

CATALYST SELECTION FOR HYDROTREATING DIESEL FUEL FROM RESIDUE HYDROCRACKING

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ABSTRACT

Six commercial catalysts ($\text{NiMo}/\text{Al}_2\text{O}_3$ and $\text{NiW}/\text{Al}_2\text{O}_3$) were evaluated for the simultaneous reduction of the aromatics and sulfur contents in the diesel fraction (177°C - 343°C) of a hydrocracked atmospheric residue.

The reactions were carried out in a fixed bed reactor operating in an upflow mode. Optimal operating variables were established to maximize aromatics conversion and sulfur removal. In order to rank catalysts according to their performance, short term screening runs were performed. The two best catalysts were selected for which long term runs were carried out. Though the hydrotreated products for all catalysts met required specifications, the optimal operating conditions used in this study were more severe than processing conditions used in existing hydrotreating units.

INTRODUCTION

Diesel fuel properties are said to have an effect on the quantity and type of air polluting emissions from diesel engines. Specifically, the sulfur and aromatics contents of diesel fuels are singled out as the main sources of particulate emissions⁽¹⁾. In Canada, the contribution of diesel particulates to the total discharges from transportation and industrial diesel engines was estimated at 29 and 23 thousand tons respectively per year⁽²⁾. In California, new and stringent emission standards are already set and other states are expected to follow California's example.

To comply with these new regulations, the oil refining industry has been evaluating a number of options to limit the sulfur and aromatics contents of diesel fuels. One way of achieving this goal involves a two-stage process: initial desulfurization with a deep desulfurization-type catalyst (Co-Mo/alumina) followed by aromatics saturation. The second stage may use a Ni-Mo/alumina or noble metal catalyst. Desulfurization would protect the noble metal catalyst against sulfur poisoning⁽³⁾.

On the other hand, there are new sulfur tolerant catalysts that would achieve both aromatics saturation and sulfur removal in one step⁽³⁻⁵⁾.

The work reported in this paper is part of a project to evaluate available commercial catalysts for simultaneously reducing sulfur and aromatics in diesel oil fractions to be produced at the Bi-Provincial Upgrader (BPU) in Lloydminster, Sask., Canada⁽⁶⁾. This

grassroots facility will upgrade a feedstock containing a 50/50 volumetric blend of Lloydminster/Cold Lake heavy oils to synthetic crude.

The project focused on attaining the proposed specifications for sulfur and aromatics contents in diesel fuel fractions. The selected approach was to study a one-step hydrotreating process using our particular feedstock and several new generation catalysts claiming to achieve the specified reductions.

EXPERIMENTAL

Equipment: Hydrotreating experiments were carried out in a stainless steel tubular fixed bed reactor operated under the following experimental conditions: upflow mode, diluted catalyst bed (reaction zone = 225 mL), isothermal and plug flow, and once through. The experimental system, including the reaction unit, was described and illustrated elsewhere⁽⁷⁾.

Catalysts: All commercial catalysts except one (catalyst B) were of the Ni-Mo type on alumina carrier. Catalyst B was a layered arrangement of Ni-Mo and Ni-W catalysts supplied by the same source. Catalyst companies provided a catalyst they considered the most suitable to treat our feedstock. There were no apparent dissimilarities in catalyst properties based on vendor information.

Feedstock: The feedstock was the fraction boiling between 177°C - 343°C obtained from a hydrocracked 50/50 volumetric blend of Cold Lake/Lloydminster residue. The hydrocracked material was distilled on a TBP unit according to procedures described in ASTM D-2892. The properties of the average feed are given in Table 1.

Analytical Methods: Specific gravities were measured at 15.5°C using a Paar DMA instrument. Dynamic viscosities were determined at 25°C on a Brookfield DV II apparatus. Carbon and hydrogen were determined commercially on a Perkin Elmer 240B analyzer. Trace nitrogen was obtained by chemiluminescence using an Antek Model 771 analyzer, while trace sulfur was measured by microcoulometry using a Dohrmann instrument, model MCTS 130. The total per cent aromatics was determined by the fluorescent indicator adsorption (FIA) method (ASTM D-1319). Simulated distillations were performed according to ASTM D-2887. Low resolution mass spectrometry (MS) analyses for aromatic types were determined commercially by ASTM D-3239. Cetane number was determined by ASTM D613 and Aniline Point by ASTM D611.

RESULTS AND DISCUSSIONS

The initial part of the study included catalyst activity runs to select the process conditions which produced a liquid product meeting the specifications established for the BPU middle distillate fraction (177°C - 343°C)⁽⁶⁾. These values correspond to, among others, sulfur content in product at 1000 wppm max. and cetane number at 40 min.

The base conditions chosen after the initial runs were: $T = 380^{\circ}\text{C}$, $P = 12.4 \text{ MPa}$ and $\text{LHSV} = 0.75 \text{ h}^{-1}$. A single catalyst (A) was used for all the initial runs.

The catalyst screening program involved experiments to rank six commercial catalysts according to their efficiencies in sulfur and aromatics conversions. Each catalyst was tested at base conditions and at various temperatures, pressures and liquid hourly space velocities (LHSV) to determine the influence of these parameters on catalyst performance. All experiments were performed using the same hydrogen-to-feed ratio ($1000 \text{ Std.m}^3/\text{m}^3$).

The properties determined on the total liquid product obtained from each run included measurements of density, viscosity, sulfur and nitrogen content, simulated distillation, total aromatics by FIA and elemental analysis. The properties of the average feedstock and of the products obtained at base conditions are shown in Table 1.

AROMATICS CONVERSION

The aromatics content of the total liquid product was used (instead of the cetane number) to compare catalyst activities. The FIA method was used to measure concentrations of aromatics in feed and products. To confirm the FIA results and to expand the information on aromatics distribution, additional analyses using Robinson and Cook's mass spectrophotometric technique⁽⁸⁾ were performed only on products obtained at base conditions. Table 2 shows the aromatics content of hydrotreated products determined by both procedures. The level of aromatics concentration recorded by the MS method was lower than that observed using FIA. The difference may be attributed to some of the problems observed with the FIA method: the analysis includes as aromatics other compounds such as diolefins and sulfur, nitrogen and oxygen containing materials⁽⁹⁾. Nevertheless, the trend observed with FIA for aromatics reduction with different catalysts was confirmed by MS results and, in addition, it was observed that conversion of diaromatics and polyaromatics to monoaromatics was almost complete.

The reduction in total aromatics with increase in reaction pressure is a well known aspect of the hydrotreating process^(9,10). In our work, the effect of pressure on aromatics conversion was studied over a wide pressure range at base values of temperature and LHSV (Figure 1). Our results indicate that in order to get aromatic conversions above 50% (or concentrations below 20 vol%), one has to operate at a pressure above 10 MPa. At higher pressures all catalysts exhibited higher aromatic conversions, confirming that the hydrogenation reaction is very much favored by pressure. Catalysts B and C clearly outperformed the others with respect to aromatics reduction. On the other hand, catalysts B and C also presented better hydrocracking activities by producing lighter fractions in the total liquid product (Table 1).

The influence of reaction temperature on aromatics conversion in middle distillate fractions has been studied before⁽¹¹⁻¹³⁾. An optimum temperature of 380°C was determined⁽¹²⁾ to achieve a maximum aromatics conversion. The base temperature found by us agrees with the optimum temperature previously measured. Our study covered the $350 - 380^{\circ}\text{C}$ temperature range, at base values of pressure and LHSV.

Again catalysts B and C exhibited the best activity for aromatics saturation (Figure II). Aromatics conversion increased linearly with reaction temperature for all catalysts tested in the program. Even at the lowest end of the temperature range (350°C) catalyst B achieved aromatics conversion above 65% (or concentrations of 15 vol%). At 365°C, all catalysts attained conversions exceeding 50% which correspond to concentrations below 20 vol%.

The effect of LHSV on aromatics conversion, at base values of temperature and pressure, is shown in Figure III. At low LHSV, all catalysts achieved conversions above 80%. At the highest LHSV tested, 1.0 h⁻¹, the conversion level surpassed 60% (or aromatics concentration below 18 vol%). Based on equal amount of conversion, the LHSV influence on aromatics reduction is not as marked as that produced by pressure or temperature.

According to the results presented, clearly aromatics saturation was more dependent on pressure than on any other parameter. Also, some of the combinations of the operating conditions reduced the aromatics concentration below the levels established in impending specifications for diesel fuels. The severe process conditions at which these requirements were met are, however, out of line with the operating parameters of existing diesel hydrotreating units.

SULFUR AND NITROGEN CONVERSIONS

Under all experimental conditions tested, sulfur conversions exceeded 90%. At base conditions removal of sulfur surpassed 94% (Table 1). Therefore, the target sulfur concentration was easily achieved by all catalysts at the operating conditions used. On the other hand, nitrogen conversions above 99% (corresponding to less than 5 wppm in product) were achieved in all of the runs performed. No significant differences were observed in the catalysts' performance from the point of view of sulfur and nitrogen removal.

INFLUENCE OF CATALYST PROPERTIES

The catalysts' properties were determined in an attempt to find the origin of the differences observed in catalysts' performance. We wished to compare the various conversions for each catalyst on an equal basis. The basis chosen was the unit surface area conversion. The catalyst components believed to affect in greater extent the conversions were nickel, molybdenum, phosphorus and tungsten. In Figure IV, the [Ni + Mo(W) + P] weight per unit surface area was plotted against the conversion for the same area. The results demonstrated that catalysts exhibiting higher coverage per unit area (B and C) were the ones performing better as far as aromatics, sulfur and nitrogen conversions are concerned. There was little correlation for independent components suggesting the existence of a synergism effect among all these elements.

CATALYST DEACTIVATION EXPERIMENTS

Long term runs of approximately 1000 hours were carried out using the two best catalysts from the screening experiments (B and C). The purpose of this task was to

study the rate of deactivation of the selected catalysts at base conditions. No marked difference in catalysts' performance was found except for hydrogen consumption (Table 3). It was the original intent of this part of the study to project catalyst life based on a deactivation curve. However, this was not possible because within the length of the runs, little deactivation occurred. The layered bed of NiMo and NiW on alumina (catalyst B) showed lower hydrogen consumption for similar aromatics conversions. The cetane number of liquid products showed similar results.

CONCLUSIONS

All six commercial catalysts studied satisfied upcoming specifications on the sulfur content for diesel fuels. Also, at base conditions, all catalysts reduced the aromatics content of the feed to less than 20 vol%. The operating conditions at which these requirements were met are, however, out of line with the operating conditions of existing diesel hydrotreating units. This implies that a single stage process for hydrotreating middle distillates can only meet the impending specifications with a new reactor designed and built specifically for these operating conditions.

Two out of six catalysts (B and C) outperformed the others in aromatics conversion. It was found that the activity of these catalysts showed marked dependence on the total coverage of definite fresh catalyst components. After the catalyst deactivation experiments, the choice between catalysts B and C was based on economics because they exhibited similar technical performance.

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TABLE 1

AVERAGE FEEDSTOCK AND PRODUCT PROPERTIES AT BASE CONDITIONS

	FEED STOCK	PROD. A	PROD. B	PROD. C	PROD. D	PROD. E	PROD. F
Density (g/cm ³)	0.8554	0.8308	0.8282	0.8251	0.8333	0.8266	0.8503
Viscosity (cP)	3.2	2.0	2.6	2.3	2.7	2.7	3.6
Carbon (wt%)	86.96	86.01	85.38	85.67	86.13	85.99	86.14
Hydrogen (wt%)	12.23	13.27	13.77	14.22	13.80	13.92	13.30
Sulfur (wppm)	3858	112	181	195	138	82	64
Nitrogen (wppm)	752	5	<1	<1	2	1	<1
Sim. Distribut. (wt%):							
IBP - 177°C	0.9	4.7	6.8	5.8	4.7	5.6	3.5
177 - 249°C	39.6	44.3	47.7	48.2	37.3	47.4	27.5
249 - 343°C	58.6	50.1	43.7	44.7	57.0	45.6	64.1
343 - 524°C	0.9	0.9	1.8	1.3	1.0	1.4	4.9

Notes: (i) A, B, C, D, E, F are commercial catalysts;

(ii) Base Conditions: T = 380°C; P = 12.4 MPa; LHSV = 0.75 h⁻¹

TABLE 2
TOTAL AROMATICS AT BASE CONDITIONS

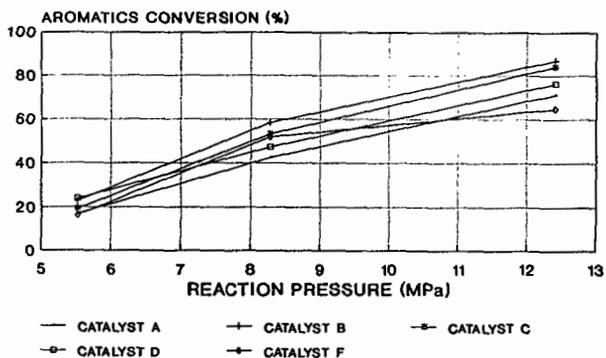
	FEED- STOCK	PROD. A	PROD. B	PROD. C	PROD. D	PROD. E	PROD. F
F.I.A. (vol.%)	43.6	12.5	6.0	7.1	11.2	9.8	17.0
Mass Spec. (wt%):							
Monoaromatics	30.60	7.31	2.18	5.08	7.74	9.29	11.12
Diaromatics	5.59	0.18	0.07	0.09	0.17	0.18	0.43
Polyaromatics	0.05	0.01	0.00	0.08	0.13	0.03	0.61
Aromatic Sulfur	0.74	0.03	0.04	0.00	0.02	0.00	0.12
Total Aromatics	36.98	7.53	2.29	5.25	8.06	9.50	12.28

TABLE 3
LONG TERM RUNS, AVERAGE QUALITY OF TOTAL LIQUID PRODUCTS

CATALYST	B	C
Cetane Number (ASTM D613)	50.3	50.7
Aniline Point, °C (ASTM D611) Modified	70.70	71.25
Sulfur (wppm)	259	174
Nitrogen (wppm)	3	<1
FIA Aromatics (vol%)	5.1	4.6
Aromatics Conversion (%)	84.40	87.50
Sulfur Conversion (%)	91.07	94.00
Nitrogen Conversion (%)	99.39	99.93
Density (g/cm ³)	0.8240	0.8225
API Gravity	40.2	40.5
Viscosity (cP)	2.4	2.4
Carbon (wt%)	85.98	86.25
Hydrogen (wt%)	13.56	13.74
H ₂ Consumption:		
L H ₂ /L feedstock	56.2	74.6
(SCF H ₂ /BBL feedstock)	(315)	(419)

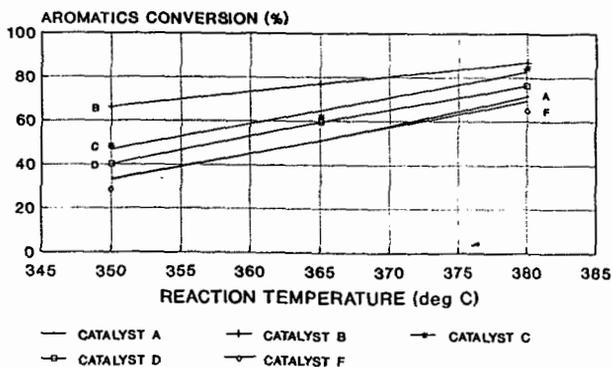
Note: Operating Conditions: T = 380°C; P = 12.4 MPa; LHSV = 0.75 h⁻¹

FIGURE I: EFFECT OF REACTION PRESSURE ON AROMATICS CONVERSION



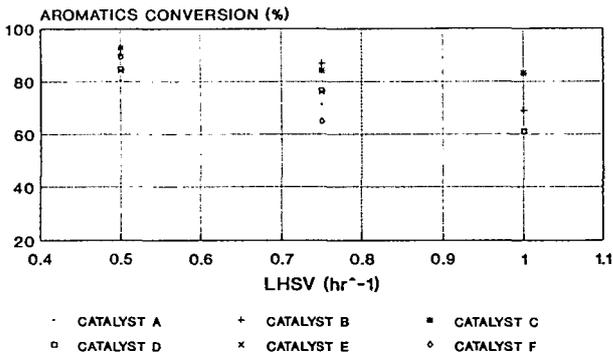
Temperature = 380 deg C
 LHSV = 0.75 hr⁻¹

FIGURE II: EFFECT OF REACTION TEMPERATURE ON AROMATICS CONVERSION



Pressure = 12.4 MPa
 LHSV = 0.75 hr⁻¹

FIGURE III: EFFECT OF LHSV ON AROMATICS CONVERSION



Temperature = 380 deg C
 Pressure = 12.4 MPa

FIGURE IV: CONVERSION AS A FUNCTION OF CATALYST COMPONENTS COVERAGE

