

## [Regular Paper]

## Hydrothermal Cracking of Furfural Extract into Middle Distillate Using Ni/Silica-alumina and Ni/Molecular Sieve Hybrid Catalyst

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Heavy residual products in petroleum refineries are a useful source of hydrocarbons, so are a potential substrate for producing middle distillates by hydrocracking technology to increase the supply of transportation fuels. This study used highly refractory furfural extract of lube oil containing 96.0 vol% aromatics with 4.63 wt% S, and 0.15 wt% N with a pour point of +30°C to produce middle distillates through catalytic hydrothermal cracking. The effect of various parameters such as temperature, hydrogen partial pressure, residence time and amount of catalyst were studied with 250 g feed and 25 g nickel-loaded catalyst of 20 : 80 ratio of silica-alumina (A) and molecular sieves 13X (Z) as cracking site and nickel metal serves as hydrogenation site. The maximum yield of middle distillates was 26.4 wt% at temperature 400°C, pressure 10.0 MPa, initial hydrogen partial pressure 9.0 MPa, and residence time 15 min.

**Keywords**

Furfural extract, Hybrid catalyst, Silica-alumina, Molecular sieve 13X, Middle distillate, Hydrothermal cracking

**1. Introduction**

The hydrocracking process is very important in the commercial production of various transportation fuels such as gasoline, diesel and kerosene, etc. The versatility of this process makes it easy to equilibrate the supply and demand of fuels such as gasoline, diesel, and jet fuel. The main objective of hydrothermal conversion is the reduction of the average carbon number, and the isomerization of linear to branched paraffins is desirable to improve the quality of the different petroleum fractions. The refiner must select the best processing option for any crude oil based on economic and quality considerations, as well as the product demand pattern<sup>1)</sup>, quality of crude available and environmental legislation requiring “clean fuel.”

Hydrocracking is considered to be the most economic way of converting heavy ends to quality fuels, especially to middle distillates. In fact, hydrocracking is the only option to balance the demand as well as product quality to present requirements. Hydrocracking has also been developed to provide flexible refining of less valuable petroleum stocks such as residue, cycle

oil, gas oil and blends from coal, shale and tar sand<sup>2),3)</sup> to lighter products. Catalyst development for the hydrothermal cracking of heavy oil showed that basic MgO supported catalyst and neutral activated carbon supported catalyst achieved better results than acidic SiO<sub>2</sub> supported catalyst using nickel as the active metal<sup>4)</sup>. Hydrocracking of vacuum gas oil using highly dispersed metals such as Ni, Ni-Mo supported on 13X molecular sieves and mesoporous MCM-41 found that higher temperatures promote coke formation whereas lower pressures produce middle distillate<sup>5),6)</sup> with mild acidity. Refractory cycle oil feed was easily hydrocracked over SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Ce exchanged Y-zeolite containing Ni and Mo to jet fuels<sup>7)</sup>. Ultrastable Y zeolite catalyst forms more middle distillates compared to commercial LZY-82 catalyst<sup>8)</sup>. Our studies using mixed feed of cycle oil and reduced crude oil with hybrid catalysts such as amorphous SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and 13X molecular sieves (ratio 20 : 80) achieved a better performance with the highest yield of middle distillate<sup>9)</sup>. Various catalysts for cracking, amorphous SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>-SiO<sub>2</sub>, USY-zeolite, ZSM-5, etc., and catalysts for hydrogenation, Ni, Mo, W, Pt, Pd, etc., have been studied<sup>10)</sup>. Improving the catalyst to increase the economy of the process technology and improve the quality of the products remains challenging.

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Table 1 Properties of Feedstock

Parameters	Values
Phase (at room temperature)	Semisolid
Specific gravity [15°C/15°C]	0.9861
Viscosity at 38°C [10 <sup>-6</sup> m <sup>2</sup> ·s <sup>-1</sup> ]	1006.00
°API	11.99
Total sulfur [wt%]	4.63
Nitrogen [wt%]	0.15
Ramsbottom carbon residue [wt%]	1.82
Aromatics [vol%]	96
Carbon to hydrogen ratio	8.21
Pour point [°C]	+30
Boiling range [°C]	220-570

Furfural is used as a solvent in Haldia Refinery, India, to upgrade the viscosity index (VI) of lube oil. Furfural extract of lube oil (FELOH) contains heavy aromatic compounds, which have very low lube potential and are refractory to cracking. The by-product extracts with a high aromatic content can be used for carbon black feedstock, rubber extended oils and other non-lube applications in which this feature is desirable. This type of by-product is usually used in the Haldia Refinery for road surfacing material mixed with bitumens. However, the by-product has great potential for conversion into desirable transportation grade fuel by hydrothermal cracking technology.

The present study investigated the hydrothermal cracking of the lube oil extract with hybrid catalyst to maximize the middle distillate yield under different reaction conditions and also to assess the catalyst stability.

## 2. Experimental

### 2.1. Feed and Catalyst Preparation

Feed was collected from the furfural extract of the lube oil plant, Haldia Refinery, Kolkata, India, and was designated as (FELOH), with the characteristics according to ASTM standard methods of analysis listed in **Table 1**. Catalyst preparation used commercially available 13X molecular sieves and silica-alumina made in the laboratory. The silica-alumina ratio was maintained at 70 : 30 for both catalysts. The ammonium form of the 13X molecular sieves was prepared by ion-exchange of the sodium form, then dried and calcined to give the protonated H-form by treatment with ammonium nitrate solution. Both supports were loaded with 5% nickel metal by impregnation with nickel nitrate. Specific surface area was measured by a simplified single point BET technique by N<sub>2</sub> adsorption using a Sorpty 1750 (M/S Carlo Erba Strumentazione, Italy). Pore volume and pore size were measured using a Quantachrome porosimeter (Autoscan 60 K, USA). Acidity was measured by a titration method. The detailed method of preparation

Table 2 Properties of Catalyst

Items	Molecular sieve 13X loaded with nickel	Silica-alumina loaded with nickel
Surface area [m <sup>2</sup> /g]	240.2	108.30
Total pore volume [m <sup>3</sup> /g]	0.3750	0.0409
Total acidity [mmol/g]	0.455	0.564

of the catalyst and its characterization techniques have been described elsewhere<sup>11</sup>. The characteristics of the catalysts are shown in **Table 2**.

### 2.2. Reaction Procedure

Experiments were carried out in a rocking type laboratory scale batch reactor of 1 litre capacity. Details of the reactor and the assembly of other parts have been described elsewhere<sup>5</sup>. The reactor was charged with the required amounts of feed and catalyst, and closed. The reactor was purged with nitrogen gas to ensure an oxygen-free environment inside the reactor. Initially, the desired pressure was maintained with hydrogen or nitrogen or both. The purity of hydrogen and nitrogen were 99.6% and 99.5%, respectively. The total pressure was maintained with nitrogen only. Pressure was measured by the pressure gauge, and the valve was kept closed properly and checked for any leakage. After ensuring that the system was leak proof, the thermocouple was inserted in the proper position, and the heater switched on. A variac was used to control the reactor temperature. After attaining the desired temperature, rocking of the reactor was started and continued for the residence time. At the end of the residence time, gas and vapor from the reactor were passed through an ice-cooled spiral condenser. The liquid product was condensed and the non-condensable gaseous product passed through a scrubbing system containing 10% NaOH solution for H<sub>2</sub>S absorption. The remainder of the gas was passed through a wet gas meter and finally released to the atmosphere. The schematic flow diagram is shown in **Fig. 1**. The liquid product was analyzed by IS/ASTM standard methods for petroleum products.

### 2.3. Coke Determination

The amount of coke was determined as the toluene insoluble materials. Solid product was separated with toluene by extraction (3 × 100 ml) and dried in an oven at 120°C overnight. The weight increment of the catalyst was considered to be the amount of coke.

### 2.4. Regeneration of Catalyst

Catalyst regeneration was performed in a tubular furnace using a glass reactor. Spent catalyst placed in a glass reactor and slowly heated by passing air at 30 ml/min up to 500°C and kept at this temperature for about 1 h with a constant flow of air.

### 2.5. Sulfur Determination

Sulfur concentration was measured by combusting

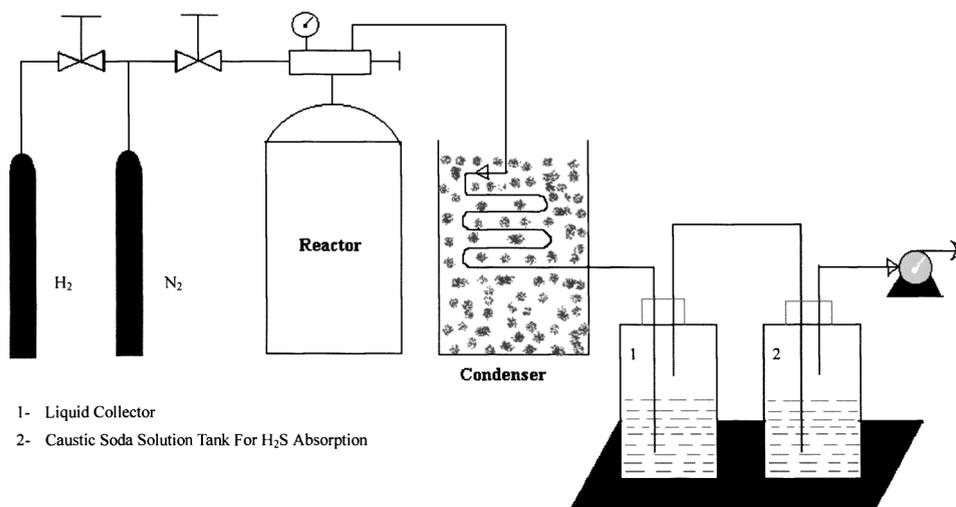


Fig. 1 Schematic Flow Diagram of the Experimental Set-up

the sulfur compounds in the presence of oxygen in a bomb calorimeter. Sulfur was finally determined from the weight of the BaSO<sub>4</sub> precipitated out using 10% BaCl<sub>2</sub> solution.

### 3. Results and Discussion

The present study investigated the characteristics of the furfural extract of lube oil from Haldia Refinery (FELOH) as a hydrothermal cracking feedstock, including overall conversion, yield of middle distillates, product distribution and properties of the middle distillates as functions of temperature, hydrogen partial pressure, residence time, catalyst amount and stability of catalyst. The catalyst supports of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (A) and 13X molecular sieves (Z) were used in the ratio of 20 : 80 based on our earlier work<sup>9)</sup> with 5% nickel as the active metal. The product distribution was calculated as wt% of feed and different cuts were expressed as: Light Distillate (LD) IBP-150°C, Middle Distillate Light (MDL) 150-250°C, Middle Distillate Heavy (MDH) 250-320°C, Heavy Distillate (HD) B. P. 320°C+ and coke (a solid carbonaceous product containing complex hydrocarbons).

#### 3.1. Effect of Temperature

The effect of temperature on hydrothermal cracking of refractory type feedstock (FELOH) was studied at 350-435°C as shown in Fig. 2. Studies were made at each temperature using 250 g feedstock and 25 g of 20 : 80 hybrid catalyst of nickel loaded A : Z, with total pressure 7.0 MPa, partial pressure of hydrogen 5.0 MPa and residence time 15 min. Experimental data show that at 350°C, the percentage conversion was only 20% but increased to 88% at 435°C. Gross hydrocracked product and the yield of middle distillate were maximum at 400°C, but the percentage of conversion was

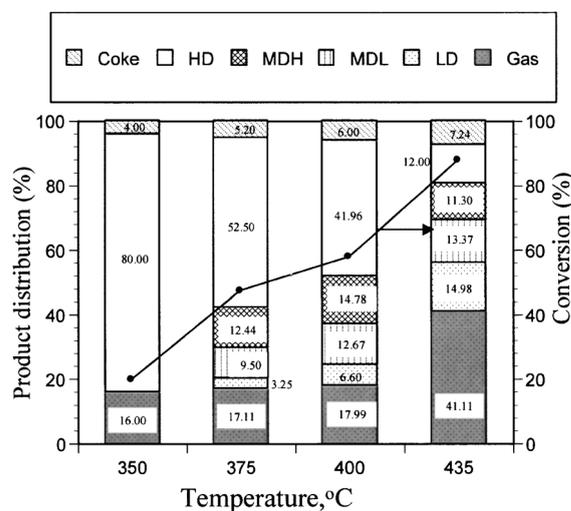


Fig. 2 Effect of Temperature on Percentage Conversion and Product Yield

only 58.03%. Yield of the middle distillate of 250-320°C cut was highest at 400°C and that of the 150-250°C cut was highest at 435°C. Therefore, the cracking reaction was more predominant than hydrogenation reaction above 400°C and greatly increasing the yield of light distillate and gaseous product. The yield pattern indicates that working temperature is extremely important in the hydrocracking of FELOH for production of middle distillates since operation at 350°C resulted in the lowest conversion of 20%, which is not adequate for cracking of such refractory type feedstock thus giving rise to the maximum yield of heavy distillate.

#### 3.2. Effect of Hydrogen Partial Pressure

The effect of hydrogen partial pressure was studied

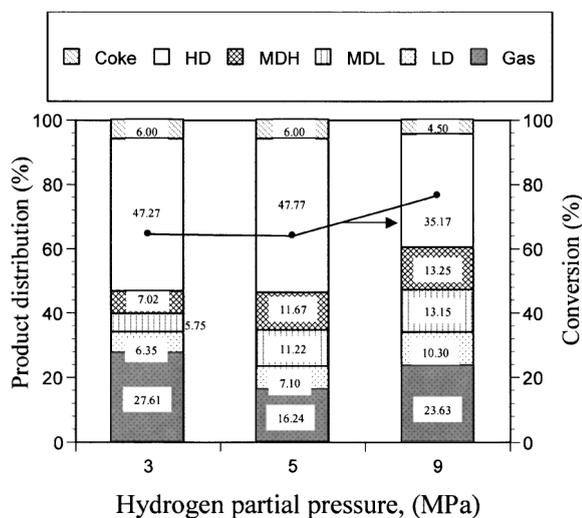


Fig. 3 Effect of Hydrogen Partial Pressure on Percentage Conversion and Product Yield

at a predetermined total pressure of 10 MPa. The results of hydrogen partial pressure variation are shown in Fig. 3. Hydrogen partial pressure is important during catalytic hydrothermal cracking. The experimental data show that the yield of middle distillate increased with corresponding increase of light distillate at higher hydrogen partial pressures from 3.0 to 9.0 MPa at 400°C. The percentage conversion was maximum with minimum yield of heavy distillate at a hydrogen partial pressure of 9.0 MPa. The yield of the 150-250°C cut and 250-320°C cut were also maximum at higher pressures. The quality of products also improved for middle distillates with increased hydrogen partial pressure, thus improving the smoke point, cetane index, etc. The smoke point of the 150-250°C cut was 16.0, 18.0, 19.0 mm and the cetane index of the 250-320°C cut was 44.0, 45.0 and 46.0 at hydrogen partial pressures of 3.0, 5.0 and 9.0 MPa, respectively. This indicates that hydrogen consumption has increased at higher pressure with rapid saturation of hydrocracked products, whereas the yield of coke decreased from 6.0 to 4.5%. Higher hydrogen pressure may have suppressed coke formation with rapid hydrogenation of cracking products. Higher hydrogen pressure remarkably suppressed coke yield during hydrothermal cracking reactions, probably due to catalytic quench of free radicals formed in thermal cracking reaction with decreasing the conversion<sup>12)</sup>. Our experimental results show that variation of hydrogen pressure from 3.0 to 5.0 MPa had little effect on conversion and coke yield. Further increase of hydrogen pressure increased the percentage of conversion from 52.22 to 64.82% with decreased coke yield from 6.0 to 4.5%. Therefore, the hydrogen effect on conversion and coke may depend on the characteristics of the feedstock. Therefore, hydro-

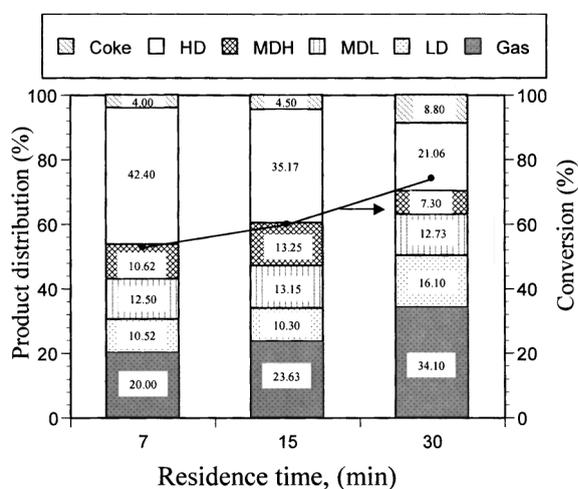


Fig. 4 Effect of Residence Time on Percentage Conversion and Product Yield

gen is a key component, which has great influence on simultaneous hydrogenation and cracking reactions in the hydrocracking process and also on the properties of products. Operating the process at higher hydrogen pressure will cause high hydrogen consumption, and high cost of reactor construction in compensation for the reduced coke yield, aromatics, sulfur, etc. with increasing smoke point and cetane index of middle distillate.

### 3.3. Effect of Residence Time

Residence time varied from 7 to 30 min at a total pressure of 10 MPa under a hydrogen partial pressure of 9.0 MPa at 400°C. The results of residence time variation are shown in Fig. 4. The yield of middle distillate increased with increased residence time up to 15 min after which the yield of middle distillate again decreased. The maximum yield of middle distillate was 26.40% at a residence time 15 min. The percentage of conversion and coke formation were maximum at a residence time of 30 min. The results reveal that simultaneous cracking and hydrogenation are favored for a residence time of 15 min giving the highest yield of middle distillate, beyond which secondary cracking reactions occur, as shown by the highest yield of gas and light distillate. The lowest yield of middle distillate at 30 min indicates that the hydrogenation reaction is suppressed favoring the cracking reaction beyond a residence time of 15 min.

### 3.4. Effect of Catalyst Amount

The effect of catalyst amount on hydrocracking of FELO<sub>H</sub> feedstock was studied with 10, 25 and 50 g of 20 : 80 of A : Z hybrid catalyst at 400°C, total pressure 10 MPa, and hydrogen partial pressure of 9.0 MPa, using 250 g feedstock. The results are shown in Fig. 5. The percentage of conversion gradually increased with increasing weight of catalyst. Conversion

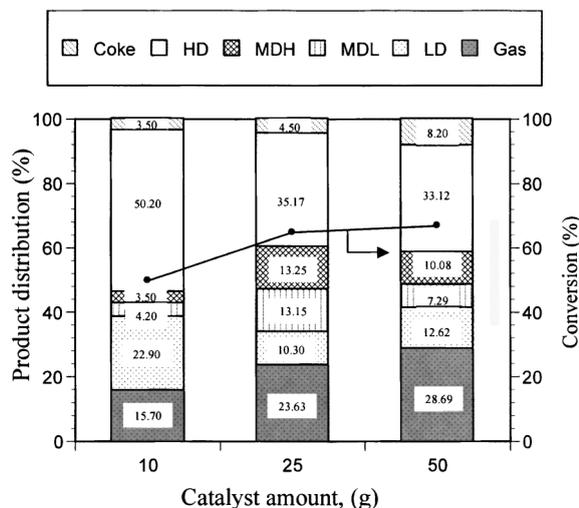


Fig. 5 Effect of Catalyst Amount on Percentage Conversion and Product Yield

increased from 49.8 to 64.83% with increasing amount of catalyst from 10 to 25 g. Further increases of catalyst from 25 to 50 g caused the percentage of conversion to slightly increase to 66.88% (Fig. 5). Coke and gaseous products increased from 4.5 to 8.2% and from 23.63 to 28.69%, respectively. Coke and gaseous product are not desired products in the hydrocracking process. Therefore, there is a compromise in selecting the amount of catalyst for hydrothermal cracking reaction. Maximum coke deposition with higher amounts of catalyst might be due to maintaining non isothermal heating inside the reactor, resulting in thermal cracking predominating over catalytic cracking as supported by the increase of gaseous product, coke and decrease of the middle distillates. Increased catalyst amount results in higher bulk surface area and more active sites, which may cause side reactions, and enhance coke formation. The percentage yield of middle distillates was maximum at 26.40% using 25 g of catalyst within the range of catalyst amounts studied. The entire feedstock is in contact with the catalyst surface occupying the maximum void space of the catalyst when 25 g catalyst was used, so effective hydrogenation and cracking reaction occurred giving the maximum yield of 150-250°C cut and 250-320°C cut. The catalyst amount of 10 g exhibited the lowest conversion and 50 g did not show much improvement. Since the feedstock is highly refractory, small portions of feedstocks were in contact with the catalyst surface but not occupying the pores of 10 g catalyst. On the other hand, the entire catalyst surface of 50 g catalyst is in good contact with the feedstock occupying the zeolite-rich catalyst pores as far as possible, but a large temperature gradient across the catalyst bed would result in lower percentage yield of middle distillates. The yield

Table 3 Assessment of Catalyst Activity and Stability

Items	Catalyst		
	Fresh	Spent	Regenerated
Percentage conversion	64.83	63.00	64.00
Gas	23.63	30.40	25.00
Light distillate (IBP-150°C)	10.30	8.15	10.10
MDL (150-250°C)	13.15	11.21	12.5
MDH (250-320°C)	13.25	11.24	11.60
Heavy distillate (320°C+)	35.17	37.00	36.00
Coke	4.5	2.00	4.80
% saturation in MDL [vol]	78.00	75.00	76.00
Smoke point of MDL [mm]	19.0	16.0	17.0
Total sulfur in MDL cut [wt%]	0.50	—	—
% saturation in MDH [vol]	75.00	70.00	69.00
Cetane index of MDH	46.0	40.0	40.0
Total sulfur in MDH cut [wt%]	0.95	—	—

Parameters: Temperature, 400°C; Total pressure, 10 MPa, hydrogen partial pressure, 9.0 MPa; Residence time, 15 min; Feed 250 g and catalyst 25 g of 20 : 80 nickel loaded A : Z hybrid catalyst.

and properties of middle distillates using 25 g catalyst may indicate that isothermal conditions were maintained, which leads to hydrogenation-cracking reactions producing quality middle distillates within the allowable specifications.

### 3.5. Study of Catalyst Stability

In any catalytic process, catalyst on-stream life time is very important to consider in view of cost effectiveness. The longer life of the catalyst increases suitability for use without much affecting the conversion and yield of middle distillates. Experiments were carried out to assess the stability of fresh, spent and regenerated catalyst for the hydrocracking of FELO<sub>H</sub> feedstock, temperature 400°C, total pressure 10 MPa, hydrogen partial pressure 9.0 MPa and residence time 15 min. Feed to catalyst ratio was maintained at 10 : 1 with 20 : 80 nickel loaded A : Z hybrid catalyst. The results are tabulated in Table 3. The conversion and yield of middle distillates with spent and regenerated catalyst were lower compared to using fresh catalyst. However, the spent catalyst, when regenerated, showed improvement in activity, and the conversion and yield of middle distillates were 64.0% and 24.1%, respectively, which are less by only 0.83% and 2.3%, respectively, compared to those using fresh catalyst. Sulfur concentration was determined with fresh catalyst was 0.5% for the 150-250°C cut and 0.95% for the 250-320°C cut. Therefore, the activity of nickel loaded hybrid catalyst does not fall drastically on hydrocracking of FELO<sub>H</sub>. Regeneration by burning of coke restored catalyst activity but not to the level of fresh catalyst, which might be due to permanent poisoning and deactivation of the catalyst. Deactivation by coke deposition was rapid during the early process<sup>12</sup>, but was reduced significantly for spent catalyst. The percent-

age of coke deposition was lower in spent catalyst compared to fresh catalyst which might be due to the reduced activity and effectiveness of the spent catalyst, so reducing the cracking severity. On the other hand, coke was deposited probably on the surface only of spent catalyst, because coke was already deposited inside the pores during the early process time. **Table 3** shows that variation of the saturation percentage for the 150-250°C cut was within 3.0% and that for the 250-320°C cut was within 6.0% using fresh, spent and regenerated catalyst under the given conditions. Therefore, the spent catalyst even after use for a residence time of 30 min was not been greatly poisoned due to the deposition of carbon and had not lost activity to a great extent, as shown by the low variation in yield of middle distillates, percentage of conversion and product properties. Such findings clearly indicate that these types of catalysts are quite stable when used under the given operating conditions.

#### 4. Conclusions

The present study reveals that the feedstock of refineries containing higher percentage of refractory type aromatic compounds and heteroatoms have great potential for hydrocracking to yield middle distillates. The furfural extract of lube oil used as feedstock did not undergo favorable hydrocracking reactions below 400°C, but beyond 400°C cracking reactions were more predominant giving higher yields of gas and light distillates. The maximum yield of middle distillates was found at 400°C using parameters such as total pressure 10 MPa, hydrogen partial pressure 9 MPa, residence time 15 min, feed 250 g and catalyst 25 g of 20 : 80 of A : Z. The feedstock was refractory but underwent favorable hydrocracking reactions at higher total pressure and higher hydrogen partial pressure producing higher percentages of middle distillates. The pres-

ent investigation further revealed that the nickel loaded 20 : 80 catalyst of A : Z did not lose much activity, even after a residence time of 30 min under the operating conditions, thus maintaining stability to a large extent. Therefore, catalytic hydrothermal technology is an attractive pathway for economic utilization of highly refractory heavy residual products of petroleum refineries to meet the need for global transportation fuels.

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## 要 旨

## Ni 担持シリカ-アルミナ/Ni 担持モレキュラーシーブハイブリッド触媒を用いたフルフルール抽出液の水素化熱分解による中間留分の製造

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石油精製所で生産される重質残さ成分は、水素化分解を行うと中間留分を製造できるため、輸送燃料製造に有効利用可能な有用な炭化水素源である。本論文では、芳香族成分: 96.0 vol%, S: 4.63 wt%, N: 0.15 wt% を含み、流動点: +30°C である潤滑油基油フルフルール抽出液を原料とし、高屈折率な重質油原料の触媒水素化熱分解試験を系統的に論じた。実験は反応温度、水素分圧、滞留時間、触媒量をパラメーターとして、主に原料供給量 250 g に対し、ともにニッケルを担持したシリカ-アル

ミナと、モレキュラーシーブ 13X を 20:80 の割合で混合したハイブリッド触媒 25 g を充填して行い、これらパラメーターの効果について考察した。なお、系内ではシリカ-アルミナ担体とゼオライト担体は分解活性を有し、担持金属ニッケルは水素化サイトとして働く。

その結果、400°C, 10 MPa, 初期水素分圧 9.0 MPa, 滞留時間 15 分において、中間留分の収量が 26.4 wt% で最大となった。

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