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A COMPARATIVE STUDY OF Fe CATALYSTS, ZnCl2 CATALYSTS AND ZnCl2- PROMOTED Fe CATALYSTS FOR HYDROCRACKING OF ATHABASCA BITUMEN

W.A.O. Herrmann, L.P. Mysak and K. Belinko

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A COMPARATIVE STUDY OF Fe CATALYSTS,

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HYDROCRACKING OF ATHABASCA BITUMEN

by

W.A.O. Herrmann*, L.P. Mysak** and K. Belinko

ABSTRACT -

Tests were carried out during thermal hydrocracking of Athabasca bitumen on certain catalysts produced from inexpensive raw materials. Two classes were investigated: iron catalysts (Class I) and zinc chloride-promoted catalysts (Class II). These experiments were carried out in a batch autoclave. The reaction temperature varied from 385° C to 455° C at an H₂ pressure of 13.8 MPa. Reaction times ranged from 30 to 210 minutes.

The products obtained by using these catalysts were analyzed and compared with those using two conventional catalysts and those with no catalyst. The highest conversion was achieved with an Fe-lignite catalyst. The next most active was found to be 100% ZnCl₂. The latter produced a smaller amount of HC gas and significantly less sulphur in the product, and may therefore be considered more desirable.

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ETUDE COMPARATIVE DE L'UTILISATION DES CATALYSEURS AU FER, DES CATALYSEURS A ZnC1₂ ET DES CATALYSEURS A PROMOTEUR ZnC1₂ POUR L'HYDROCRAQUAGE DU BITUME DE L'ATHABASCA

PAR

W.A.O. Herrman*, L.P. Mysak** et K. Belinko***

RESUME

Des essais, portant sur certains catalyseurs obtenus à partir de matériaux bruts bon marché, ont été effectués au cours de l'hydrocraquage thermique des bitumes de l'Athabasca. Deux catégories de catalyseurs ont été étudiés: des catalyseurs dont l'élément actif est le fer (catégorie I) et des catalyseurs à promoteur de chlorure de zinc (catégorie II). Ces expériences ont été faites dans un autoclave en opération discontinue. La température de réaction variait de 385° à 455° C, sous une pression d'hydrogène de 13,8 MPa. Les temps de réaction variaient de 30 à 210 minutes.

Les produits obtenus en utilisant ces catalyseurs ont été analysés et on les a comparés avec les produits obtenus sans catalyseurs ou en présence de deux catalyseurs conventionnels. La conversion la plus élevée a été celle effectuée avec catalyseur de lignite et de fer. La seconde étant celle activée par le chlorure de zinc à 100%. Ce dernier donne une plus petite quantité d'hydrocarbures et nettement moins de soufre: par conséquent, son utilisation serait plus souhaitable.

Droits de la Couronne réservés

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INTRODUCTION

A major concern at CANMET (Canada Centre for Mineral and Energy Technology) in the growing demands for energy in Canada, has been the refining of bitumen and other residual oils. Efforts at the Energy Research Laboratories have been directed at processing these feedstocks, both by catalytic methods (1-3) and by non-catalytic or thermal hydrocracking techniques (4,5). In developing these technologies, the primary aim has been to generate a clean distillate product while at the same time ensuring that the process is economically feasible.

A comparative study of non-catalytic and catalytic hydrocracking of bitumen was recently undertaken by Logie and Denis (6). A conclusion reached was that bitumen does not readily lend itself to conventional catalytic hydrocracking, mainly because of rapid catalyst deactivation. The nature of the fouling material makes catalyst regeneration economically unwarranted, and consequently a cheap once—through catalyst would be required.

Evaluation studies of various catalysts for liquid phase hydrogenation of Weyburn crude oil were reported in a previous publication (7). In this report, the catalytic activities of various inexpensive raw materials of Canadian origin are compared in hydrocracking of Athabasca bitumen. The catalysts are grouped into two classes: - Class I - Fe-based catalysts, and Class II - ZnCl₂-promoted Fe catalysts. The application of ZnCl₂ catalysts to the hydrocracking of polynuclear hydrocarbons and coals is well documented (8,9). The results obtained with Class I and Class II catalysts are compared with those obtained with ZnCl₂ alone, and with other more conventional catalysts.

EXPERIMENTAL PROCEDURE

Apparatus

The reaction vessel used was a stirred autoclave having a capacity of 2 litres (Fig. 1). The allowable working pressure was $34.5\,$ MPa at a maximum temperature of about 485° C. The contents of the vessel were stirred by a magnetically operated impeller rotating at 1250 rpm.

The autoclave was heated by an external heating coil and the assembly was insulated. The inside temperature was measured by means

of a thermocouple inserted in a well, extending from the top closure to about 5.1 cm from the bottom. The outside skin temperature was measured by a thermocouple placed against the vessel wall midway in the heated portion.

A smaller high pressure vessel was used as a product receiver. An 800-litre plastic container was used as a gas holder for sampling the gases after each experiment.

An Inconel liner was used in the autoclave to prevent corrosion of the vessel wall during experiments involving the ZnCl₂ catalysts. Approximately 500 gm of Athabasca bitumen, containing 1.5 wt % catalyst, was charged to the autoclave and the system evacuated. The vessel was then pressurized with hydrogen and checked for leaks. The hydrogen pressure at ambient temperature was chosen to approximate 13.8 MPa at the operating temperature of the experiment. Once the reaction temperature was attained, hydrogen was admitted periodically into the vessel to replace any consumed hydrogen and to maintain the desired pressure. In testing Class I catalysts, some of the experiments were designed to study the effect of simultaneously changing the reaction temperature and time. Runs at 385°C, 425°C and 440°C were carried out for 3.5 hours, 3 hours and 1.5 hours, respectively. Otherwise, the experiments were conducted at 425°C for various periods of time.

On completion of the experiment, the product was discharged from the reaction vessel by pressure difference into the cold product receiver, so that the reaction could be quenched immediately after the required time had elapsed.

When the system reached ambient temperature, the gases were metered into the plastic gas holder and a representative sample was collected for analysis. The product receiver was subsequently pressurized to about 2.1 MPa, thereby forcing the liquid product into a collecting bottle. Any solid material remaining in the autoclave was collected and weighed.

Catalyst Preparation

Class I

German grude catalyst has been successfully used in Germany for the liquid phase hydrogenation of refractory petroleum residual oils. The grude catalyst was prepared from a Winkler generator dust and consisted of fine fly ash particles covered with a thin layer of carbon (7). This generator dust was impregnated with a saturated solution of FeSO₄ so that in the dried cat-

alyst, the concentration of $\operatorname{Fe}_2 0_3$ was about 11.8%.

In the preparation of the carbon black support catalyst, the support material was impregnated with a specific quantity of FeSO_4 to make the surface concentration of $\operatorname{Fe}_2\operatorname{O}_3$ approximately the same as that of the German grude. The required quantity of ferrous sulphate was dissolved in water and the carbon slowly added to this solution with stirring. This resulted in a paste which was subsequently dried in a vacuum drying oven and then ground in a ball mill and screened to minus 325 mesh.

A similar procedure was followed to produce the Fe-lignite catalyst.

A fourth catalyst used in this work was an iron oxide residue obtained from Sherritt-Gordon Mines Ltd. of Fort Saskatchewan, Alberta, which was rejected from the leaching of the concentrate of nickel-copper-cobalt ores. A sample of this residue was ground and screened to minus 325 mesh. The surface area of this iron oxide residue catalyst (about 75 m 2 /g) was found to be approximately half that of the other catalysts and for this reason, twice as much iron oxide residue was used in the experiments to provide a basis for comparison with the other catalysts.

A chemical analysis of the various Class I catalysts is presented in Table 1.

Class II

In the preparation of Class II catalysts, the same iron oxide residue used as a Class I catalyst was used as the support material. The required amounts of ZnCl₂ were dissolved in distilled water and the pH adjusted to 6.5 with addition of sodium carbonate. Iron oxide was then added to this solution and the mixture dried in a vacuum oven. The dried products were ground and screened to minus 325 mesh.

Various concentrations of ${\rm ZnCl}_2$ were used to promote the iron oxide support, ranging from 1% to 25%. A 100% ${\rm ZnCl}_2$ catalyst was also tested.

RESULTS

Some physical and chemical properties of the Athabasca bitumen feedstock used in these studies are presented in Table 2. Assessment of the catalysts was generally based on the following criteria:

- (1) the yield of total liquid products boiling above 40°C
- (2) the percentage of residue boiling above 418°C
- (3) the nature of this high boiling residue characterized by the Conradson carbon formation
- (4) the degree of hydrogenation as indicated by the per cent sulphur content in the kerosene fraction $(250^{\circ}-333^{\circ}C)$

Details of operating conditions for runs with various Class I and Class II catalysts are summarized in Tables 3 and 4, respectively. Data for $+418^{\circ}$ C residuum was calculated by dividing the difference in residuum content between feed and product by the residuum content in the feed.

In terms of $+418^{\circ}\mathrm{C}$ residuum conversion, the most active Class I catalyst was found to be Fe-lignite (Fig. 2). Conversion of residuum with this catalyst ranged from 25% at $385^{\circ}\mathrm{C}$ (3.5 hr) to approximately 80% at $445^{\circ}\mathrm{C}$ (1.5 hr). The Fe-carbon black and the iron oxide residue catalysts were found to be slightly better than the German grude catalyst. In the case of the ZnCl_2 -promoted catalysts, conversion was generally found to increase with increasing concentration of ZnCl_2 (Fig. 3). At the higher operating temperatures, both the iron-based catalyst and the ZnCl_2 -promoted catalyst appeared to reach approximately the same level of conversion.

The specific gravity of the liquid products obtained using the various catalysts is plotted as a function of reaction temperature and time in Fig. 4 and 5. Of the four Class I catalysts, Fe-lignite and Fe-carbon black catalysts were found to yield the lightest liquid product. In general, the specific gravity of the liquid products obtained with the Class II catalysts was found to be inversely proportional to the concentration of ZnCl₂. As in the case of +418°C residuum conversion, the specific gravity of the liquid products for all catalysts appeared to converge at the higher operating temperatures.

Figures 6 and 7 show the variation in gasoline content (fraction boiling below 200°C) produced as a function of reaction temperature and time

for the various catalysts investigated. The trend in results was found to be approximately similar to that of residuum conversion. Fe-lignite was again found to yield the largest gasoline fraction. Of the Class II catalysts, those with the highest ZnCl₂ concentration were generally found to produce more gasoline.

All four Fe-based catalysts were found to produce approximately the same quantity of hydrocarbon gases (Table 3). In the case of ${\rm ZnCl}_2$ -promoted catalysts, the amount of hydrocarbon gas produced at operating temperatures below 435°C was greatest with the 100% ${\rm ZnCl}_2$ and least with the 1% ${\rm ZnCl}_2$ catalysts (Fig. 8). At reaction temperatures above 435°C, the amount of hydrocarbon gas produced was approximately the same for all ${\rm ZnCl}_2$ concentrations.

Of the four Class I catalysts, the Fe-carbon black catalyst was found to produce the least sulphur containing product in all cases (Table 3) and there was little difference in desulphurizing abilities between the remaining three catalysts. The results reported in Table 4 for ${\rm ZnCl}_2$ -promoted catalysts revealed that the product with the least sulphur content was produced with the 100% and 25% ${\rm ZnCl}_2$ catalysts. The sulphur content of the products using the other Class II catalysts did not appear to vary with the concentration of ${\rm ZnCl}_2$ in the catalyst.

Table 5 compares the product distribution obtained with three different catalysts and for one case without a catalyst. These experiments were all conducted under similar operating conditions, i.e., 425°C at 13.8 MPa pressure for 45 minutes. The data indicate that conversion of +418°C-residuum was significantly altered by the presence of a catalyst during the hydrocracking process. Furthermore, in the case of the non-catalytic experiments, the formation of coke-like deposits on the walls of the autoclave was quite pronounced. Such coke-like formation was not evident in experiments involving catalysts. The most notable contribution of the Nalcomo 471 (Co-Mo) catalyst was in sulphur removal from the products (Table 5). The sulphur content of each fraction was considerably lower than for any of the other catalysts investigated.

DISCUSSION

In hydrocracking of bitumen, the primary aim is to convert the heavy residuum material into distillable fractions without generating excessive amounts of HC gases or coke-like material. To ensure the efficiency of this process, it is desirable to maximize the cracking reactions that can occur, and to ensure proper hydrogenation of the cracked products. To minimize hydrogen consumption, it is often desirable to have hydrogenation occur by H-transfer reactions. However, the H-donors will invariably be the large unsaturated molecules of the system and dehydrogenation of these molecules will render them likely candidates for coke formation. Conditions must therefore be established so that sufficient amounts of active hydrogen are made available to suppress the formation of coke.

A substance that will actively catalyze the cracking and hydrogenation reactions which occur during thermal hydrocracking will undoubtedly contribute to a higher yield of HC gases or lower boiling fractions in general. This results in a greater consumption of hydrogen with little improvement in product quality. Therefore, in selecting a catalyst, it is not only important to consider residuum conversion but also to take into account the amount of lower boiling fractions produced.

The results of this study appear to favour Fe-lignite as the most active of the Class I catalysts. This is indicated not only by the higher conversion levels achieved, but also by the lower gravity of the product and the larger gasoline fraction obtained.

The differences in conversion of +418°C residuum for the various Class I catalysts appeared to diminish at the higher temperatures. It is possible that, at the high temperatures, the rate of cracking of residuum material is so great that any catalytic effects are not readily apparent. Under these conditions, a greater concentration of catalyst might better show up any catalytic effects. It is interesting to note, however, that differences in the amount of the gasoline fraction produced with the various Class I catalysts are still quite pronounced at the higher reaction temperatures (Fig. 6). This may suggest that the catalysts are still active towards hydrogenation reactions, thereby ensuring that the cracked radicals undergo hydrogenation as opposed to polymerization.

The results reported for the Class II catalysts demonstrated the catalytic activity of the ${\rm ZnCl}_2$. Conversion of $+418^{\rm O}{\rm C}$ -residuum was greatest for 100% ${\rm ZnCl}_2$ and least for 1% ${\rm ZnCl}_2$. Conversion was found to be approximately the same for all Class II catalysts at the higher operating temperatures. This would again indicate that the catalytic effect was masked by the thermal effect.

The amount of lower boiling fractions, e.g., gasoline and HC gases produced was found similar for all ${\rm ZnCl}_2$ -promoted catalysts at the higher operating temperatures (Fig. 7 and 8). It may therefore be concluded that, unlike the Fe catalysts, the ${\rm ZnCl}_2$ -promoted catalysts may not be as active towards hydrogenation reactions.

In Table 5, the product distributions for Fe-lignite, 100% $\rm ZnCl_2$, Nalcomo 471 and for a non-catalytic case are compared under similar operating conditions. Although differences in conversion between $\rm ZnCl_2$ and Fe-lignite are not appreciable, Nalcomo 471 and the non-catalytic case show a significantly lower conversion. In comparing product quality for Fe-lignite and $\rm ZnCl_2$ catalyst, the latter produced a lesser amount of HC gas and a lower sulphur content, and might therefore be considered a more desirable choice.

CONCLUSIONS

The autoclave experiments described in this report show that catalysts for thermal hydrocracking of bitumen can be produced from relatively inexpensive Canadian raw materials. These catalysts are capable of suppressing the formation of coke-like material in the reactor, and give results comparable to more conventional catalysts used in hydrocracking of bitumen and other heavy oils.

Fe-lignite was found to be the most active of all the catalysts investigated. The most active Class II catalyst was $100\%~\rm ZnCl_2$. This catalyst had a distinct advantage over the Fe-lignite catalysts in that fewer HC gases were generated during the hydrocracking process. Furthermore, the sulphur content of the various fractions obtained with the $\rm ZnCl_2$ catalyst was significantly lower than for Fe-lignite.

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TABLE 1

Ash Analysis of Class I Catalysts

Analysis wt %	German Grude	Fe-Carbon Black	Fe-Lignite	Iron-Oxide Residue
Ash content	51.38	11.84	18.46	100.00
Ash analysis				
sio_2	2.09	Ni1	0.96	10.34
A1 ₂ 0 ₃	1.59	0.31	1.38	1.24
Fe ₂ 0 ₃	11.76	11.43	11.53	82.01
TiO2	0.27	0.08	0.14	0.13
P ₂ 0 ₅	0.23	0.17	0.19	0.23
Ca0	21.72	0.01	1.11	0.42
MgO	2.88	0.19	0.56	4.72
so ₃	9.61	0.02	2.46	0.74
Na ₂ 0	0.62	0.01	0.38	0.08
к ₂ 0	Nil	Nil	0.02	0.09
ZnO	Trace	Trace	Trace	Trace
NiO	Ni1	Trace	Trace	Trace
Cr ₂ 0 ₃	Trace	Nil	Trace	Trace
Mn ₃ 0 ₄	0.13	0.02	0.03	·Trace
Combustibles	48.62	88.16	81.54	0

TABLE 2

Analysis of the Athabasca Bitumen Feedstock

Specific gravity 60/60°F	1.009
Sulphur (wt %)	4.63
Viscosity (cSt at 210°F)	152.2
Conradson Carbon Residue (wt %)	12.8
Pentane insolubles (wt.%)	16.0
Benzene insoluble (wt %)	0.9
Chlorine (wt %)	0.013
Gasoline fraction vol % up to 200°C	0.53
Naphtha fraction vol % 20 0 -250 ⁰ C	2.23
Specific gravity	0.858
Sulphur wt %	1.43
Kerosine fraction vol % 250-333°C	11.86
Specific gravity	0.902
Sulphur wt %	1.92
Fuel oil fraction vol.% 333-418°C	18.57
Specific gravity	0.951
Sulphur wt %	3.10
Heavy fuel oil fraction vol % 418-524°C	19.08
Specific gravity	0.989
Sulphur wt %	3.77
Residuum vol % + 524°C	47.73
Specific gravity	1.076
Sulphur wt %	6.21

It should be noted that the residuum content of the autoclave products was measured at a temperature of +418°C. Therefore at this cut temperature, the residuum in the Athabasca bitumen would be 66.81 vol.%.

TABLE 3 Pitch Conversion Results for Class I Catalysts

Feed Residue ($\pm418^{\circ}$ C) wt % = 69.6

Catalyst	Reaction Temp	Reaction Time	Conversion of +418 ^O C Residuum	Gas Formed	S in Total Product	Kerosene Fraction	S in Kerosene Fraction	Conradson Carbon in Residuum
	; -		wt % of feed	wt % of Feed	wt %	vol % of total prod	wt %	Fraction wt %
Fe-carbon black	385	3.5 hr	20.88	2.38	3.66	14.6	2.41	18.6
Fe-lignite	385	11	25.21	1.57	3.91	17.4	2.57	21.4
Fe ₂ 0 ₃ residue	385	11	19.22	1.04	3.86	14.5	2.46	18.9
German grude	385	**	19.07	1.10	3.85	15.3	2.53	19.8
 Fe-carbon black	425	3 hr	72.52	7.39	2.25	22.5	2.25	28.93
Fe-lignite	425	! !	74.84	7.94	2.46	21.3	2.54	34.53
Fe ₂ 0 ₃ residue	425	ti .	71.98	6.52	2.53	22.9	2.30	31.12
German grude	425	**	69.97	7.16	2.44	22.0	2.37	28.13
Fe-carbon black	440	1.5 hr	81.52	10.96	2.27	19.1	3.02	37.40
Fe-lignite	437	* ************************************	79.58	.10.82	2.62	16.6	3.12	36.60
Fe ₂ 0 ₃ residue	444	TT .	77.20	12.24	2.55	19.4	2.91	34.55
German grude	441	"	79.92	10.56	2.52	18.0	2.97	-35.40
Fe-lignite	425	40 min	51.11	4.77	3.53	22.0	2.63	28.83
Fe-lignite	425	60 min	58.34	5.13	3.27	22.7	2.51	31.2
Fe-lignite	425	90 min	64.12	5.28	3.94	21.0	2.43	32.3
							<u>:</u>	

Feed Residue (+418 $^{\circ}$ C) wt % = 69.6

Catalyst	Reaction Temp °C	Reaction Time	Conv. of +418 C Residuum wt % of feed	Formed	S in Total Product wt %		Kerosene	Conradson Carbon in Residuum Fraction wt %
99% Fe ₂ 0 ₃ & 1% ZnCl ₂	385 420 445	45 min	3.32 23.55 69.82	0.41 1.41 6.11	4.28 3.76 2.91	9.3- 12.9 21.2	2.17 2.44 2.53	20.9 23.6 31.1
98% Fe ₂ 0 ₃ & 2% ZnCl ₂	385 421 445	11 11 . 11	8.14 37.49 70.65	1.54 2.41 6.28	4.20 3.38 2.85	10.0 18.0 22.	2.25 2.40 2.66	19.5 22.5 34.3
96% Fe ₂ 0 ₃ & 4% ZnCl ₂	385 423 443	11 11	5.07 39.63 71.69	1.41 2.54 6.53	4.30 3.42 2.79	9.8 20.0 20.9	2.29 2.41 2.70	20.14 24.41 35.13
90% Fe ₂ 0 ₃ & 10% ZnCl ₂	385 422 445	11 11	6.97 45.30 70.37	1.60 2.96 6.59	4.37 3.19 2.98	8.8 22.8 19.9	2.25 2.35 2.77	21.06 22.88 32.3
85% Fe ₂ 0 ₃ & 15% ZnCl ₂	400 426 446	11 11	12.20 45.23 72.88	2.56 2.94 6.52	4.38 3.60 2.91	12.4 20.2 33.9	2.56 2.51 2.84	20.5 23.8 31.7
75% Fe ₂ 0 ₃ & 25% ZnCl ₂	403 427 446 455	" " 10 min	13.93 44.28 71.70 58.38	2.46 2.88 5.96 5.29	4.28 3.28 2.64 3.10	12.0 18.8 20.4 19.5	2.40 2.34 2.64 2.60	20.4 21.4 33.4 21.66
100% ZnCl ₂	410 430 446	45 min	27.62 55.43 72.57	3.03 3.16 6.03	3.30 2.70 2.64	14.5 21.8 20.3	2.20 2.20 2.58	11.9 23.4 32.7

TABLE 5

Product Fraction Comparison to +532°C*

	No Catalyst		Nalcon	Nalcomo 471		Fe-Lignite		ZnCl ₂	
Boiling Range °C	Wt.%	Wt.7s	Wt.%	Wt.7s	Wt.%	Wt.7S	Wt.7	Wt.7s	
RT-100	1.29	-	2.08	0.13	3.43	0.46	2.89	0.19	
100-200	9.13	1.52	9.59	0.34	14.88	1.38	11.63	0.69	
200-250	6.81	1.68	10.23	0.86	7.68	1.68	9.13	1.40	
250-275	7.36	2.09	7.04	1.42	6.12	1.94	6.42	1.98	
275-332	13.82	2.20	11.42	1.58	15.04	2.75	16.98	2.00	
332-361	8.37	2.84	10.14	1.79	9.21	3.21	9.36	2.30	
361-391	6.24	3.15	6.77	1.94	4.61	3.36	4.44	2.56	
391-421	7.11	3.52	7.89	2.10	7.96	3.60	7.06	2.72	
421-532	16.62	4.00	11.35	2.56	14.66	4.46	19.38	3.50	
+532	23.37		23.54		15.58		12.70		
% conversion of (+421°C) residuum	42.5		49.9		56.6		53.9		

^{*} These experiments were carried out at 425°C, H₂ pressure of 13.8 MPa and a reaction time of 45 minutes.

STIRRED AUTOCLAVE

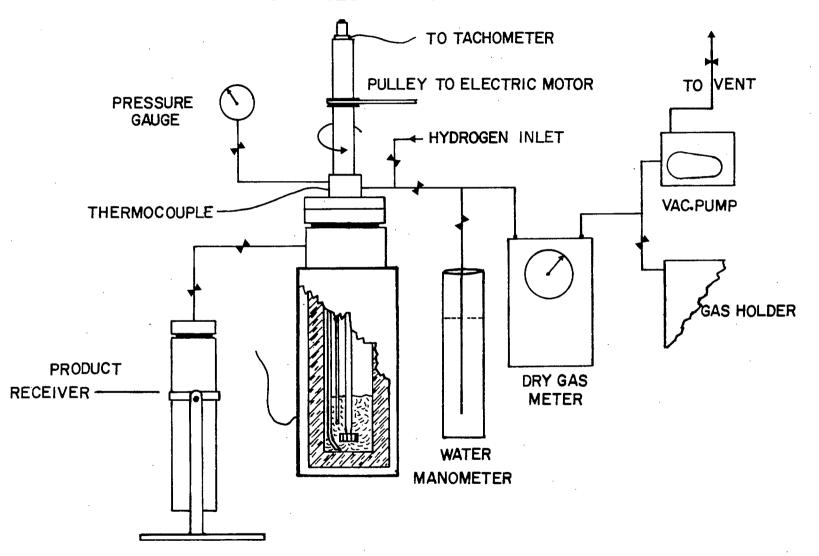


FIGURE 1 - Experimental Apparatus

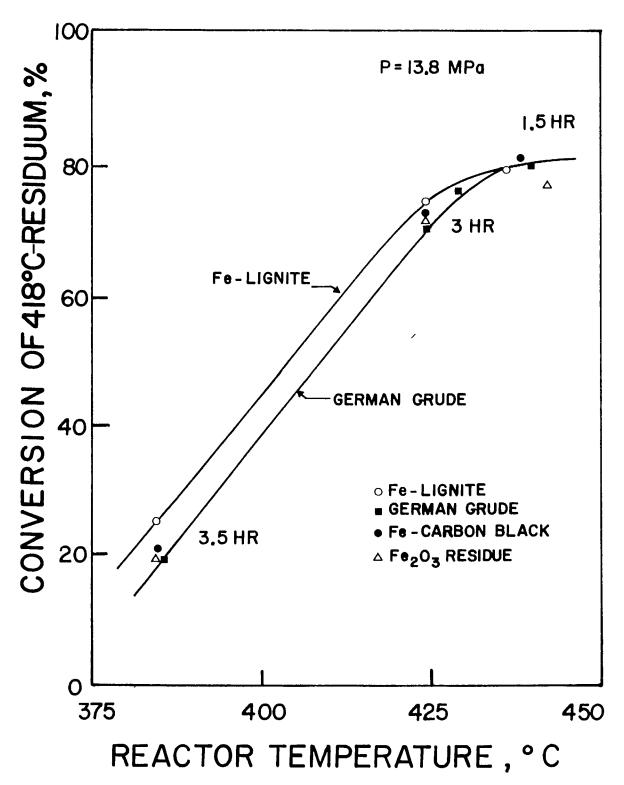
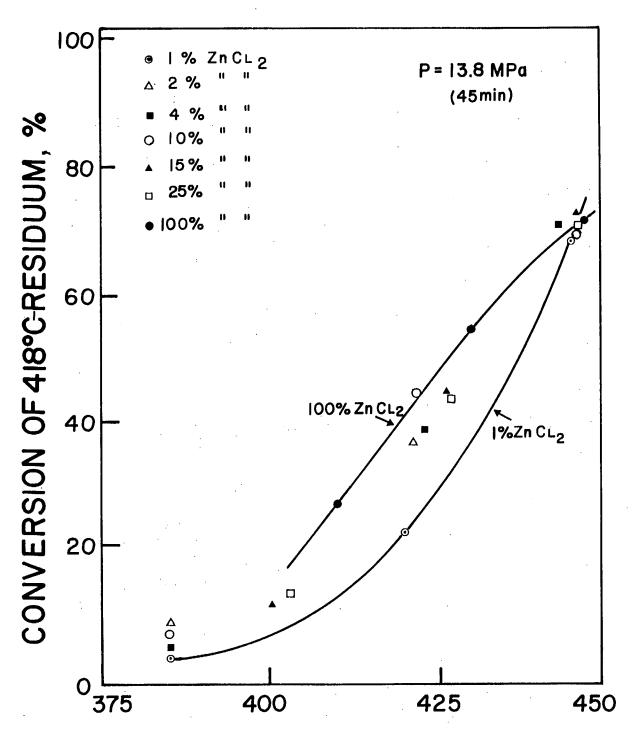
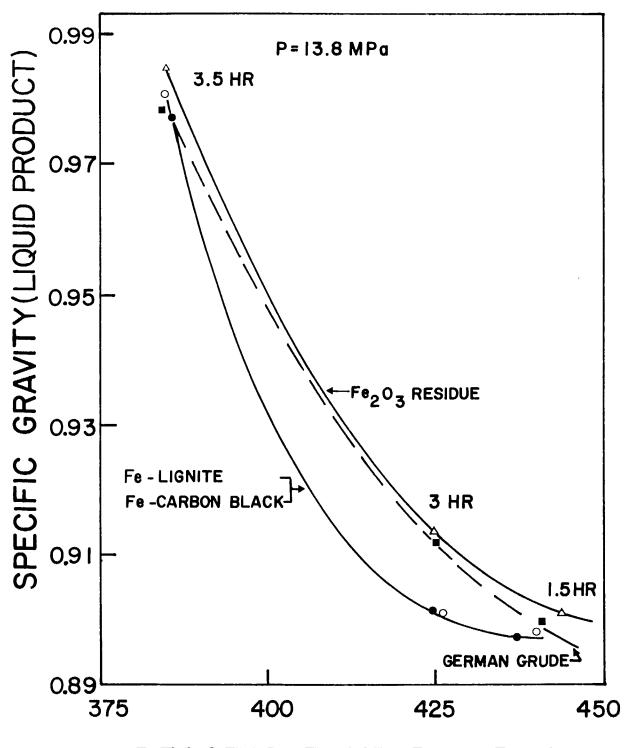


FIGURE 2 - $\frac{\text{Per Cent Conversion Versus Reaction Temperature}}{\text{for Class I Catalysts}}$



REACTOR TEMPERATURE, °C

FIGURE 3 - Per Cent Conversion Versus Reaction Temperature for Class II Catalysts



REACTOR TEMPERATURE,°C

FIGURE 4 - Specific Gravity of Liquid Product for Class I Catalysts

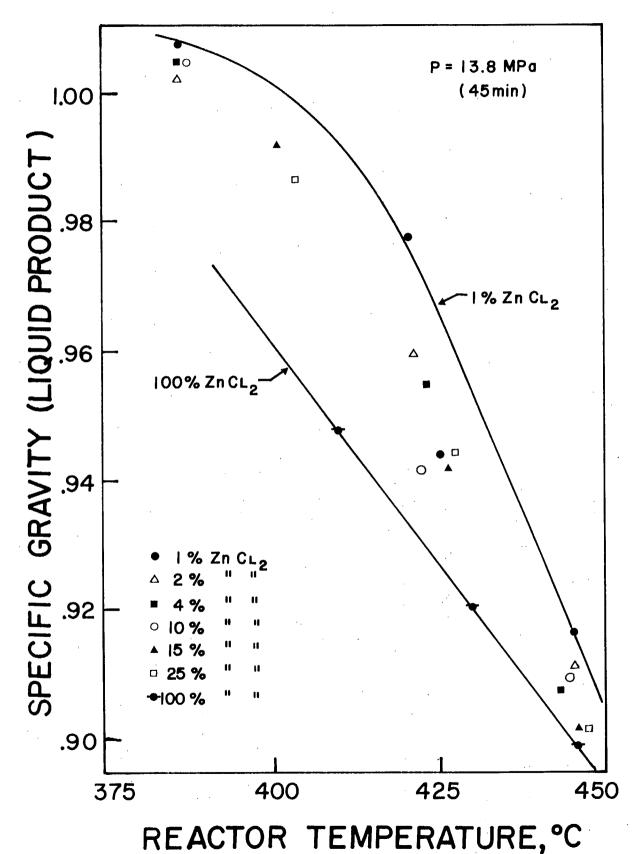
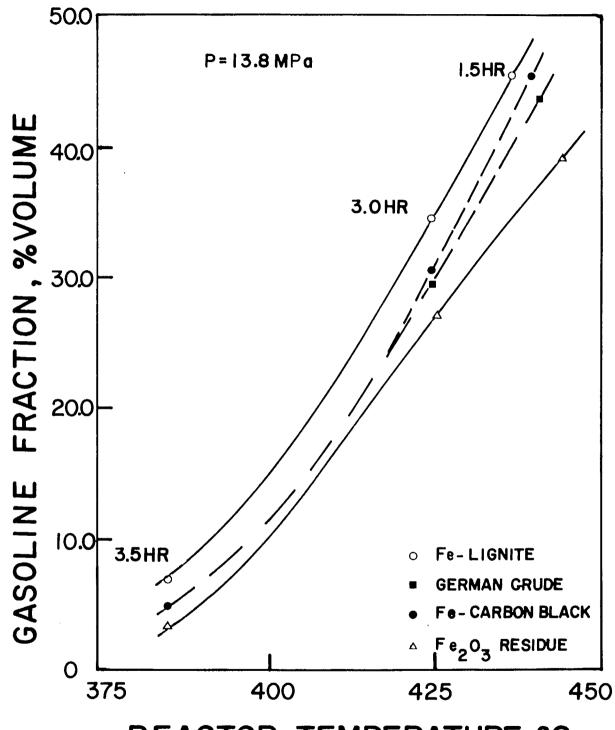
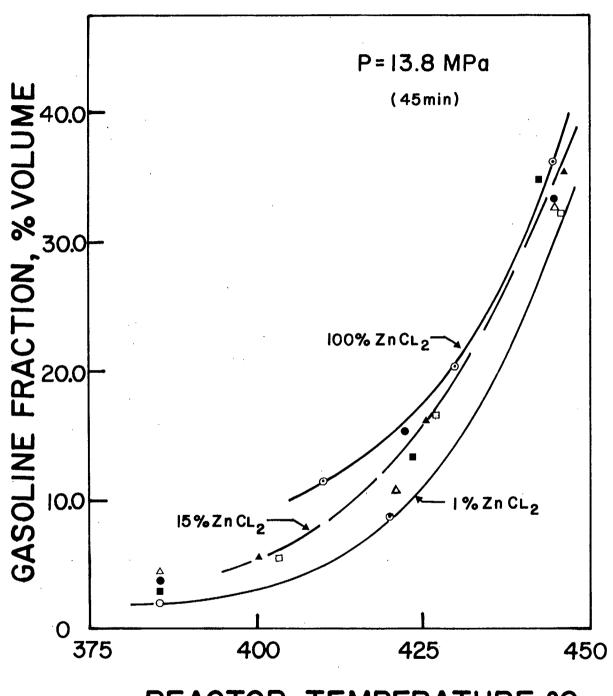


FIGURE 5 - Specific Cravity of Product for Class II Catalysts



REACTOR TEMPERATURE, °C

FIGURE 6 - Per Cent Gasoline Fraction Versus Reaction Temperature for Class I Catalysts



REACTOR TEMPERATURE,°C

FIGURE 7 - Per Cent Gasoline Fraction Versus Reaction
Temperature for Class II Catalysts

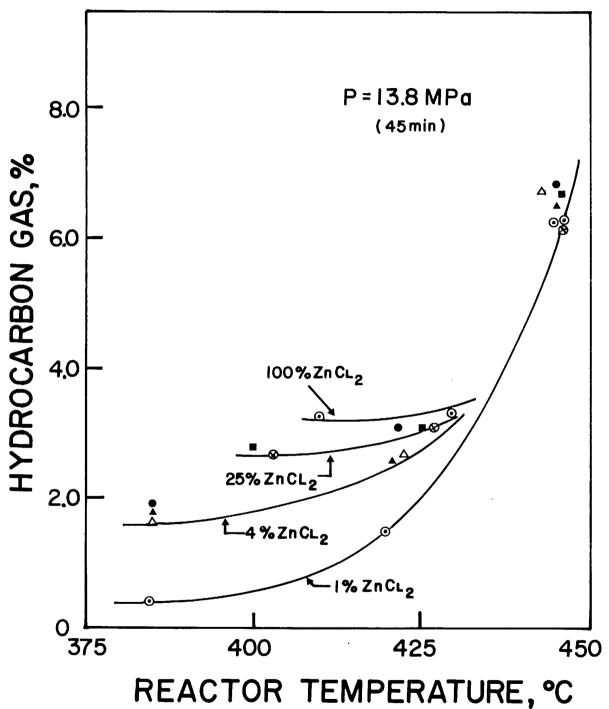


FIGURE 8 - Per Cent HC Gas Formed at Different Reaction Temperatures for Class II Catalysts

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