely, the larger the particles of the catalyst the more rapid is their settling against the upward-flowing liquid feed and their concentration at the bottom of the reaction vessel becomes greater than that at its top. The hydrogenation of oil is an exothermic reaction, the removal of the high heat of reaction of about 250 kcal per kg of oil feed is very difficult. Consequently, too high a catalyst concentration often leads to a runaway temperature condition that necessitates an immediate shut-down.

Unlike the catalyst, used in either a vapour phase fixed or fluidized bed operation, which is freely separable from the oil and may be regenerated, the liquid phase catalyst suspended in a heavy asphaltic oil, is very difficult to separate from the liquid and cannot be regenerated. Therefore, the catalyst must be discharged continuously or periodically from the hot catchpot together with the residual liquid product. It is then usually separated from the heavy oil by coking. Reclaiming the catalyst from the ash after burning has not yet become economically feasible, the catalyst must be inexpensive.

Of the many catalysts tried so far in Germany and elsewhere for the liquid phase hydrogenation of refractory petroleum residual oils, molybdenum and iron grudes have been the most successful. These catalysts consist of ammonium molybdate or iron sulphate supported on grude, a finely divided carbonaceous powder. The grude was a former waste product from the Winkler process for producing water and producer gas from lignite char. This carbonaceous dust from the gas generator precipitates in the "dust separator" and contains about 55% carbon and 45% fly ash. It has a surface area of approximately $150 \text{ m}^2/\text{g}$ and is slightly alkaline. The molybdenum grude is impregnated with ammonium molybdate solution and dried. The resulting product contains 2% MO_3 . The iron grude is impregnated with ferrous sulphate solution and the dried product contains 10% of iron as Fe_2O_3 . The iron grude was less expensive, so it was used in the commercial plants in Germany.

Unfortunately the German grude catalyst support is not available in Canada. Therefore the problem is to find a liquid phase catalyst of Canadian origin that is economically price and, at the same time, is equally as efficient as the German iron grude.

METHOD OF TESTING CATALYSTS

A continuous pilot plant is cumbersome to operate, requires operating personnel and consumes too much time, so it is more efficient to use a small batch autoclave to do preliminary tests on a large number of catalytic materials to weed out those which do not meet a minimum standard of efficiency. Obviously, the batch autoclave experiment does not simulate a continuous operation because the feed materials (oil and hydrogen) are not continuously charged to the autoclave and the duration of the experiment is, of necessity, arbitrarily limited. However, the results obtained are valid, in that sound comparisons can be made.

In order to assess the results of the catalyst tests, a suitable selection of criteria must be chosen in order to judge the quality of the products of the reactions and the effectiveness of the catalyst. In testing catalysts, the activity of the catalyst is determined by the quality and quantity of the various products.

As stated previously, the purpose of the tests is to obtain a good liquid-phase catalyst for the production of a suitable vapour-phase feed from a vacuum residual oil. The required specifications for the vapour phase feed will depend on the desired end-products. In this case it is assumed that the objective is to produce motor gasoline, jet fuel, and diesel fuel. But, in order to obtain the required specifications of the vapour phase feed, the reaction conditions of the liquid phase operation will depend on the nature of the liquid phase feed.

In the treatment of residual oil by hydrogen in the liquid phase, several reactions may take place:

1. elimination of foreign molecules, S, N, and O as H_2S , NH_3 and H_2O respectively;
2. cracking of the asphaltenes and other heavy components into lighter compounds, resulting in a lowering of the molecular weight;
3. hydrogenation of the resulting unsaturated hydrocarbons;
4. formation of gaseous hydrocarbons; and
5. polymerization of the unsaturated hydrocarbons and aromatics to form heavy polynuclear compounds and carbon.

The second and fourth reactions are endothermic, while the three others are exothermic. The first three are the desired reactions, while the last two must be reduced to a minimum.

An increase in the operating temperature and reaction time will increase all these reactions, but an increase in pressure will tend to suppress the undesirable fourth and fifth reactions. For the catalyst testing program a suitable temperature, pressure, and contact time must be chosen which will promote the desirable reactions and minimize the undesirable ones. At the same time, the temperature must be sufficiently high to give a reasonably efficient reaction time.

The use of a catalyst in the liquid phase hydrogenation of residual oils will profoundly affect the various reactions outlined above. An efficient catalyst will possess selectivity, in order that the desired reactions will be promoted while the undesirable ones will be suppressed. The catalyst will materially lower the required temperature to bring about the necessary cracking and hydrogenation to convert the heavy oil components to a suitable vapour phase feed. The lower temperature will suppress the formation of gaseous hydrocarbons, polynuclear compounds, and carbon.

It is well known that in the hydrogenation of oil the heat given off by the exothermic reactions exceeds the heat absorbed by the endothermic reactions. Therefore there will be a net evolution of heat. By noting this heat, the activity of the catalyst may be readily observed while the reaction is proceeding; the greater the activity of the catalyst, the quicker the heat of reaction is released. Because the heat loss from the outside of the autoclave is approximately constant, the greater is the difference in temperature between the reactants and the outside wall of the reaction vessel. The latter temperature is determined by the controller setting, so the former temperature which varies.

The hydrogen consumption may also be used as an indication of the activity of the catalyst during the reaction. Throughout the reaction, hydrogen is consumed and gaseous hydrocarbons are formed. A catalyst of the desired selective activity will result in the hydrogen consumption being greater than the formation of light hydrocarbon gases and this will be shown by a drop in the reaction pressure.

In view of the foregoing consideration of the various reactions involved in the liquid phase hydrogenation of residual oils, the following criteria, based on the production of an average vapour phase feed, were selected as a theoretical standard for judging the activity of the catalyst.

1. No residual coke should be produced and the formation of carbon as a fine powder should be minimal.
2. The formation of gaseous hydrocarbons should be as low as practicable.
3. The liquid product, which would constitute the vapour phase feed, should have the following specifications:

(a) specific gravity	0.840 - 0.860
(b) sulphur content	3 wt % maximum
(c) pentane insoluble content	2 wt % maximum
(d) distillation range	
oil fraction up to 175°C (347°F)	25 wt % maximum
oil fraction up to 200°C (392°F)	35
residuum above 325°C (617°F)	40
residuum above 350°C (660°F)	35

It will be noted that no specification is given for the yield of oil product. The oil yield, of course, depends upon the amounts of hydrocarbon gas and residual carbonaceous residue produced, and the less of these the more efficient is the catalyst.

EXPERIMENTAL APPARATUS

The catalyst tests were carried out in a 2-litre, vertical, batch autoclave rated at 5000 psi maximum working pressure at 850°F (454°C). The autoclave was provided with a thermocouple well, a pressure gauge, a liquid sample dip-tube, a gas inlet or outlet opening, and a rotary stirrer. The autoclave was heated by means of a cylindrical electric heater, the heating controlled by means of an iron-constantan thermocouple contacting the outside wall of the autoclave. The temperature of the reaction was recorded by an iron-constantan thermocouple inserted in the thermocouple well. A schematic diagram and an illustration of the equipment is shown in Figures 1 and 2 respectively. The pressure receiver was used only for the quantitative experiments after the qualitative tests

The agitation of the contents of the autoclave was accomplished by a special type of stirring mechanism. The vertical hollow shaft of this stirrer

was attached to an impeller with six vertical radial blades located about one inch above the bottom of the autoclave. The centrifugal effect produced by the rotation of the shaft at 540 rpm withdrew gas from the space above the liquid and into an inlet hole at the top of the shaft. The gas passed down the hollow shaft and was discharged below the impeller so that it bubbled upward through the liquid back into the gas space. The velocity of the flowing gas along with the rotation of the impeller were sufficiently great to produce a violent agitation of the liquid contents of the autoclave.

In order to determine the effectiveness of this stirrer, a test was conducted in which 42 grams of a powdered catalyst was added to 1225 grams of naphtha of 0.730 specific gravity. This gravity of the naphtha duplicated as closely as possible the gravity that the liquid phase feed oil would have at reaction temperature and pressure. A hydrogen pressure of 800 psi was applied. With the stirrer in operation, a 100-ml sample of the suspension was taken from the bottom of the autoclave. It was found that the sample contained 3.1 wt % of the catalyst. This compares well with the calculated amount of 3.4 wt % that was added to the naphtha. Because a little solid-free naphtha remained in the dip-tube and a small sample of the dispersion was taken, the result of this test was considered very good and indicated that the operation of the stirrer was satisfactory.

OILS USED FOR CATALYST TESTS

Weyburn crude oil from Saskatchewan is a typical Canadian crude oil that would be suitable for refining by the hydrogenation process as it is a high-sulphur asphaltic oil. The analysis of the crude oil is given in Table 1. The vacuum residuum boiling above 427°C (801°F) was used for the catalyst tests. The analysis of this residual oil is shown in Table 2. The sulphur content is 4.4 % and the amount of the pentane insoluble portion is 16.6 %.

The above residual oil was used for Experiments 1 to 54 inclusive. The supply was then exhausted, so a similar residual oil was used for the remaining experiments with the exception of Experiment 55. This residual oil, obtained from the Shell Oil Company of Canada, was the vacuum bottoms from the distillation of Weyburn crude oil. The analysis of this residual oil is shown in Table 2. It is similar to the former feed oil but is a little heavier and higher in pentane solubles and sulphur content.

Table 1
Analysis of Weyburn Crude Oil

Specific gravity, 60°/60°F	0.891	A.P.I. gravity, 60°F	27.3
Sulphur, wt %	2.41	Pour point, °F	45
Saybolt Universal Viscosity, sec		Molecular Weight (calculated)	211
at 100°F	66 (12.1 cSt)	Carbon residue, (Conradson),	
at 78°F	110 (22.9 cSt)	wt %	6.4

DISTILLATION, U. S. Bureau of Mines Routine Method

Stage 1 - Distillation at atmospheric pressure, 760 mm Hg
First drop 45°C (113°F)

Fraction No.	Cut at °C	at °F	Per cent	Sum per cent	Specific gravity 60°F	Degrees A.P.I. 60°F	Correlation index	Aniline point °C	Viscosity S.U. 100°F	Cloud test °F
1	50	122	-	-	-	-	-	-		
2	75	167	2.8	2.8	0.686	74.8	16	-		
3	100	212	4.0	6.8	0.720	65.0	21	50.0		
4	125	257	4.9	11.7	0.748	57.7	26	44.5		
5	150	302	4.3	16.0	0.764	53.7	26	47.8		
6	175	347	4.3	20.3	0.779	50.1	26	51.2		
7	200	392	4.1	24.4	0.794	46.7	27	54.0		
8	225	437	4.2	28.6	0.810	43.2	29	57.0		
9	250	482	3.4	32.0	0.826	39.8	31	59.3		
10	275	527	5.8	37.8	0.844	36.2	35	62.0		

Stage 2 - Distillation continued at 40 mm Hg pressure

11	200	392	2.7	40.5	0.866	31.9	41	63.0	39	20
12	225	437	5.4	45.9	0.876	30.0	42	64.5	44	40
13	250	482	5.1	51.0	0.891	27.3	46	66.4	55	55
14	275	527	4.8	55.8	0.902	25.4	48	69.2	77	70
15	300	572	6.7	62.5	0.917	22.8	52	73.0	141	85
Residuum			35.5	98.0	1.015	7.9				

Carbon residue of residuum 15.9 %

Carbon residue of crude 6.4 %

APPROXIMATE SUMMARY

	Percent by vol	Specific gravity	Degrees A.P.I.	Viscosity S.U. 100°F
Light gasoline	6.8	0.706	68.9	
Total gasoline and naphtha	24.4	0.752	56.7	
Kerosine distillate	4.2	0.810	43.2	
Gas oil	17.5	0.854	34.2	
Nonviscous lubricating distillate	9.4	0.885-0.908	28.4-24.3	50-100
Medium lubricating distillate	7.0	0.908-0.927	24.3-21.1	100-200
Viscous lubricating distillate	-	-	-	Above 200
Residuum	35.5	1.015	7.9	
Distillation loss	2.0			

Table 2

Analysis of Weyburn Vacuum Residuums

	Residuum above 427°C (801°F)	Shell Vacuum Bottoms
Specific gravity, 60°/60°F	1.021	1.047
Pour point, °F	100	Too high
Softening point (Ring and ball in water), °F		134.5
Ash, wt %	0.03	0.03
Viscosity, Kinematic at 230°F, cSt		2,005
210°F, cSt	347	4,600
180°F, cSt	932	20,000*
100°F, cSt	50,000*	7,000,000*
Pentane insolubles, wt %	16.6	24.8
Benzene insolubles, wt %	0.06	1.4
Carbon, wt %	84.2	84.7
Hydrogen, wt %	10.4	10.0
Sulphur, wt %	4.4	4.7
Nitrogen, wt %	0.3	0.6
Molecular weight (calculated)	810	890

*Extrapolated.

In Experiment 55, the bitumen separated from the Athabasca bituminous sands of Northern Alberta was utilized as the feed oil. The analysis of this oil is shown in Table 3. This bitumen was extracted in the experimental plant of the University of Alberta which was situated on the Clearwater River near McMurray. Approximately 50 % of the bitumen boils below 300°C at 40 mm Hg pressure and it contains 5.8 % sulphur.

Table 3

Analysis of Athabasca Bitumen

Specific gravity, 60°/60°F	1.030	Saybolt Fural viscosity, sec.	
A.P.I. gravity, 60°F	5.88	at 210°F	820
Sulphur, Wt %	5.8	at 250°F	236

Distillation, U. S. Bureau of Mines Routine Method

Distillation at atmospheric pressure, 760 mm Hg

Fraction No.	Cut at		Percent	Sum percent	Specific gravity 60°F	Degrees A.P.I. 60°F	Viscosity S.U. 100°F	Viscosity S.U. 212°F	Cloud test °F
	°C	°F							
1	50	122							
2	75	167							
3	100	212							
4	125	257							
5	150	302	0.9						
6	175	347	0.8	1.7	0.809	43.4			
7	200	392	1.1	2.8	0.823	40.4			
8	225	437	1.1	3.9	0.848	35.4			
9	250	482	4.1	8.0	0.866	31.9			
10	275	527	11.9	19.9	0.867	31.7			

Distillation continued at 40 mm Hg pressure

11	200	392	1.6	21.5	0.878	29.7	36	32	below 0
12	225	437	3.2	24.7	0.929	20.8	66	36	below 0
13	250	482	6.1	30.8	0.947	17.9	118	39	below 0
14	275	527	6.4	37.2	0.958	16.2	178	42	below 0
15	300	572	10.6	47.8	0.972	14.1	508	52	

Residuum 49.5 97.3

Carbon residue of residuum 39.6 %

Carbon residue of crude 19.6 %

Approximate Summary

	Percent by vol	Specific gravity	Degrees A.P.I.
Light gasoline	0.0		
Total gasoline, naphtha and kerosene distillate	2.8	0.818	41.5
Gas oil	19.0	0.867	31.7
Nonviscous lubricating distillate	4.3	0.901-0.940	25.6-19.0
Medium lubricating distillate	8.5	0.940-0.959	19.0-16.1
Viscous lubricating distillate	13.2	0.959-0.981	16.1-12.7
Residuum	49.5		
Distillation loss	2.7		

DEVELOPMENT OF EXPERIMENTAL PROCEDURE

In order to establish a satisfactory standard experimental procedure and to select a suitable set of operating conditions for the catalyst testing program, a series of four preliminary experiments were done. In these experiments in which the German iron grude was used as the catalyst, the residuum above 427°C from Weyburn crude was used as the feed oil and 5,000 psi was used as the operating pressure; the influence of the equipment and the effect of the over-all reaction, as influenced by the temperature and reaction time were studied. The charge consisted of one-half litre of the feed oil and 1.5 wt % of catalyst. A series of temperatures were chosen from 395° to 454°C to represent an adequate range. It should be noted that this range is lower than the corresponding range that would be employed in a continuous operation, because a batch experiment requires a lower temperature because the oil remains in the autoclave during the experiment. In order to vary the reaction time, samples of the liquid product were withdrawn from the bottom of the autoclave through the dip-tube into small 200-ml pressure receivers when the reaction temperature was reached and at various time intervals after this initial point. At the end of the experiment the autoclave was allowed to cool to room temperature, the pressure was released and the autoclave opened. The remaining oil product was then removed as the final sample.

The specific gravity of these samples was determined to give an approximate indication of the progress of the reactions. The results are shown in Table 4 and Figure 3. The specific gravity versus time curves show that, in every case, the specific gravity at first decreased with the time; but then, as shown by the three higher temperatures, a minimum point was reached and the specific gravity increased. At temperatures of 435 and 454°C, the minimum specific gravity occurs between 30 and 40 minutes. This shows, that up to this particular time, the desirable cracking and hydrogenation reactions predominated but after this period, the undesirable aromatization reactions probably increased. The specific gravity curves also show that above 435°C the minimum specific gravity is not materially improved and the aromatization reactions increased with the temperature.

Table 4

Results of Preliminary Experiments Using Iron Grude as Catalyst

Experiment No.	1	2	5	4
Reaction temp , °C	395	423	434	454
Total reaction time, min	120	180	350	275
Reaction time, min	0	0	0	0
Sp gr, 60/60°F	0.980	0.994	0.890	0.932
Reaction time, min	10	15	15	15
Sp gr, 60/60°F	0.953	0.945	0.873	0.876
Reaction time, min	25	30	40	32
Sp gr, 60/60°F	0.937	0.924	0.856	0.851
Reaction time, min	45	45	90	70
Sp gr, 60/60°F	0.925	0.906	0.867	0.876
Reaction time, min		75	190	130
Sp gr, 60/60°F		0.886	0.873	0.903
Reaction time, min		120	290	225
Sp gr, 60/60°F		0.883	0.886	0.963
Reaction time, min	120	180	350	275
Sp gr, 60/60°F*	0.890	0.889	0.900	0.979

*Final sample

One further preliminary experiment, No. 6, was done on the same amount of the feed oil and of the iron grude catalyst. The temperature controller was set to give a reaction temperature of approximately 435°C. The graph of the inside temperature, as measured by the thermocouple in the thermocouple well, showed a steady rise during the heating-up period. At a certain point before the reaction temperature had been reached the inside temperature rose more sharply, then maintained a more or less steady temperature until a point was reached when it decreased abruptly to approximately the temperature where it had formerly started to rise sharply. At this point, the heating was stopped and the autoclave and its contents allowed to cool. This temperature gradient is indicative of the nature of the chemical reactions taking place. At first, the beneficial exothermic hydrogenation reactions predominated but, later, the endothermic reactions, mainly hydrocarbon gas formation, increased. It is considered that the point of minimum specific gravity of the oil product is reached during the sharp decrease in the temperature. As a consequence of this characteristic progress of the chemical reactions, it was decided that the duration of future experiments would not be on the basis of an arbitrary specified time but would be logically determined by the specific variation in the temperature. Therefore the points where the temperature started to rise sharply and finished falling abruptly were taken as the beginning and end of the reaction period, respectively. Then the elapsed time between these two points would be the reaction time. The reaction temperature was the average temperature throughout the reaction time.

In Experiment 6 it was attempted to obtain an operating temperature of 435°C. But unfortunately the extent of the exothermic heat of reaction rendered this impossible with the result that the actual average temperature was 454°C. The duration of this experiment was 50 minutes.

After the test and before cooling and release of the pressure, a sample of the gaseous product from the vapour space above the liquid product in the autoclave was withdrawn. Then, the liquid product was removed through the dip-tube. In cooling to room temperature, most of the vapour sample had

condensed. The analysis of these two oil products are given in Table 5. The sampling of the vapour and liquid phase portions was done to find out the properties of these two oil products which would constitute, in a continuous process, the feed to the vapour phase stage and the residual oil collected in the hot catchpot, respectively.

The analysis of the vapour phase portion of the oil product shows that the sulphur and pentane insoluble contents have been drastically reduced. On the other hand, the oil is much too light, 83 % boiling in the gasoline range up to 177°C and only 7 % remaining as the residuum above 357°C. Unfortunately this result is due to the nature of the batch type of experiment with which it is difficult to duplicate a continuous operation. On the other hand, useful comparative results can be obtained from batch experiments and for this purpose the standard procedure is to collect the total oil product at room temperature and pressure. In noting the yields of gaseous, liquid, and solid products and in comparing the analysis of the oil product with that of the oil feed, the extent of the hydrogenation and, thus, the effect of the catalyst may be determined.

EXPERIMENTAL PROCEDURE USED FOR TESTS

Except where otherwise noted, for each experiment approximately half a litre of the feed oil was weighed into the autoclave and 1.5 wt % of the catalyst (with or without a support) was added. The rated maximum working pressure of the autoclave, 5,000 psi, was used as the operating pressure. After heating the autoclave until the inside temperature had reached 100°C, the stirring was commenced. At this time hydrogen was then added until the pressure was 5,000 psi.

During the heating-up period and throughout the duration of the experiment, the pressure never rose above 5,000 psi. But on the contrary, because of the hydrogen consumption, the pressure continually decreased. When the pressure dropped to 4,800 psi, additional hydrogen was added until the pressure reached 5,000 psi again.

After the experiment, the autoclave was allowed to cool. When the inside temperature had reached 350°C, the stirring was stopped. When the autoclave had reached room temperature, the pressure was released by discharging

Table 5

Result of Preliminary Experiment Using Iron Grude as Catalyst

Experiment No.	6	
Oil feed	Residuum above 427°C from Weyburn crude	
Reaction temp, °C	454	
Reaction time, min	50	
Oil product	Product from vapour at reaction <u>temp and pressure</u>	Product from liquid at reaction <u>temp and pressure</u>
Sp gr, 60/60°F	0.750	1.026
Sulphur, wt %	1.2	4.8
Pentane insolubles, wt %	0.1	32.2
Distillation range, vol %		
Gasoline fraction, up to 350°F (177°C)	82.8	14.0
Diesel fraction, 350 - 675°F (177 - 357°C)	9.8	41.0
Residuum, above 675°F (357°C)	7.4	45.0
Coke	None	

the gas. The autoclave was opened and the oil product removed for analysis. The presence of any coke in the bottom of the autoclave was noted.

QUALITATIVE TESTS ON VARIOUS CATALYSTS

Before any quantitative tests were made, a series of qualitative tests were made on various catalysts in order to estimate their quality. In these tests, the Weyburn vacuum residuum above 427°C (801°F) was used as the feed oil. The specific gravity, sulphur content, and, in some experiments, the pentane insoluble portion of the oil product were determined, but the yields of the gaseous, liquid, and solid products were not calculated. The main criterion for the evaluation of the catalysts in these tests was the production of coke. If no coke was formed, the catalyst was considered to have passed the qualitative test and was eligible for further testing. In those experiments where no coke was produced, the solid residue was a fine black powder, which consisted mainly of the catalyst with a small amount of carbon. In these tests, the distillation range (Engler) of the oil product was also determined. The temperature range of the oil fractions were arbitrarily chosen as follows:

Experiments 1 to 20

gasoline fraction	up to 350°F (177°C)
diesel fraction	350 - 675°F (177° - 357°C)
residuum	above 675°F (357°C)

Experiments 21 to 52

gasoline fraction	up to 350°F (177°C)
diesel fraction	350 - 680°F (177 - 360°C)
residuum	above 680°F (above 360°C)

Experiments 53 to 66

gasoline fraction	up to 200°C (392°F)
jet fuel fraction	200 - 250°C (392° - 482°F)
diesel fraction	250 - 325°C (482° - 617°F)
residuum	above 325°C (617°F)

Test on Iron Grude

In order to have a standard for comparing the results of the various catalysts tested, Experiment 7 was made using 1.5 % of the German iron grude. The grude had been impregnated with FeSO_4 and contained 10 % Fe as Fe_2O_3 . The

properties of the iron grude are as follows:

Surface area, m ² /g	150								
pH value	7.2								
Ash, %	51.5								
Analysis of Ash, % iron grude:									
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	SO ₃
2.1	2.5	11.4	20.0	3.3	0.0	0.0	trace	0.1	9.9

Approximately half the iron grude is mineral matter, the remainder is probably carbon. The 11.4 % of Fe₂O₃ contains the 10 % iron promoter. The results of the test are shown below:

Results of Test Using Iron Grude as Catalyst

Experiment No.	7
Oil feed	Residuum above 427°C from Weyburn crude
Reaction temp, °C	443
Reaction time, min.	70
Oil product	
Sp gr, 60/60°F	0.915
Sulphur, wt %	3.1
Pentane insolubles, wt %	9.0
Distillation range, vol %	
Gasoline fraction, up to 350°F (177°C)	33.0
Diesel fraction, 350 - 675°F (177 - 357°C)	43.3
Residuum, above 675°F (357°C)	23.7
Coke	none

As was expected with this efficient catalyst, no coke was produced in the bottom of the autoclave. The results of the analysis of the oil product show that the specific gravity has been reduced from 1.021 to 0.915, the sulphur from 4.4 to 3.1 %, and the pentane insolubles from 17 to 9 %. The gasoline fraction up to

177°C was 33 vol % and the residuum above 357°C was 24 vol %.

It would have been desirable to have the specific gravity and the pentane insolubles lower and the distillation range higher. But no coke was formed and the sulphur was adequately reduced, so the results are considered satisfactory.

It will be noted that the properties of the oil product did not measure up to the ideal specifications referred to previously (Page 8). As mentioned above, this was not to be expected from a batch operation. However, these results with iron grude as the catalyst will be used as a practical standard of comparison for the other catalysts tested in the qualitative series.

Test on a Semi-Anthracite Coal as a Support for a Molybdenum Promoter

It was thought that a low-volatile coal might be suitable as a catalyst support. In Experiment No. 8, the German grude support was replaced by a semi-anthracite coal from the Cascade area in Alberta. The sample of coal was obtained from Canmore Mines Limited, Canmore, Alberta, and is a representative low-volatile Canadian coal. Molybdenum, which is considered superior to iron, was used as the promoter. In choosing this catalyst, an attempt was made to make one somewhat similar to the German molybdenum grude. The analysis of the coal on the dry basis is as follows:

Proximate analysis, %

Ash	13.2
Volatile Matter	11.6
Fixed carbon (by diff)	75.2

Ultimate analysis, %

Carbon	80.1
Hydrogen	1.9
Sulphur	0.8
Nitrogen	1.1
Ash	13.2
Oxygen (by diff)	2.9

The coal was ground to minus 200 mesh and impregnated with an ammonium molybdate solution. The dried product contained 2 % Mo as MoO_3 . The properties of the catalyst, support plus promoter, are as follows:

Surface area, m ² /g	108									
pH value	9.0 (support only)									
Ash, %	14.9									
Analysis of ash, % of support plus promotor:										
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	SO ₃	MoO ₃
7.1	4.2	0.8	trace	trace	trace	0.1	0.1	0.2	trace	2.0

It will be noted that this catalyst is quite different from the iron grude. The latter contains about 51 % ash which is high in iron and calcium. But the Mo catalyst supported on Canmore coal has a much lower ash content, 15 %, and the composition of the ash is quite different - the iron is replaced by molybdenum and there is only a trace of calcium. Furthermore, the surface area is much lower and the ground coal support is more alkaline.

The results of the test are shown in Table 6. A large residue of coke in the form of a hard cake was produced in the bottom of the autoclave in this experiment. The shape of this compact residue and the stream lines on the top surface indicate that the polynuclear compounds had precipitated out of the oil solution and had formed a solid residue during the early stages of the reaction. This coke-like residue consisted of approximately 88 wt % of benzene insoluble material which showed that it was mostly carbon. The coke formation was probably the result of the coal support having a lower surface area and a higher specific gravity than the German grude.

The analysis of the oil product shows that the reduction in the gravity and sulphur content was much the same as with the iron grude. But the pentane insolubles were higher.

As a result of the considerable amount of coke formation, the semi-anthracite coal, when used as a catalyst support, did not pass the qualitative test and is therefore definitely inferior to the German grude.

Tests on Three Carbonaceous Supports with Molybdenum as Promoter

Three inexpensive carbonaceous materials of Canadian origin were tested as a catalyst support: a sample of acetylene black from Shawinigan Chemical Limited, Montreal, Quebec; a commercial graphite of 98.7 % purity obtained from

Table 6

Results of Tests on Carbonaceous Supports with Molybdenum as Promoter

Support	<u>Semi- Anthracite Coal</u>	<u>Acetylene Black</u>	<u>Graphite</u>	<u>Lignite Char</u>
Experiment No.	8	16	19	14
Oil feed	Residuum above 427°C from Weyburn crude	Residuum above 427°C from Weyburn crude	Residuum above 427°C from Weyburn crude	Residuum above 427°C from Weyburn crude
Reaction temp, °C	431	465	466	457
Reaction time, min	60	35	35	45
Oil product				
Sp gr, 60/60°F	0.924	0.871	0.875	0.894
Sulphur, wt %	3.2	2.5	3.0	3.3
Pentane insolubles, wt %	13.0			
Coke	Large residue of compact coke	Large residue of granular coke	Large residue of granular coke	Large residue of granular coke

Cyanamid of Canada Limited, Montreal, Quebec; and a lignite char from Dominion Briquettes and Chemicals Limited, Winnipeg, Manitoba. The acetylene black is produced by the thermal decomposition of acetylene. The graphite is a by product from the manufacture of calcium cyanamide from calcium carbide. The lignite char is obtained from the carbonization of lignite by the Lurgi low-temperature process. The lignite was obtained from the Bienfait mine in Saskatchewan operated by the Manitoba and Saskatchewan Coal Company Limited. The properties of the acetylene black and the graphite are shown below:

	<u>Acetylene black</u>	<u>Graphite</u>
Surface area, m ² /g	62*	13*
pH value	5.9	6.5
Ash, %	0.1	1.5
Volatile matter, %	0.9	0.6
Fixed carbon, %	99.0	97.9

*Support plus molybdenum promoter.

Compared with the iron grude, it is seen that both materials impregnated with the promoter, are very much lower in surface area. The materials themselves are mildly acidic and have very little ash.

The analysis of the lignite char (dry basis) is as follows:

Ash	9.8 %
Volatile matter	13.0
Fixed carbon (by diff)	77.2
Sulphur	0.7
Nitrogen	1.1

Before impregnation with the promoter, the lignite char was ground to minus 200 mesh. The three catalyst supports were impregnated with a 2 % Mo promoter in the same manner as was done with the Canmore coal. The properties of the impregnated lignite char are as follows:

Surface area, m ² /g	24
pH value	9.1*
Ash, %	11.6

Analysis of ash, wt % of support plus promoter:

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	SO ₃	MoO ₃
2.7	0.6	0.8	3.0	0.6	0.4	0.2	0.1	0.1	1.1	2.0

*Support only.

The surface area and the ash content of this catalyst is also much lower than that of the iron grude.

The results of the tests, as shown in Table 6, were similar to those of Experiment 8 with the semi-anthracite coal, that is, a large amount of coke was produced. With each of the three supports, a large residue (100 to 125 grams) of granular coke was found in the bottom of the autoclave. As was the case in Experiment 8, the reduction of the specific gravity and sulphur content of the oil was considered satisfactory.

Tests on Four Carbonaceous Supports with Iron as Promoter

The same three carbonaceous materials, as were used in the above tests, were used again in these tests with the addition of a fourth (a "magnetic" carbon black obtained from United Carbon Company, Houston, Texas). According to the manufacturer's advertisement, iron is incorporated into the carbon black particles

by a special method. In a private communication from the company, it is stated that the iron is combined with the carbon during the formation of the carbon black, and the analysis of the product indicates a predominance of Fe_2O_3 with a lesser content of other iron oxides. The analysis of this material, as submitted by the company, is as follows:

Surface area, m^2/g	155
pH value	7.7
Ash, wt %	12.6
Ultimate analysis, %	
C	86.5
Fe	8.7*
S	1.2
H	0.3
Others, (by diff)	3.3
*11.6 % as Fe_2O_3	

The pH of the sample received was found to be 6.4.

It will be seen that the surface area and the iron content as Fe_2O_3 of this catalyst are much the same as of the iron grude. On the other hand, the catalyst is a little acidic and the ash content is about one quarter of that in the iron grude.

The lignite char, the graphite and the acetylene black were impregnated with an FeSO_4 solution and the dried product contained 10 % Fe as Fe_2O_3 . The magnetic carbon black was used as received.

The results with iron as the promoter, as shown in Table 7, were much the same as with molybdenum. In every case, a compact coke residue was produced in the bottom of the autoclave. In spite of the fact that the surface area and the iron content of the magnetic carbon black were similar to those of the iron grude, the results were no better than with the three other catalysts. Perhaps the slight acidity was responsible for the coke formation.

The acetylene black was a little acidic (pH 5.9), so it was thought that this support might be improved by making it slightly alkaline. This was done by adding sufficient lithium carbonate solution during the impregnation

Table 7

Results of Tests on Carbonaceous Supports with Iron as Promoter

Support	Acetylene Black	Graphite	Lignite Char	Magnetic Carbon Black	Acetylene Black with LiCO_3 added
Experiment No.	18	15	20	35	37
Oil feed	Residuum above 427°C from Weyburn crude	Residuum above 427°C from Weyburn crude	Residuum above 427°C from Weyburn crude	Residuum above 427°C from Weyburn crude	Residuum above 427°C from Weyburn crude
Reaction temp, °C	459	456	464	460	455
Reaction time, min	35	40	40	35	40
Oil product					
Sp gr, 60/60°F	0.899	0.826	0.856	0.864	0.839
Sulphur, wt %	3.0	2.2	3.2	2.9	2.4
Distillation range, vol %					
Gasoline fraction, up to 350°F (177°C)					47.0
Diesel fraction, 350 - 680°F (177 - 360°C)					31.2
Residuum, above 680°F (360°C)					21.8
Coke	Large residue of compact coke	Large residue of compact coke	Large residue of com- pact coke	Large residue of com- pact coke	None

of the support with the iron promotor to produce a catalyst with a calculated pH value of 8. However, by actual test, the pH value was found to be 10.1.

The results of the hydrogenation tests are shown in Table 7. Raising the pH value to 10.1 seemed to have a marked beneficial effect upon the results because no coke was formed. A fine black dust of the catalyst and carbon were noticed in the bottom of the autoclave. The oil product was also lighter and contained less sulphur. However, the distillation range showed about twice as much gasoline as is desired in the oil product.

Tests on De-Ashed Lignite as a Support for Molybdenum and Iron

Because the lignite char proved to be no worse than the other Canadian supports, it was considered that the lignite itself might be superior to the char. During the hydrogenation reactions, those parts of the lignite particle that are easily attacked would be converted to volatile components and would leave a relatively porous structure behind, as in the hydrogenation of coal, the lignite would acquire a higher surface area, and its effectiveness as a catalyst support might be enhanced.

For these tests, lignite from the Bienfait mine in Saskatchewan was ground to minus 200 mesh. The analysis of the lignite (dry basis) is as follows:

Proximate analysis, %

Ash	16.2
Volatile matter	42.7
Fixed carbon (by diff)	41.1

Ultimate analysis, %

Carbon	63.2
Hydrogen	2.8
Sulphur	1.1
Nitrogen	1.2
Ash	16.2
Oxygen (by diff)	15.5

Ash analysis, %:

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	Mo ₃ O ₄	SO ₃
34.9	19.6	7.0	27.5	3.7	2.6	0.4	0.5	1.2	0.3	11.6

In order to eliminate any possible deleterious influence of the inorganic constituents in the first two tests, the lignite was treated by flotation with perchlorethylene to reduce the ash content from 16 % to 7 % on the dry basis. This was followed by a mild hydrochloric acid extraction which further reduced the ash content to approximately 1 %. To neutralize the acid remaining after the water wash, the lignite was washed with a LiCO₃ solution. Separate samples of the de-ashed lignite were then impregnated, as before, with molybdenum, 2 % as MoO₃, and iron, 10 % as Fe₂O₃. The properties of these catalysts (support plus promoter) are as shown:

Promoter	Molybdenum	Iron
pH value	4.7	2.7
Ash, wt %	0.8	0.8

The de-ashed lignite has a very low ash content and is acidic in spite of the neutralizing treatment.

The results of the hydrogenation tests are as follows:

Promoter	<u>Molybdenum</u>	<u>Iron</u>
Experiment No.	31	26
Oil feed	Residuum above 427°C from Weyburn crude	Residuum above 427°C from Weyburn crude
Reaction temp, °C	454	452
Reaction time, min	40	45
Oil product		
Sp gr, 60/60°F	0.878	0.862
Sulphur, wt %	2.3	2.7
Distillation range, vol %		
Gasoline fraction, up to 350°F (177°C)	41.8	43.7
Diesel fraction, 350 - 680°F (177 - 360°C)	34.2	35.0
Residuum, above 680°F (360°C)	24.0	21.3
Coke	none	none

The results of these two experiments were very gratifying because no coke was produced in the bottom of the autoclave. As was the case with the iron grude, a small amount of fine black powder was noticed which contained the residue of the promoter and the lignite mineral matter.

It is considered that this favourable result was due to the greatly increased surface area which the lignite obtained during the initial reacting period. This supports the assumption that the lignite was converted to a porous structure which would greatly improve its effectiveness as a catalyst support. It is commonly believed that an acidic catalyst would favour the precipitation of the polynuclear compounds to form a coke residue. But in this experiment, in spite of the acidity of the catalyst, no coke was produced. If the surface area is great, the acidity of the catalyst may not be a serious defect.

The analysis of the oil products show that the specific gravity and sulphur reductions were good. But the distillation range shows that the gasoline fraction up to 350°F is higher than it was with the German iron grude.

Although molybdenum is considered to be a little superior to iron as a promoter, the results of these two tests show little difference between them.

In the above two tests, the lignite was de-ashed to eliminate any possible detrimental action of any of the mineral constituents. In order to find out if this treatment is necessary, the lignite containing all the ash was used in the third experiment. However, in order to neutralize any acidity, a weak solution of sodium hydroxide was added during the impregnation of the support with the promoter. Only iron as 10 % Fe_2O_3 was used.

The results of the test are as follows:

Experiment No.	52
Oil feed	Residuum above 427°C from Weyburn Crude
Reaction temp, °C	459
Reaction time, min	60
Oil product	
Sp gr, 60/60°F	0.837
Sulphur, wt %	3.1
Coke	Small amount of soft residue

The results of this test were not quite as good as those of the first two. However, no hard coke was produced and only a small amount of soft residual matter. The sulphur and gravity reduction of the oil product were much the same. Perhaps a larger amount of catalyst might eliminate the soft residue.

Tests on Cellulose and Lignosol as Supporters for an Iron Promoter

Tests were done using two commercial finely divided materials (cellulose and lignosol) as supports: these are plentiful in Canada and are relatively cheap. Cellulose was chosen as it was considered beneficial to deposit the promoter on the outside of the fine cellulose fibres so that the active catalytic sites would be more accessible to the large oil molecules than if, as usually, the promoter were deposited on the inside surfaces of a porous support. The cellulose used for the test was obtained in the form of standard Whatman filter tablets. The filter tablets were pulped with water and then impregnated, as in the previous tests, with iron, 10 % as Fe_2O_3 . To

increase the pH value, the catalyst was washed with a weak NaOH solution and then air dried. In spite of the alkaline wash, the pH value of the prepared catalyst was only 3.1.

Lignosol is the trade name for a commercial product obtained from wood lignin. It was thought that its partial solubility in the oil would increase the intimate contact of the promoter with the oil. The finely powdered lignosol was obtained from Lignosol Chemicals Limited of Quebec City. The lignosol was also impregnated with iron as 10 % Fe_2O_3 .

The results of the hydrogenation tests are as follows:

Support	Cellulose	Lignosol
Experiment No.	43	50
Oil feed	Residuum above 427°C from Weyburn Crude	Residuum above 427°C from Weyburn Crude
Reaction temp, °C	451	461
Reaction time, min.	50	65
Oil product		
Sp gr, 60/60°F	0.837	0.856
Sulphur, wt %	2.7	3.3
Coke	Large residue of compact coke	Large residue of compact coke

The results show that the reduction of specific gravity and sulphur content of the oil product were satisfactory. On the other hand these two catalyst supports must be considered unsuitable because of the coke formation in the bottom of the autoclave.

Tests Using Molybdenum Benzoate, Iron Phenolate, and Iron Oxalate as Catalysts

It was considered that a metal compound which would dissolve in the feed oil in the molecular form would produce the largest surface area possible. Therefore molybdenum benzoate, iron phenolate, and iron oxalate which were readily soluble in the feed oil were selected for these tests. The pH value of the molybdenum benzoate was found to be 3.1. With the first two catalysts, the amount of the catalyst was 1.5 wt % of the feed oil which was the residuum

above 427°C from Weyburn crude oil. With the iron oxalate, the catalyst amounted to 3.75 wt % of the feed oil, which was the Shell vacuum bottoms from Weyburn crude oil. The results of the hydrogenation tests are shown in Table 8.

Table 8

Results of Tests Using Molybdenum Benzoate,
Iron Phenolate, and Iron Oxalate as Catalysts

Catalyst	Molybdenum benzoate	Iron Phenolate	Iron Oxylate
Experiment No.	34	53	63
Amount of Catalyst, wt % of feed oil	1.5	1.5	3.75
Oil feed	Residuum above 427°C from Weyburn Crude	Residuum above 427°C from Weyburn Crude	Shell vacuum bottoms from Weyburn Crude
Reaction temp, °C	458	464	444
Reaction time, min	40	55	120
Oil product			
Sp gr, 60/60°F	0.857	0.849	0.892
Sulphur, wt %	3.0	2.4	2.3
Pentane insolubles, wt %		3.0	5.7
Distillation range, vol %			
Gasoline fraction, up to 200°C (392°F)			32.0
Jet fuel fraction, 200 - 250°C (392 - 482°F)			13.9
Diesel fuel fraction, 250 - 325°C (482 - 617°F)			18.5
Residuum, above 325°C (617°F)			35.6
Coke	Large residue of compact coke	Small residue of compact coke	None

Of these three catalysts, the iron oxalate was the only one which did not produce any coke, the residue being a fine black powder. As coke was formed with the other two catalysts, more iron oxylate was used. Perhaps this suppressed coke formation. The analysis of the oil product from this test shows that the desulphurization was good and that the distillation range was satisfactory.

The results of the tests with molybdenum benzoate and iron phenolate were disappointing as both failed to pass the qualitative test of producing no coke. However, less coke was produced with the iron phenolate. It is possible that, if the amount of the catalyst was increased as it was with the iron oxalate, the coke formation would have been eliminated.

Tests Using Specific Vapour Phase Catalysts

It was considered of interest to try hydrogenating catalysts which have proved effective in the fixed-bed vapour phase operation. Two commercial catalysts were selected: Ruhroel Catalyst No. K536 from Germany and Union Oil Company catalyst, Type N-H768 from the United States. The Ruhroel catalyst consisted of molybdenum, zinc, and chromium oxides deposited on a support of an acid-treated diatomaceous earth. The Union Oil Company catalyst was composed of cobalt molybdate on an alumina support. Both catalysts were obtained in pelleted form and were ground to less than 200 mesh. The pH of the Union Oil catalyst was found to be 5.7.

The results of the hydrogenation tests are as follows:

Catalyst	Union Oil	Ruhroel
Experiment No.	39	59
Amount of Catalyst, wt % of feed oil	1.5	1.5
Oil feed	Residuum above 427°C from Weyburn Crude	Shell vacuum bottoms from Weyburn Crude
Reaction temp, °C	458	464
Reaction time, min	40	95
Oil product		
Sp gr, 60/60°F	0.866	0.835
Sulphur, wt %	2.6	2.5
Pentane insolubles, wt %		2.2
Distillation range, vol %		
Gasoline fraction, up to 350°F (177°C)	47.2	
Diesel fraction, 350 - 680°F (177 - 360°C)	31.0	
Residuum, above 680°F (360°C)	21.8	

Gasoline fraction, up to 200°C (392°F)	56.0
Jet fuel fraction, 200 - 250°C (392 - 482°F)	9.5
Diesel fraction, 250 - 325°C (482 - 617°F)	10.2
Residuum, above 325°C (617°F)	24.3
Coke	none

As expected, neither of these catalysts produced coke and the reduction of the specific gravity and sulphur content of the oil product were satisfactory. On the other hand, the production of the gasoline fraction was much too high. Both these catalysts are very efficient for the liquid as well as for the vapour phase hydrogenation operation. However, their cost price is too high to use for the liquid phase from which catalyst recovery and regeneration is uneconomical.

Tests Using an Iron Oxide Residue

A very cheap catalyst material is obtainable from the Sherritt-Gordon Mines Limited of Fort Saskatchewan, Alberta. It comprises the iron oxide residue which is rejected from the leaching of the concentrate of the nickel-copper-cobalt ore. In this operation, ammonium hydroxide and air are used to separate the nickel, cobalt, and copper in an ammoniacal solution from the iron oxide and remaining gangue material at a temperature of 175°F and 5 atmospheres pressure. The solid residue is filtered and washed with water. It then passes to the tailings pond for storage and possible future use.

A sample of the iron oxide residue was dried and ground. The pH value was found to be 3.2. This material was used as the catalyst for the first five hydrogenation tests. The results are shown in Table 9. In Experiments 44, 45 and 47, the Weyburn residuum above 427°C was used as the feed oil. In Experiment 45 the amount of the catalyst was the same as used formerly, 1.5 wt % of the feed oil. But in Experiments 47 and 44, the amounts were increased to 2.5 % and 5.0 % respectively.

Table 9

Results of Tests Using Iron Oxide Residue as a Catalyst

Experiment No.	45	47	44	56	55
Amount of catalyst, wt % of feed oil	1.5	2.5	5.0	2.5	2.5
Oil feed	Residuum above 427°C from Weyburn Crude	Residuum above 427°C from Weyburn Crude	Residuum above 427°C from Weyburn Crude	Shell vacuum bottoms from Weyburn Crude	Athabasca Bitumen
Reaction temp , °C	459	471	457	457	456
Reaction time, min	45	45	35	65	60
Oil product					
Sp gr, 60/60°F	0.848	0.850	0.849	0.823	0.872
Sulphur, wt %	3.1	2.4	2.2	2.3	2.8
Pentane insolubles, wt %				1.5	3.9
Distillation range, vol %					
Gasoline fraction, up to 350°F (177°C)	47.8	47.5	43.0		
Diesel fraction, 350 - 680°F (177 - 360°C)	28.4	31.5	31.8		
Residuum, above 680°F (360°C)	23.8	21.0	25.2		
Gasoline fraction, up to 200°C (392°F)				57.2	47.1
Jet fuel fraction, 200 - 250°C (392 - 482°F)				10.0	11.2
Diesel fraction, 250 - 325°C (482 - 617°F)				10.8	12.4*
Residuum, above 325°C (617°F)				22.0	29.3*
Coke	none	none	none	none	none

*Fraction 250 - 271°C (482 - 520°F) and residuum above 271°C (520°F) measured.
Cracking started at 271°C and distillation terminated.

In spite of the acidic nature of the iron oxide residue, the results of these three experiments show that it proved to be an additional catalyst which was sufficiently effective to pass the qualitative test, as no coke was produced in any of the tests. The analysis of the oil product shows that the sulphur reduction was satisfactory but the gasoline fraction was too high. Increasing the amount of the catalyst seemed to have little effect on the results.

In Experiment 56, the Shell vacuum bottoms from Weyburn crude was used as the feed oil and the amount of the catalyst was 2.5 %. Again no coke was produced, but, in addition to the oil product, some heavy, viscous, asphaltic oil was found in the bottom of the autoclave. Otherwise the results were similar to those of Experiment 47 in which the same amount of catalyst was used. The presence of the viscous oil was probably due to the heavier feed oil.

In Experiment 55, the Athabasca bitumen was used as the feed oil and the amount of the catalyst was again 2.5 %. As this feed oil was heavier than the Shell bottoms, a larger amount of the heavy viscous oil was produced than in Experiment 56, but no coke was formed. In Experiments 56 and 55, the analysis of the oil product, including the heavy viscous oil, showed that the sulphur reduction was good but the gasoline fraction was too large. In Experiment 56, the pentane insoluble portion of the oil product was drastically reduced.

In an attempt to improve the efficiency of the catalyst, the hematite portion of the iron oxide residue was used in Experiment 64. In addition to hematite, the residue contained a little magnetite and some of the gangue material from the leaching operation. The magnetite was extracted from this residue by a magnetic separation in an aqueous suspension. The hematite portion was dried and 2.5 % was used for the test with the Shell vacuum bottoms as the feed oil. No grinding was necessary as the hematite was found to be sufficiently fine to be used as a catalyst. The results of the test are shown in Table 10.

In comparing the results of this experiment with those of Experiment 56 where the same amount of the iron oxide residue was used, it will be seen that no coke was formed and that the residue was a black powder.

The sulphur reduction in the oil product was practically the same. Due to the

Table 10

Results of Tests Using Various Iron Catalysts

Catalyst	Hematite Portion of Iron Oxide Residue	Hematite Portion of Iron Oxide Residue with Promoters added	FeS Prepared from FeSO ₄	FeS Commercial
Experiment No.	64	60	61	62
Amount of Catalyst, wt % feed oil	2.5	2.5	1.5	1.5
Oil feed	Shell vacuum bottoms from Weyburn Crude	Shell vacuum bottoms from Weyburn Crude	Shell vacuum bottoms from Weyburn Crude	Shell vacuum bottoms from Weyburn Crude
Reaction temp , °C	431	451	449	452
Reaction time, min	125	60	110	75
Oil Product				
Sp gr, 60/60°F	0.902	0.840	0.849	0.831
Sulphur, wt %	2.4	2.3	2.0	2.3
Pentane insolubles, wt %	8.1	2.0	2.4	1.6
Distillation range, vol %				
Gasoline fraction, up to 200°C (392°F)	22.5	53.3		
Jet fuel fraction, 200 - 250°C (392 - 482°F)	10.1	12.6		
Diesel fraction, 250 - 325°C (482 - 617°F)	16.3	13.9		
Residuum, above 325°C (617°F)	51.1	20.2		
Coke	none	none	Large residue of compact coke	Small amount of soft residue

lower temperature, the gasoline fraction was reduced to a satisfactory yield, but the pentane insolubles, 8.1 %, were too high. The inclusion of the non-magnetic gangue material in the hematite may have contributed to this undesirable high yield of pentane insolubles.

In a further attempt to improve the efficiency of the catalyst, in Experiment 60 the hematite portion of the iron oxide residue was used with the addition of five promoters - Al, Mg, Ca, K, and Sn. The hematite was impregnated with a solution containing the nitrates of these metals and then dried. As a percentage of the hematite, the amounts of the promoters were calculated as 2.2 % $\text{Al}(\text{OH})_3$, 1.2 % MgO , 0.8 % $\text{Ca}(\text{OH})_2$, 0.7 % K_2O , and 0.4 % Sn. This catalyst is similar to the synthetic ammonia catalyst. As in Experiment 64, 2.5 % of the promoted catalyst was used with the Shell vacuum bottoms. The results, as shown in Table 10, were much the same as in Experiment 56 when the whole iron oxide residue was used. No coke was formed, and the sulphur and pentane insolubles reduction were the same. However, the pentane insolubles were much lower than they were in Experiment 64. This is probably the result of the beneficial effect of the promoters in neutralizing the bad effect of the gangue material.

Tests on Iron Sulphide

In Experiment 61, the FeS was precipitated from a solution of FeSO_4 by ammonium sulphide solution in an atmosphere of H_2S . The FeS was dried in an atmosphere of hydrogen and then heated in an atmosphere of H_2S at 500°C for one hour in order to render it more active. In Experiment 62, a sample of commercial FeS was ground in a ball mill to minus 200 mesh size. This was reduced in H_2S at 500°C for one hour to increase its activity.

The feed for these tests was the Shell vacuum bottoms and the catalyst amounted to 1.5% of the feed. The results are shown in Table 10.

The precipitated FeS produced a large amount of hard coke but the commercial FeS produced some soft residual matter. In both cases the desulphurization was satisfactory. The reason for the superiority of the commercial FeS over the precipitated type is not apparent. However, the results show that iron oxide is a better catalyst than iron sulphide because neither coke nor soft residual matter is produced from using the former.

Test Using no Catalyst

A final experiment was made on the Shell vacuum bottoms without using a catalyst. The results were as follows:

Catalyst	none
Experiment No.	58
Oil feed	Shell vacuum bottoms from Weyburn Crude
Reaction temp , °C	455
Reaction time, min	60
Oil Product	
Sp gr, 60/60°F	0.826
Sulphur, wt %	2.4
Pentane insolubles, wt %	2.0
Coke	Large residue of compact coke

As expected a very large amount of coke was produced but the desulphurization was good.

Conclusions

Of the twenty-one catalysts tested, nine produced neither any coke nor a soft residue. The cheapest of these were the de-ashed Bienfait lignite with an iron promoter and the Sherritt-Gordon iron oxide residue. It is quite probable that the lignite itself, without de-ashing, would also be an equally good catalyst support. The hydrogenation tests with all the nine catalysts showed that the desulphurization and the reduction in the specific gravity was good but the gasoline fraction in the oil product was too large.

This latter defect could probably be corrected in a continuous operation. The high surface area (about $150 \text{ m}^2/\text{g}$) is the most important requirement

of a catalyst support, and a slightly alkaline pH is desirable but is of secondary importance.

QUANTITATIVE TESTS ON VARIOUS CATALYSTS

In these quantitative experiments, the more important catalysts, which had successfully passed the previous qualitative tests, were tested again. The oil feed for all the tests was the Shell vacuum bottoms from Weyburn crude oil.

EXPERIMENTAL PROCEDURE USED FOR TESTS

In these tests, a modified and extended procedure was employed. In order to accelerate the cooling of the product oil, when the experiment had terminated, a product receiver was introduced. This permitted the immediate withdrawal, after the termination of the test, of the portion of the oil product which was liquid at the reaction temperature, that is, the highest-boiling fraction. By this action, further reactions such as cracking, polymerization, and precipitation of heavy polynuclear compounds were considerably reduced but not entirely eliminated.

As in the former tests, about 500 ml of the feed oil and 1.5 wt % of the catalyst (support and promoters) were added to the autoclave. The method of operation during the test was the same as before. At the end of the experiment, the valve in the tubing connecting the autoclave dip-tube and the receiver was opened and the liquid portion of the oil product was discharged into the receiver. A portion of the product vapours and gases passed into the receiver until the two pressures became equalized. The apparatus was then left to cool overnight. Next morning the autoclave and receiver were opened and the liquid and solid products were removed and weighed. In most cases, the oil product in the receiver separated into two portions: a top layer of a fluid oil fraction, which could easily be decanted, and a heavy, viscous, asphaltic bottom layer which had to be removed with a spatula. The product remaining in the autoclave consisted of a light oil condensate, any carbonaceous residue produced during the reaction, and the catalyst powder. The light oil from the autoclave was added to the decanted oil from the receiver to be designated the oil product.

The heavy viscous oil from the receiver was designated the asphaltic product and the solid residue, including the catalyst, was designated carbonaceous residue. From the weights of the feed oil and products, the yields of oil product, asphaltic product, and carbonaceous residue were calculated. The specific gravity, sulphur content, pentane insolubles, and distillation range of the oil product were determined. In these series of experiments the boiling range of the various oil fractions were as follows:

gasoline fraction	up to 200°C (392°F)
jet fuel fraction	200 - 250°C (392 - 482°F)
diesel fraction	250 - 325°C (482 - 617°F)
residuum	above 325°C (617°F)

It should be noted that, in these tests the asphaltic product was not added to the oil product before the analysis as was done in the qualitative tests.

In all these experiments, there was unfortunately a slight leak from the packing gland of the stirring mechanism, which resulted in a small continuous escape of product oil vapours to lessen the yield of oil product.

Tests on the Standard Iron Grude and the Two Vapour Phase Catalysts

Three catalysts, which had previously given good results without any coke formation, were used in the first series of tests. These comprised the German iron grude, used as a standard for comparison purposes, the Union Oil Company cobalt molybdate on alumina, and the Ruhroel K536 catalyst (molybdenum, zinc and chromium on diatomaceous earth). The first one is a specific liquid phase catalyst and the latter two are specific vapour phase catalysts. The results of the tests are shown in Table 11.

As in the qualitative tests, all three catalysts gave good results as evidenced by the lack of coke formation. In each case, the appearance of the solid residue as a black powder confirmed the fact that it was composed of the inorganic residue of the catalyst with a minimum content of carbon residue. The Union Oil catalyst produced the highest yield of oil product, 79 %, but no asphaltic product. The other two catalysts produced some

Table 11

Results of Tests Using Iron Grude and Vapour Phase Catalysts

Catalyst	Iron Grude	Ruhrroel	Union Oil
Experiment No.	71	69	70
Reaction temp, °C	459	461	462
Reaction time, min	105	80	130
Oil feed, g	522.0	535.5	552.5
Oil product, g	311.2	328.0	436.0
Asphaltic product, g	72.8	89.0	0.0
Carbonaceous residue, g	15.0	38.0	6.0
Appearance of carbonaceous residue	black powder	black powder	black powder
Coke	none	none	none
Products, wt % oil feed			
Oil	59.6	61.2	78.9
Asphaltic	13.9	16.6	0.0
Carbonaceous residue	2.9	7.1	1.1
Oil product			
Specific gravity, 60/60°F	0.856	0.829	0.937
Sulphur, wt %	1.6	1.7	0.9
Pentane insolubles, wt %	3.4	2.3	6.4
Distillation range, Engler, vol %			
Gasoline fraction, up to 200°C (392°F)	47.5	49.8	35.4
Jet fuel fraction, 200 - 250 °C (392 - 482°F)	11.0	12.5	10.6
Diesel fraction, 250 - 325°C (482 - 617°F)	10.0	10.7	15.5
Residuum, above 325°C (617°F)	31.5	27.0	38.5
Asphaltic product			
Pentane insolubles, wt %	85.4	74.9	

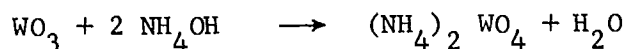
asphaltic products, so their oil product yields were less. The sulphur reduction in the oil product of 4.7 to 1.7 % and less was excellent and the reduction of the pentane insolubles from 25 to 6.4 % was good. The amount of the gasoline fraction in the oil product from the Union Oil catalyst test was satisfactory. But because the asphaltic product was not included in the oil product from the other two tests, the gasoline fraction percentage was too high in the case of the other two catalysts.

Of the three catalysts, the Union Oil cobalt molybdate on alumina produced the best results; because the solid residue was the lowest, no asphaltic product was produced, and, therefore, the oil product yield was the highest. The lower oil yield with the iron crude catalyst resulted from a higher gas loss as well as the yield of asphaltic product.

Tests on Hematite Portion of Iron Oxide Residue with Various Promoters

The hematite portion of the Sherritt-Gordon iron oxide residue had produced no coke in the previous qualitative experiments, therefore, it was used in these four tests. In these experiments, several promoters were used to improve the efficiency of the iron oxide catalyst. Two tests were made with small additions of tungsten and two with additions of tungsten, chromium and zinc. The tungsten and chromium acted as the hydrogenation promoters, whereas the zinc neutralized the acidic chromium compound and is cheaper than the more commonly used nickel.

In the first two experiments, the amount of tungsten (as WO_3) used was 0.8 % and 1.15 % respectively by weight of the hematite. In preparing the catalyst according to the following equation, the required amount of WO_3 was added to the appropriate amount of ammonium hydroxide and excess water to produce ammonium tungstate, which is soluble in water.



The hematite was mixed with the ammonium tungstate solution and dried. The amount of the catalyst, consisting of the support and promoter, used for the test was 1.5 wt % of the feed oil.

In the last two experiments, equal amounts of tungsten were used with added chromium and zinc. In Experiment No. 68, the amount of Cr_2O_3 was 2.0 % of the hematite and the amount of ZnO was 5.0 % of the hematite. In Experiment No. 74, the chromium and zinc was reduced as the tungsten was increased, that is, from 7.0 % to 4.9 %. The individual amounts of chromium and zinc, 1.4 % and 3.5 % respectively, were in the same proportion as before. In preparing the catalyst, the water soluble salts were used: $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ and ZnSO_4 . To ensure that the promoters were added to the hematite in the proper amounts, the preparation was done in three steps: each of the three ingredients in turn were added to the hematite as a water solution and then dried. As before the amount of the hematite plus promoters was 1.5 wt % of the feed oil. The results of the tests are shown in Table 12.

In comparing the results of Experiments 67 and 73, it is evident from the much smaller amount of the carbonaceous residue, that the small increase in the amount of tungsten resulted in a marked increase in the efficiency of the catalyst. The lower oil yield in Experiment 73 is due to the higher amount of asphaltic product. The small decrease in the carbonaceous residues of Experiments 68 and 74 shows that the addition of chromium and zinc had only a slightly beneficial effect on the catalytic efficiency. The reason for the higher yields of asphaltic product in Experiments 73 and 68 is not apparent. The sulphur reduction in all the experiments is satisfactory. The temperature of 433°C in Experiment 67 was too low as evidenced by the high pentane insolubles and the lower volatility of the oil product.

It is considered that the hematite portion of the iron oxide residue, with tungsten as a promoter, is a satisfactory catalyst. The efficiency of this catalyst was not as good as the Union Oil cobalt molybdate on alumina but compares very favourably with the German iron grude. In a continuous operation, the hematite portion of the iron oxide residue or the iron oxide residue itself, both without the addition of any promoters, would probably prove to be an adequate catalyst.

Table 12

Results of Tests Using Hematite Portion of Iron Oxide Residue with Promoters

Catalyst	Hematite portion of iron oxide residue + 0.8 % W	Hematite portion of iron oxide residue +1.15 % W	Hematite portion of iron oxide residue +0.8 % W 2.0 % Cr 5.0 % Zn	Hematite portion of iron oxide residue +1.15 % W 1.4 % Cr 3.5 % Zn
Experiment No.	67	73	68	74
Reaction temp , °C	433	458	460	462
Reaction time, min	125	120	90	195
Oil feed, g	553.0	516.7	578.5	602.5
Oil product, g	435.0	319.6	389.0	407.3
Asphaltic product, g	23.4	76.9	105.4	25.6
Carbonaceous residue, g	36.6	11.6	33.5	9.0
Appearance of carbonaceous residue	black powder	black powder	black powder	black powder
Coke	none	none	none	none
Products, wt % oil feed				
Oil	78.7	61.8	67.2	67.6
Asphaltic	4.2	14.9	18.2	4.2
Carbonaceous residue	6.6	2.2	5.8	1.5
Oil product				
Specific gravity, 60/60°F	0.939	0.850	0.860	0.922
Sulphur, wt %	2.2	1.6	2.3	1.3
Pentane insolubles, wt %	9.9	2.6	3.8	7.4
Distillation range, Engler, vol %				
Gasoline fraction, up to 200°C (392°F)	15.2	46.0	48	33.9
Jet fuel fraction, 200 - 250°C (392 - 482°F)	11.3	12.5	14	15.7
Diesel fraction, 250 - 325°C (482 - 617°F)	15.5	14.0	13	20.0
Residuum, above 325°C (617°F)	58.0	27.5	25	30.4
Asphaltic product				
Pentane insolubles, wt %			79.5	

Tests Using Lignite as a Support for Iron and Cobalt Molybdate on Alumina

In the previous qualitative tests, de-ashed lignite with an iron promoter did not produce any coke in the solid residue. In these four tests, lignite was again used as the supporting material for the promoter. In the first experiment, No. 72, the same de-ashed and neutralized lignite was used with the same amount of iron deposited on it, 10 % as Fe_2O_3 , as was used in Experiments 26 and 31. The ash had been reduced to 0.8 % and a solution of FeSO_4 had been used to impregnate the lignite.

In Experiments 80 and 79, lignite particles were considerably smaller. Formerly, in Experiments 26, 31 and 72, the lignite had been ground to minus 200 mesh. In these experiments, the washed lignite with an ash content of 7 % was ground with water in a colloid mill. In Experiment 80 the lignite was again impregnated with FeSO_4 as 10 % Fe_2O_3 . In Experiment 79 the lignite was first impregnated with 15 % Al_2O_3 in the form of an $\text{Al}_2(\text{SO}_4)_3$ solution, then with 2 % MoO_3 in the form of an $(\text{NH}_4)_2\text{MoO}_4$ solution and finally with 0.5 % CoO in the form of a $\text{Co}(\text{NO}_3)_2$ solution. The result was a promoter similar to the Union Oil Company catalyst, cobalt molybdate on alumina.

In the fourth experiment, No. 81, another form of the lignite support was used. An attempt was made to increase the surface area by depolymerizing the lignite. This was accomplished by heating the lignite with water at 325°C for half an hour. The washed lignite with 7 % ash was put in the autoclave and distilled water was added. The autoclave was closed and heated up to 325°C with the stirrer in operation. The temperature was maintained at 325°C for half an hour while stirring. Then an iron promoter, 10 % as Fe_2O_3 , was added in the form of an FeSO_4 solution. This was transferred to the lignite by means of a feed cylinder attached to the autoclave and provided with a valve in the connecting tubing.

In each of the four tests, the amount of the lignite with the promoter was 1.5 % of the feed oil. The results of the tests are shown in Table 13.

In each test the carbonaceous residue contained no coke. As before the residue consisted of powdered carbon and catalyst. The higher oil yields and

lower yields of asphaltic product and carbonaceous residue in Experiments 80, 79 and 81 as compared with Experiment 72 showed that the catalyst was more efficient; although the lower temperature in Experiment 72 may be partly responsible for this result. Since the promoter in Experiments 72, 80 and 81 was the same, 10 % Fe_2O_3 in the form of FeSO_4 , the higher efficiency is probably because of the larger surface area of the lignite support. In Experiment 81, the 69 % yield of oil product was satisfactory but, in Experiments 80 and 79, the lower oil yields indicate an excessively high gas loss. In all the experiments, the oil product was satisfactorily low in sulphur content and pentane insolubles but, again, the volatility was high because the asphaltic product was separated from the oil product. The results of these experiments show that the efficiency of the lignite support is improved by either grinding in a colloid mill or by depolymerizing,

Tests on Commercial Carbon Blacks with Cobalt Molybdate and Iron Promoter

The German iron grude has a predominantly carbon support in a finely divided state, so two finely powdered commercial carbon blacks were used in these series of experiments. Both were obtained from the Cabot Company of Boston, Mass. and were designated as "Sterling MT" and "Carbolac I". The properties of these two carbon blacks, as given by the manufacturer's catalogue, are as follows:

Brand Name	Sterling MT	Carbolac I
Surface area, m^2/g	6	950
pH value	8.5	3.0

Because the best results so far have been obtained with the Union Oil cobalt molybdate on alumina, molybdenum and cobalt were used as the promoters in the same proportion as for the Union Oil catalyst: 2 % as MoO_3 and 0.5 % as CoO . In Experiments 75 and 76, the two carbon blacks were impregnated with these promoters in the same way as was done in Experiment 79 but omitting the alumina. In Experiments 77 and 78, Carbolac I was again used as the support for the promoters. In Experiment 77, the same cobalt molybdate on alumina

Table 13

Results of Tests Using Lignite with Iron and Cobalt Molybdate on Alumina

Catalyst	Lignite de-ashed neutralized +10 % Fe_2O_3	Lignite ground in colloid mill +10 % Fe_2O_3	Lignite ground in colloid mill +15 % Al_2O_3 2 % MoO_3 0.5 % CoO	Lignite depolymerized +10 % Fe_2O_3
Experiment No.	72	80	79	81
Reaction temp, °C	452	473	473	472
Reaction time, min	120	60	75	45
Oil feed, g	506.5	582.0	642.0	604.5
Oil product, g	191.5	319.5	364.6	417.0
Asphaltic product, g	139.0	59.0	48.0	56.5
Carbonaceous residue, g	21.4	7.0	7.6	8.0
Appearance of carbonaceous residue	black powder	black powder	black powder	black powder
Coke	none	none	none	none
Products, wt % oil feed				
Oil	37.8	54.9	56.8	69.0
Asphaltic	27.4	10.1	7.5	9.3
Carbonaceous residue	4.2	1.2	1.2	1.3
Oil product				
Specific gravity, 60/60°F	0.821	0.864	0.829	0.852
Sulphur, wt %	1.4	2.0	1.6	1.9
Pentane insolubles, wt %	1.7	3.2	2.8	2.9
Distillation range, Engler, vol %				
Gasoline fraction, up to 200°C (392°F)	56.0	59.0	63.6	55.7
Jet fuel fraction, 200 - 250°C (392 - 482°F)	11.7	9.4	9.0	11.4
Diesel fraction, 250 - 325°C (482 - 617°F)	13.5	11.9	10.5	12.5
Residuum, above 325°C (617°F)	18.8	19.7	16.9	20.4
Asphaltic product				
Pentane insolubles, wt %	74.5			

promoter was used as in Experiment 79 and it was applied to the Carbolac I in the same way. In Experiment 78, the same iron catalyst was used as in Experiments 72, 80, and 81: 10 % as Fe_2O_3 in the form of FeSO_4 , and the method of impregnation was the same. The results of the tests are shown in Table 14.

As is seen from the product yields in Experiments 75 and 76, the Carbolac I was a better supporting material than the Sterling MT. The oil product of 74 % was higher and the carbonaceous residue of catalyst powder with a little carbon was too small to weigh. When the alumina was added to the molybdenum and cobalt, the results were greatly improved. The highest yield of oil product was obtained, 92 %, no asphaltic product was produced and again the solid residue was too small to weigh. With Fe_2O_3 as the promoter, the catalytic activity was much less; the yield of oil product was 64 % and of asphaltic product was 15 %, but again the solid residue was too small to weigh. In every experiment the sulphur and pentane insolubles content of the oil product was satisfactory, but the gasoline fraction in the oil product was too large.

The results of these experiments show the beneficial effect of a large-surface catalyst. In spite of the acidity (pH3) of the Carbolac I, its high specific surface ($950 \text{ m}^2/\text{g}$) more than compensated for the acidity. The Sterling MT with a low surface area of $6 \text{ m}^2/\text{g}$ but a good pH value of 8.5 yielded much less oil product, some carbonaceous residue, but no coke. As expected, the iron promoter was less efficient than the cobalt molybdate with and without alumina. The best results were obtained from the Carbolac I with cobalt molybdate on alumina as the promoter.

Conclusions

All the catalysts tested in the quantitative experiments gave very good specific gravity, sulphur and pentane insolubles, reduction of the oil product, and no coke formation, but the yield of the gasoline fraction of the oil product was too high.

Though these results were uniform, the efficiencies of the catalysts were different as shown by the yields of oil product and carbonaceous residue. The oil product yields were between 40 % for the iron promoter on de-ashed and neutralized

Table 14

Results of Tests Using Carbon Blacks with Cobalt Molybdate and Iron

Catalyst	Sterling MT + 2 % Mo 0.5 % Co	Carbolac I + 2 % Mo 0.5 % Co	Carbolac I + 15 % Al_2O_3 2 % Mo 0.5 % Co	Carbolac I + 10 % Fe_2O_3
Experiment No.	75	76	77	78
Reaction temp, °C	451	450	460	455
Reaction time, min	155	145	95	90
Oil feed, g	729.0	611.4	674.0	714.0
Oil product, g	491.2	452.9	622.9	454.0
Asphaltic product, g	25.2	19.1	0.0	109.2
Carbonaceous residue, g	35.1	trace*	trace*	trace*
Appearance of solid residue	black powder	black powder	black powder	black powder
Coke	none	none	none	none
Products, wt % oil feed				
Oil	67.4	74.1	92.4	63.6
Asphaltic	3.5	3.1	0.0	15.3
Carbonaceous residue	4.8	trace	trace	trace
Oil product				
Specific gravity, 60/60°F	0.855	0.861	0.867	0.832
Sulphur, wt %	1.6	1.3	1.1	2.0
Pentane insolubles, wt %	2.7	4.1	4.5	1.7
Distillation range, Engler, vol %				
Gasoline fraction, up to 200°C (392°F)	46.6	47.8	42.9	57.4
Jet fuel fraction, 200 - 250°C (392 - 482°F)	12.2	11.1	11.5	12.4
Diesel fraction, 250 - 325°C (482 - 617°F)	15.5	15.5	16.2	13.1
Residuum, above 325°C (617°F)	25.7	25.6	29.4	17.1

*Too small to weigh.

lignite and 90 % for the cobalt molybdate on alumina promoter on Carbolac I, and the carbonaceous residues were between 7 % for the Ruhroel catalyst and a trace for the Carbolac support with promoters. The standard iron grude yielded approximately 60 % of oil product, the hematite portion of the iron oxide residue with tungsten, chromium, and zinc promoters yielded about 70 %, and the depolymerized lignite with an iron promoter also yielded about 70 %. The highest yield of oil product of over 90 % was obtained with the Carbolac I support with a promoter of cobalt molybdate on alumina.

In the selection of a liquid phase catalyst, the quantitative tests have shown that the weight percentage of oil yield with no coke formation is the best indication of the efficiency of a catalyst. Because Carbolac I with a cobalt molybdate promoter yielded the most oil, it clearly demonstrates that a large surface area is of most importance to the efficiency of a liquid phase catalyst; however, this catalyst is too expensive to use on a commercial scale. Therefore, it is considered that the hematite portion of the iron oxide residue or the iron oxide residue alone, either with or without promoters, and the Bienfait lignite with an iron promoter would be efficient and inexpensive liquid phase catalysts of Canadian origin.

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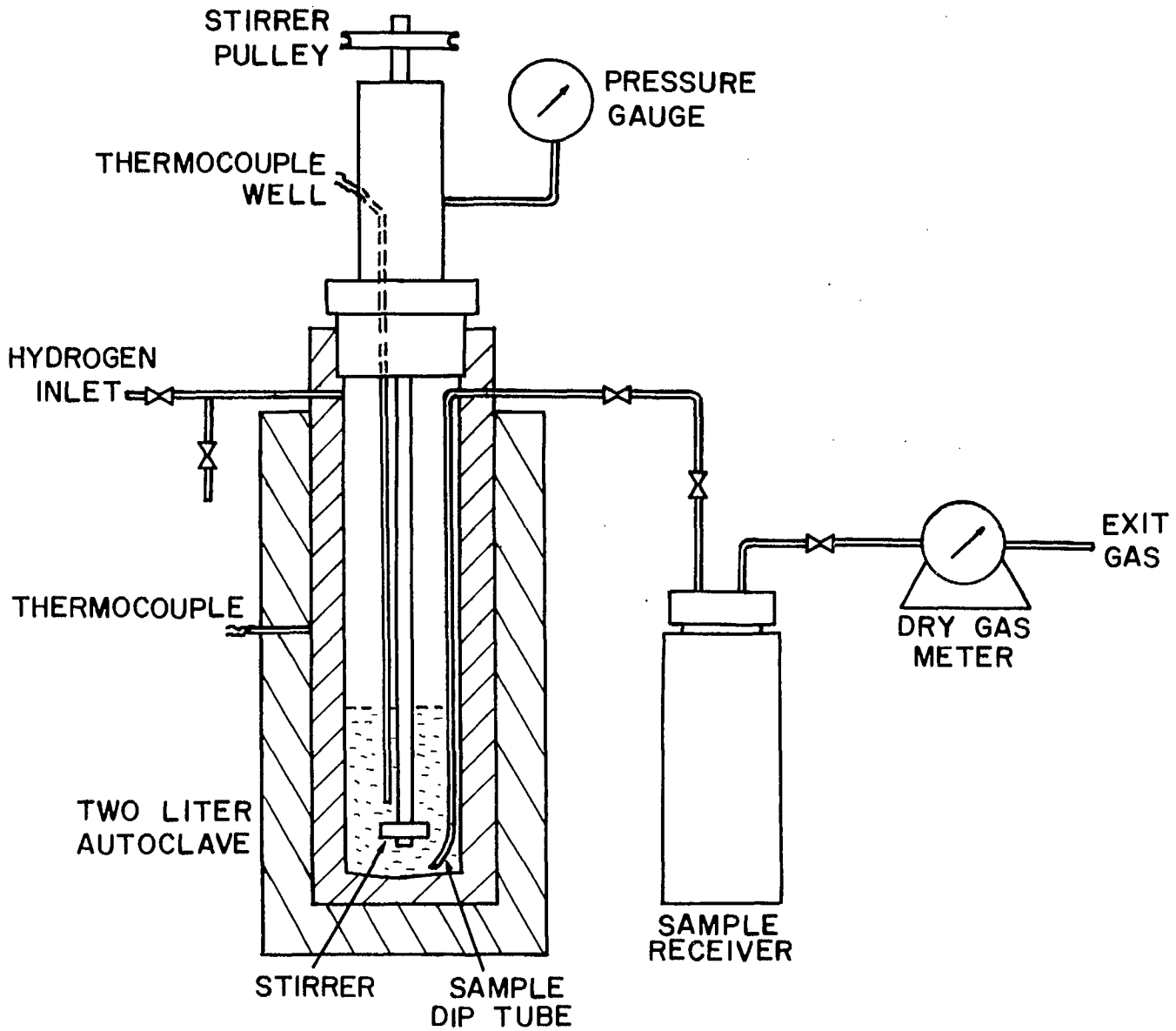


Figure 1 - Schematic diagram of experimental apparatus

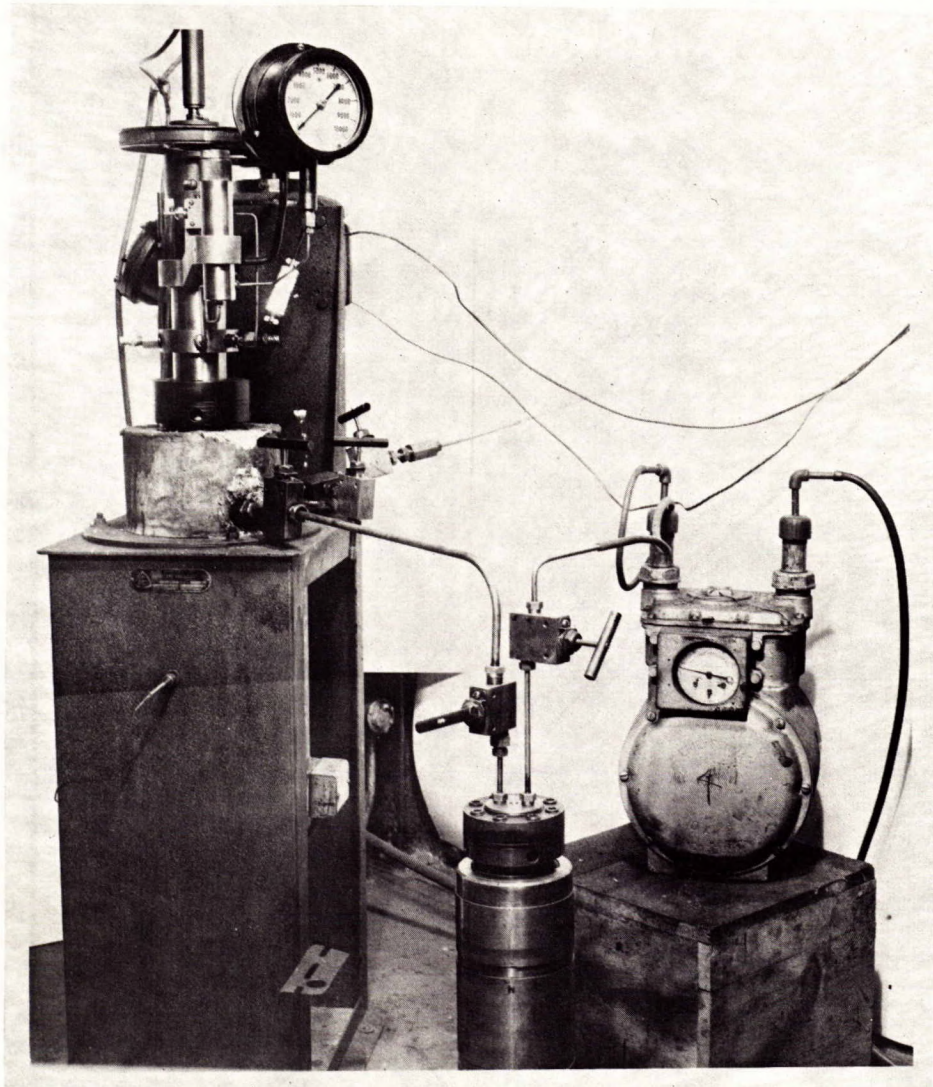


Figure 2 - Experimental apparatus

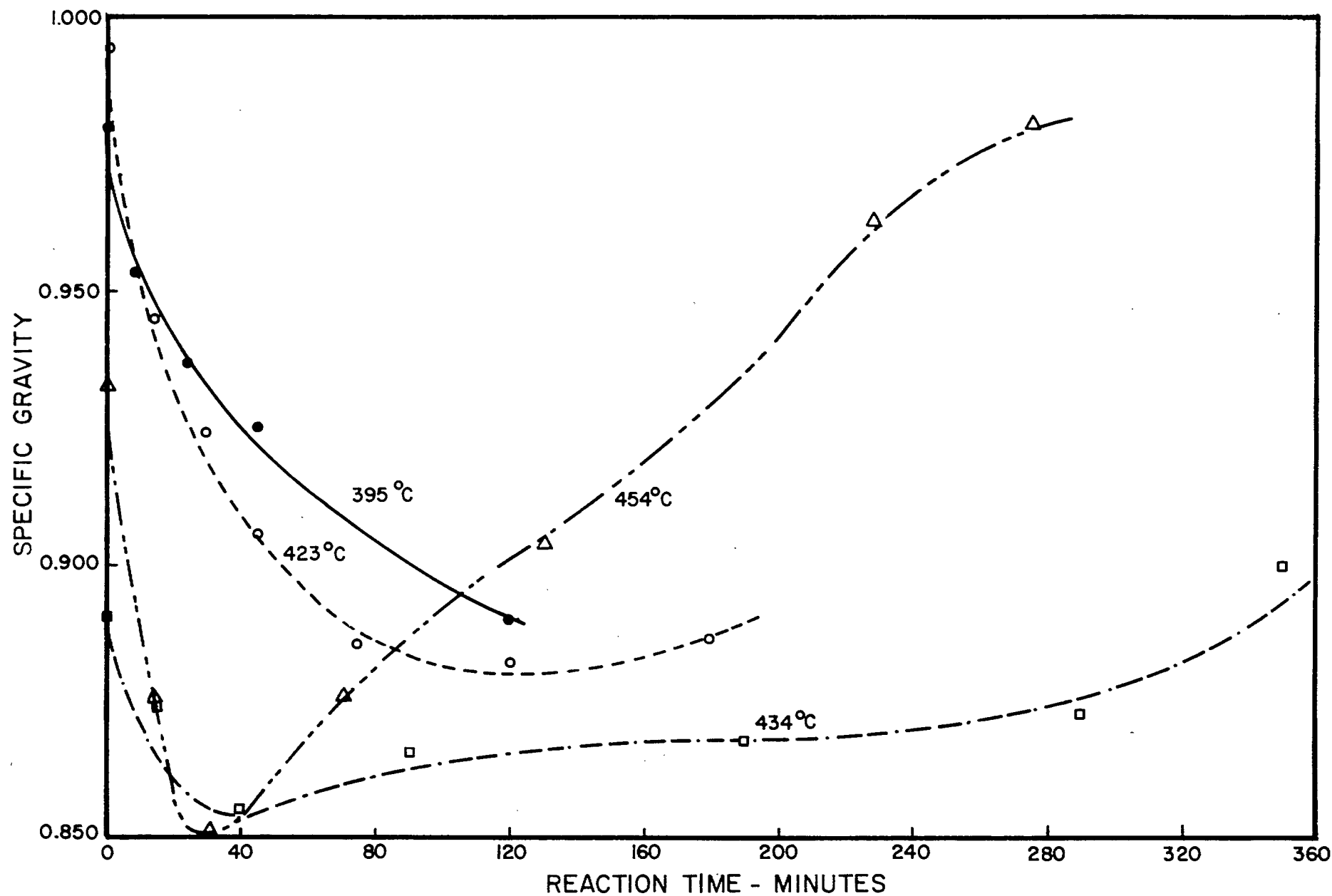


Figure 3 - Specific gravity of oil product versus reaction time at various temperatures

