

Comparison of Hydrodenitrogenation of Basic and Nonbasic Nitrogen Compounds Present in Oil Sands Derived Heavy Gas Oil

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The hydrodenitrogenation of oil sands-derived heavy gas oil has been conducted in a trickle bed reactor over a commercial Ni–Mo/Al₂O₃ catalyst in the temperature range of 365–415 °C, pressure in the range of 65–88 bar, liquid hourly space velocity in the range of 0.5–2 h⁻¹. The hydrogen/heavy gas oil ratio has been changed from 400 to 1000 mL/mL. The study was conducted to determine the effects of these variables on the relative rates of conversion of total, basic, and nonbasic nitrogen compounds. It was observed that rate of conversion of nonbasic nitrogen compounds was lower than that of basic nitrogen compounds under identical process conditions. The pressure and hydrogen/heavy gas oil ratio have a more significant effect on the conversion of nonbasic nitrogen compound as compared to their effect on the conversion of basic nitrogen compounds. The effect of excess hydrogen sulfide on the conversion of basic and nonbasic nitrogen compounds has also been studied by adding butanethiol in the feed gas oil. An increase in the quantity of butanethiol decreases the conversion of both basic and nonbasic nitrogen compounds. It was also observed that in the region of higher space time (about 1.5–2 h), the conversion of nonbasic nitrogen compound increased at a sharp rate as compared to that of basic nitrogen compounds. This may be possibly due to the generation of more basic nitrogen compounds from the nonbasic ones. The kinetics of the conversion of nitrogen compounds has also been studied in the present work.

Introduction

The gradual shortage in the supply of crude oil has created interest in finding alternate source of energy. In this context, the huge reserves of tar sands and shale oil have attracted attention in converting these materials into cleaner feedstock for producing transportation fuel.¹ This along with the advances in oil sands technology has made the economics of producing synthetic crude oil from tar sands favorable and, as a result, a spectacular growth in the oil sands operation has currently been observed.

Tar sands and shale oil contain high amounts of contaminants, especially nitrogen. Thus, the products such as heavy gas oil obtained from the processing of oil sands-derived bitumen also contain very high levels of nitrogen. The presence of nitrogen compounds in the heavy gas oil creates problem in meeting the stringent emission specifications. The presence of nitrogen compounds also adversely affects the stability of fuel during storage as well as deactivates the catalysts used in the

downstream secondary processing (such as fluid catalytic cracking and hydrocracking) of these stocks at a faster rate. Since zeolite-based acidic catalysts are used in fluid catalytic cracking and hydrocracking operations, mainly basic nitrogen compounds are responsible for deactivation of these acidic catalysts. Therefore, the nitrogen compounds present in the oil sands-derived heavy gas oil need to be removed before they are used for further processing. Catalytic hydrodenitrogenation (HDN) is perhaps the only process used commercially for reducing the levels of nitrogen content in these stocks.

In the past, numbers of researchers have studied the HDN of oil sands and oil shale-derived heavy gas oil.^{2–10} For example, Sami et al.² have studied the effect of

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temperature, pressure, and liquid flow rate on HDN efficiency of an Athabasca bitumen-derived heavy gas oil over a cobalt molybdate catalyst. They have conducted experiments in the temperature and pressure range of 300–450 °C and 600–1800 psig, respectively. It was observed that the catalyst could remove up to 92% sulfur and 72% nitrogen from the heavy gas oil under experimental conditions. They also studied the effect of different process variables such as reaction temperature, pressure, contact time, etc., on the removal of nitrogen from the heavy gas oil.

Similarly, Saban et al.⁴ have also studied the HDN of three different shale oil distillates over Co–Mo/Al₂O₃ and Ni–Mo/Al₂O₃ catalysts. They have reported that nitriles in the shale oil first undergo HDN reaction at mild operating conditions, much faster than five- and six-membered nitrogen heterocyclic compounds. Similarly, Mann et al.^{6,7} have also studied the hydrotreatment of heavy gas oil over alumina-supported Co–Mo, Ni–W, and Ni–Mo catalysts. They found that Ni–Mo/Al₂O₃ was best for removing nitrogen, though it was poorest for hydrodesulfurization. They have reported that HDN reactions over these catalysts follow a pseudo first-order kinetics.

Diaz-Real et al.⁸ have also studied the HDN of Athabasca bitumen-derived heavy gas oil over Ni–Mo, Ni–W, and Co–Mo catalysts. They have reported that data from their HDN studies fitted a pseudo first-order kinetic model satisfactorily. They reported activation energies for HDN as 25.1, 18.9, and 16.6 kcal/mol, respectively, over Ni–Mo, Ni–W, and Co–Mo catalysts. Kwak et al.⁹ have also carried out the HDN studies of a bitumen-derived liquid. They have found that their rate data fitted a kinetic model having order of reaction of 1.7. The activation energy reported by them for the HDN reaction was 94 kJ/mol.

In most of the earlier studies it was found that the rate of HDN over the existing commercial catalysts, which are used for removing nitrogen from the conventional crude oil-derived heavy gas oil, is lower in removing nitrogen from these tar sand derived stocks. Hence, there is a growing need to develop better catalysts having higher HDN activity. The development of better HDN catalysts and technology requires the knowledge about the types of nitrogen compounds, which are least reactive and hence survive in the hydrotreated product. But most of the earlier works have focused attention on the removal of total nitrogen compounds from the heavy gas oil. Only a very few studies have been conducted to understand the relative rates of removal of various types of nitrogen compounds present in oil sands-derived heavy gas oil.^{11–15}

Moreover, most of the information has been obtained from the studies using model compounds and also under conditions which are not relevant to industrial hydrotreating operations.^{13,14} The essence of the information obtained from these studies is that the nonbasic nitrogen compounds are more difficult to remove as com-

Table 1. Different Physico-chemical Properties of Heavy Gas Oil

boiling range	210–655 °C
density at 20 °C, g/cm ³	0.9859
sulfur content, wppm	41000
total nitrogen content, wppm	3900
basic nitrogen content, wppm	1600
nonbasic nitrogen content, wppm	2300
microcarbon residue, wt %	1.98
asphaltene, wt %	1.55

pared to the basic ones. The studies with model compounds, though shedding light on the fundamental aspects of HDN, cannot provide information about the situation during the HDN of actual heavy gas oil feedstock where both basic and nonbasic nitrogen compounds undergo HDN simultaneously. In addition, the situation is more complex because of the fact that besides the basic nitrogen compounds originally present in the feed heavy gas oil, these are further generated from the nonbasic nitrogen compounds through hydrogenation during hydrotreatment process.

Therefore, there is a need for a systematic study to generate information about the relative rates of various nitrogen compounds undergoing simultaneous HDN in heavy gas oil at industrially relevant hydrotreating conditions as well as about the nature of the nitrogen compounds remaining in the product after hydrotreatment.¹⁶ Hence, the present study has been undertaken to determine the relative rates of conversion of basic and nonbasic nitrogen compounds in heavy gas oil over a commercial catalyst at different levels of process parameters. Another aim of the present study was to identify the types of nitrogen compounds, which remain unconverted in the product after hydrotreatment. The kinetics of the relative rates of basic and nonbasic nitrogen compounds during the hydrotreatment of the heavy gas oil has also been studied in the present work.

Experimental Setup and Procedure

The feedstock used in the study was heavy gas oil derived from oil sands bitumen and was supplied by Syncrude Canada Ltd. The typical physicochemical properties of the heavy gas oil along with their basic and nonbasic nitrogen content is given in Table 1.

The sulfur content of the heavy gas oil was measured using combustion/fluorescence technique following ASTM 5463 procedure. Similarly, the total nitrogen content was determined following ASTM D4629 procedure using the technique of combustion/chemiluminescence. Basic nitrogen content was determined by titration with KOH. The nonbasic nitrogen content was determined from the difference between the total and basic nitrogen content. A digital precision density meter was used to measure the density of the heavy gas oil. The micro carbon residue (MCR) was determined following ASTM D4530 procedure. The asphaltene content of the heavy gas oil was found out from its pentane insolubility. The portion of the heavy gas oil not soluble in pentane was treated as the asphaltene content of the heavy gas oil.

The catalyst was trilobe-shaped commercial Ni–Mo-based alumina with a diameter of ~1.5 mm. The catalyst had a BET surface area of 160 m²/g and a pore volume of 0.5 mL/g. The surface area of the catalyst was determined in a BET surface area analyzer (Micromeritics, ASAP 2000). The pore volume of the catalyst was measured in a mercury porosimeter.

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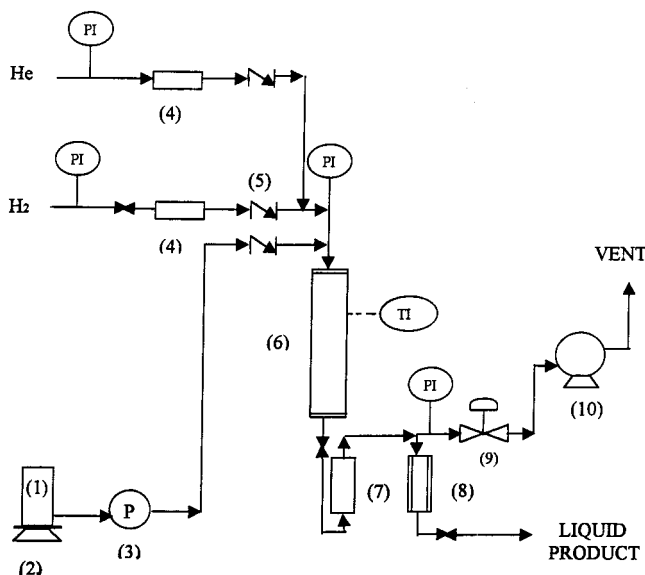


Figure 1. Schematic diagram of the experimental setup. (1) Liquid feed tank; (2) weighing balance; (3) liquid feed pump; (4) mass flow controller for hydrogen and for helium; (5) check valve; (6) reactor and furnace assembly; (7) water scrubber; (8) high pressure gas-liquid separator; (9) back pressure regulator; (10) gas flow meter.

All the experiments have been conducted in a microscale trickle bed reactor using 5 mL of catalyst. The schematic diagram of the experimental set up is shown in Figure 1. The system consisted of liquid and gas feeding sections, a high pressure reactor, a heater with temperature controller for precisely controlling the temperature of the catalyst bed, a scrubber for removing the ammonium sulfide from the reaction products, and a high-pressure gas-liquid separator. The length and internal diameter of the reactor were 240 and 14 mm, respectively.

The catalyst bed inside the reactor was diluted with 80 mesh of silicon carbide. The use of lower liquid velocity along with smaller reactor diameter and catalyst bed height causes a number of problems in testing catalysts having commercially applied shape and size in a microreactor. The major problems are poor wetting of catalyst, wall effect, and back mixing of liquid.¹⁷ It was found in our earlier studies^{17,18} that use of 80 mesh of diluent in the catalyst bed could remove all these problems of testing commercial catalyst in a microreactor using 5 mL of catalyst.

Before loading, the catalyst was dried in an oven for 4 h at 250 °C. For loading the catalyst, the reactor was packed from bottom to top in three parts. The bottom part was loaded first with 3.5 mL of 3 mm size glass beads followed by 3.5 mL of 16 mesh silicon carbide and another 3.5 mL of 60 mesh silicon carbide. Then the middle part of the bed was packed with a mixture of 5 mL of catalyst and 10 mL of 80 mesh silicon carbide. For uniform distribution, both catalyst and silicon carbide were divided into four equal parts, and small quantities of catalyst and silicon carbide were alternately loaded in the reactor with a spatula and mildly vibrating the reactor intermittently. Then the top part was carefully loaded with 3.5 mL each of 80, 46, and 16 mesh of silicon carbide.

After loading the reactor with catalyst and diluent, it was put in the unit and ~50 mL of distilled water was injected into the scrubber. The pressure of the unit was then raised to 88 bar. Helium was then fed at the controlled rate of 50 mL/min, and the temperature of the reactor was then raised to

100 °C. After the reactor had reached 100 °C, the sulfidation of the catalyst was started. The sulfidation of the catalyst was carried out using a sulfiding solution containing 2.9 vol % of butanethiol in a straight run atmospheric gas oil. Initially, the flow rate of the sulfiding solution was kept high (at 2.5 mL/min) to wet the catalyst bed. After passing sulfiding solution for 1 h at this rate, the flow rate was reduced and adjusted to maintain a LHSV of 1.0 h⁻¹. Hydrogen flow was then started corresponding to a hydrogen/sulfiding solution ratio of 600 mL/mL. Helium flow was then stopped. The temperature of the reactor was then slowly increased from 100 to 193 °C and was maintained at this temperature for 24 h. After this, the temperature of the reactor was again increased slowly to 343 °C and was then maintained at 343 °C for another 24 h.

After the sulfidation was over, the catalyst was then precoked by passing heavy gas oil at the rate of 5 mL/h. The temperature of the reactor was then increased slowly to 375 °C. The precoking of the catalyst was continued under this set of conditions for 7 days. After this initial period of precoking, the temperature of the reactor was set to the desired level and the product was collected every 24 h interval. The products were stripped with nitrogen for removing the dissolved ammonia and hydrogen sulfide and were then analyzed for their total, basic, and nonbasic nitrogen contents. The total, basic, and nonbasic nitrogen contents of the products were analyzed following the procedures described above.

Results and Discussion

This study has been conducted with a view to find out the effect of different process parameters, namely, temperature, hydrogen/gas oil ratio, pressure, hydrogen sulfide concentration, and space velocity on the relative removal rates of basic and nonbasic nitrogen compounds present in heavy gas oil. The results are discussed in the following sections. The conversions of different types of nitrogen compounds as followed in the results and discussion section are defined below:

$$\% \text{ conversion of total nitrogen} = \frac{\text{total nitrogen in feed} - \text{total nitrogen in product}}{\text{total nitrogen in feed}} \times 100$$

$$\% \text{ conversion of nonbasic nitrogen} = \frac{\text{nonbasic nitrogen in feed} - \text{nonbasic nitrogen in product}}{\text{nonbasic nitrogen in feed}} \times 100$$

$$\% \text{ conversion of basic nitrogen} = \frac{\text{basic nitrogen in feed} - \text{basic nitrogen in product}}{\text{basic nitrogen in feed}} \times 100$$

Effect of Temperature. The effect of temperature has been studied in the temperature range of 365 to 415 °C keeping pressure, hydrogen/heavy gas oil volumetric ratio, and liquid hourly space velocity (LHSV) constant at 88 bar, 600, and 1.0 h⁻¹, respectively. The results are shown in Figure 2 in which the conversion of total, basic, and nonbasic nitrogen compounds are plotted as a function of temperature.

Figure 2 shows that for the entire range of temperature studied, the conversion of nonbasic nitrogen compounds is much lower than that of basic nitrogen compounds. The conversion of total nitrogen lies between these two extreme cases. For example, at a temperature of 415 °C, the conversion of basic nitrogen compound is about 92 wt % as compared to only 67 wt % for the nonbasic nitrogen compound. Thus, the product hydrotreated at 415 °C contains mainly non-

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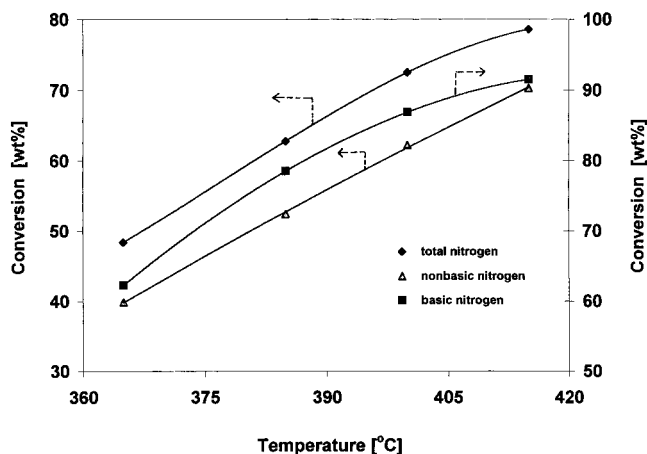


Figure 2. Effect of temperature on the conversion of total, basic, and nonbasic nitrogen compounds at a pressure of 88 bar, LHSV of 1.0 h⁻¹, and a hydrogen/heavy gas oil ratio of 600 mL/mL.

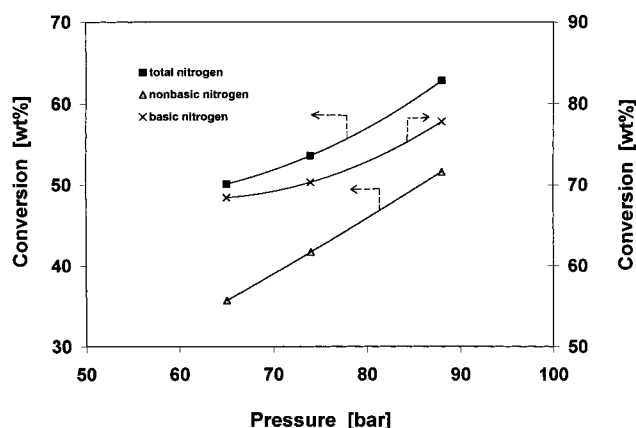


Figure 3. Effect of pressure on the conversion of total, basic, and nonbasic nitrogen compounds at a temperature of 385 °C, LHSV of 1.0 h⁻¹, and a hydrogen/heavy gas oil ratio of 600 mL/mL.

basic types of nitrogen compounds representing about 83 wt % of the total nitrogen in the product.

Figure 2 also shows that the conversion of total, basic and nonbasic nitrogen compounds increase with increase in reaction temperature. However, the rate of increase in the conversion of basic nitrogen compound is lower for the higher temperature zone (400–415 °C) than that obtained at the lower range of temperature (365–390 °C). This may be due to the generation of significant amount of basic nitrogen compounds through the hydrogenation of nonbasic ones.

It is also observed from Figure 2 that the conversion of nonbasic nitrogen compounds increases at a steady rate throughout the entire range of temperature studied. This indicates that the thermodynamic limitation for prehydrogenation of nonbasic to basic compounds does not prevail even at 415 °C.

Effect of Pressure. The effect of pressure on the relative HDN rates of basic and nonbasic nitrogen compounds have been studied by carrying out experiments at three levels of pressure viz., 65, 74, and 88 bar keeping temperature and LHSV constant at 385 °C and 1.0 h⁻¹, respectively (see Figure 3). The hydrogen/heavy gas oil volumetric ratio was maintained at 600 for all these sets of experiments.

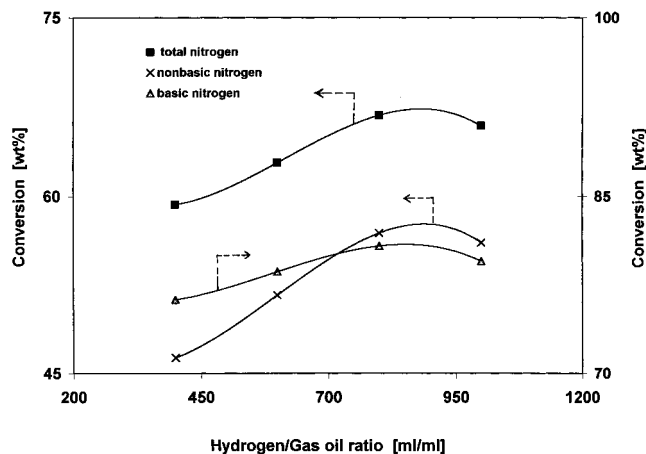


Figure 4. Effect of hydrogen/heavy gas oil ratio on the conversion of total, basic, and nonbasic nitrogen compounds at a temperature of 385 °C, LHSV of 1.0 h⁻¹, and pressure of 88 bar.

Figure 3 shows that throughout the range of pressure studied, the conversion of nonbasic nitrogen compounds is lower than that of basic nitrogen compounds. However, both the groups of compounds show increase in reactivity with increasing operating pressure. The Figure also indicates that as the reaction pressure is increased, the difference in the relative rates of conversion of these two groups of nitrogen compounds also decreases. For example, for a reactor pressure of 65 bar, the difference in the conversion of basic and nonbasic nitrogen compounds is ~26%. However, this difference increases to ~33% for a pressure of 88 bar. Similar results have also been obtained by Frost and Jensen¹⁰ on the HDN of shale oil over Co–Mo/Al₂O₃ catalyst.

Ho¹⁶ has explained this type of behavior in the conversion of basic and nonbasic nitrogen compounds as follows. At lower pressure, the conversion of basic nitrogen compounds is faster because of competitive adsorption. At higher pressure, the HDN of basic nitrogen compounds becomes relatively slow because of the conversion of nonbasic nitrogen compounds to the basic nitrogen compounds through hydrogenation, which increases with increasing pressure.

Effect of Hydrogen/Gas Oil Ratio. The hydrogen/gas oil volumetric ratio is an important parameter, which affects the hydrotreatment reactions. Though there are some reports available on the influence of hydrogen/gas oil ratio on the efficiency of hydrodesulfurization reactions, information about the effect of hydrogen/gas oil ratio on the HDN reactions specifically on the relative rates of conversion of basic and nonbasic nitrogen compounds are only few. In this study, the effect of hydrogen/heavy gas oil ratio on the conversion of basic, nonbasic and total nitrogen compounds have been studied for a range of 400 to 1000 mL/mL, at a constant pressure of 88 bar, temperature of 385 °C and a LHSV of 1.0 h⁻¹. The results are plotted in Figure 4.

It is evident from Figure 4 that the rates of conversion of basic, nonbasic, and total nitrogen increase with increase in the hydrogen/heavy gas oil volumetric ratio from 400 to 800 beyond which there is no beneficial effect of increasing the hydrogen/heavy gas oil volumetric ratio on conversions. This is because as the hydrogen/heavy gas oil ratio is increased, the partial pressure of hydrogen is increased. It is well-known that for conver-

sion of both basic and nonbasic nitrogen compounds, prehydrogenation of the heterocyclic ring is the first step in the HDN reactions.^{16,19} Thus, an increase in the partial pressure of hydrogen favors the prehydrogenation reaction and hence the conversion of nitrogen compounds. But when hydrogen is present in much excess, the reaction behaves like pseudo first order with respect to hydrogen partial pressure.

It is also to be noted from Figure 4 that the rate of increase in the conversion of nonbasic nitrogen is higher than that of basic ones. For example, for an increase in hydrogen/heavy gas oil volumetric from 400 to 800, the HDN of basic nitrogen compound increases from 76.2 to 80.8 wt %. On the other hand, the conversion of nonbasic nitrogen increases from 46.3 to 56.9 wt % for a similar change in hydrogen/heavy gas oil volumetric ratio. This indicates that the hydrogen partial pressure plays a more significant role of the conversion of nonbasic nitrogen compounds. It is also to be noted from this study that in the commercial process for the HDN of this particular heavy gas oil, the hydrogen/gas oil volumetric ratio should be maintained around 800 for achieving efficient HDN. However, this optimum value of hydrogen/heavy gas oil volumetric ratio is valid only for an operating pressure of 88 bar, temperature of 385 °C, and a LHSV of 1.0 h⁻¹. The optimum value of this ratio may change if the values of these process variables are different.

Effect of Hydrogen Sulfide Concentration. In the commercial HDN operation, hydrodesulfurization of sulfur compounds present in heavy gas oil also takes place. The byproduct hydrogen sulfide formed during hydrodesulfurization generally affects the relative rates of HDN of basic and nonbasic nitrogen compounds. Besides this, it is well-known that HDN reaction occurs over sulfided catalyst and hydrogen sulfide may be required to maintain the chemical state of the catalyst.²⁰ Therefore, considerable research is taking place to investigate the effect of hydrogen sulfide on HDN reaction.^{21–23} However, most of the studies have been conducted using model compounds such as quinoline. Such studies using model compounds have indicated that prehydrogenation reactions are slightly inhibited by hydrogen sulfide but the hydrogenolysis reactions leading to the scission of carbon–nitrogen bond were enhanced with increasing hydrogen sulfide concentration. Gultekin et al.²⁴ have reported that the presence of hydrogen sulfide enhanced the overall HDN of quinoline significantly.

Taking a lead from all these guidelines, our aim was to investigate the possibility of enhancing the HDN rate by increasing the concentration of hydrogen sulfide to a much higher level compared to that which is generally present in the reactor due to the hydrodesulfurization of sulfur compounds present in the gas oil. The generation of excess hydrogen sulfide inside the reactor was

Table 2. Effect of Butanethiol Addition to Feed on the Conversion of Total, Basic, and Nonbasic Nitrogen at a Reaction Temperature of 385 °C, Reaction Pressure of 88 Bar, LHSV of 1.0 h⁻¹, and a Hydrogen/Heavy Gas Oil Ratio of 600 mL/mL

conversion (wt %) of	butanethiol added in the feed, wt % of feed		
	0	1	3
total nitrogen	62.8	59.4	58.5
basic nitrogen	78.5	76.5	75.3
nonbasic nitrogen	51.1	47.2	46.0

accomplished by adding butanethiol in the feed heavy gas oil. The experiments were carried out at two different concentrations of added butanethiol, viz. 1 and 3 wt % of feed heavy gas oil. These experiments were carried out at a temperature of 385 °C, pressure of 88 bar, LHSV of 1.0 h⁻¹, and hydrogen/heavy gas oil volumetric ratio of 600. The results are given in Table 2 and are compared with the case in which no butanethiol is added in the feed heavy gas oil.

The results of Table 2 show that as the concentration of hydrogen sulfide is increased by adding butanethiol in the feed, the conversion of both basic and nonbasic nitrogen compounds decreases slowly. As a result, the removal rate of total nitrogen also decreases. It is also interesting to note that the effect of butanethiol addition has more prominent for the conversion of nonbasic nitrogen compound. This may be due to the fact that prehydrogenation reaction of nonbasic nitrogen compounds may be the controlling one in the HDN of heavy gas oil feedstock, and as reported earlier hydrogen sulfide has an adverse effect on the hydrogenation reaction.

The results obtained in the present study are thus contrary to those of earlier workers who have reported an enhancement in the HDN rate of different model compounds with increase in the concentration of hydrogen sulfide. However, our findings could be explained in line with the arguments provided by Nagai et al.²⁵ and Topsoe et al.²⁶ Nagai et al.²⁵ pointed out that the earlier studies, where hydrogen sulfide was observed to have a promoting effect of HDN, dealt with low hydrogen sulfide/hydrogen ratios. This suggests that with such low ratios of hydrogen sulfide/hydrogen the catalyst may not be in the fully sulfided state and hence remains in the reduced state. Thus, an increase in the concentration of hydrogen sulfide in this range improves the sulfidation of the catalyst, which in turn increases the HDN activity of the catalyst. However, when the hydrogen sulfide is in excess of completing sulfidation of the catalyst, an increase in the concentration of hydrogen sulfide leads to the decrease in HDN activity of the catalyst.

Effect of Space Velocity. The effect of space velocity has been studied by changing from 0.5 to 2.0 h⁻¹ keeping temperature, pressure, and hydrogen/heavy gas oil ratio constant at 385 °C, 88 bar, and 6000 mL/mL, respectively. The results are plotted in Figure 5 in which conversions of basic, nonbasic, and total nitrogen compounds are plotted as a function of space time (i.e., inverse of space velocity).

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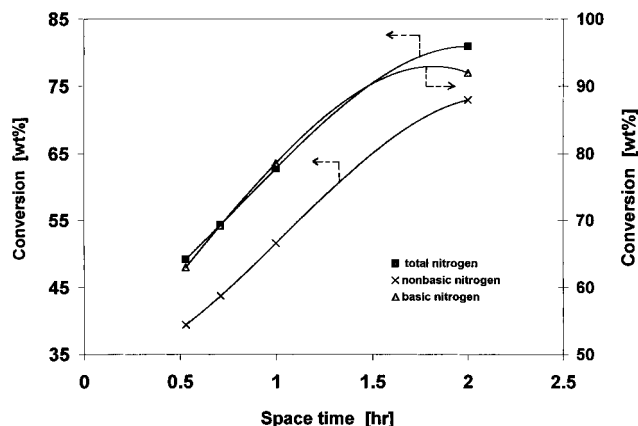
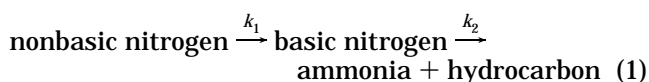


Figure 5. Effect of space time on the conversion of total, basic, and nonbasic nitrogen compounds at a temperature of 385 °C, pressure of 88 bar, and a hydrogen/heavy gas oil ratio of 600 mL/mL.

It is important to note again that the rate of conversion of nonbasic nitrogen compounds is much lower than that of basic nitrogen compounds. For example, at a space time of about 2.0 h, the conversion of basic nitrogen compound is ~92 wt % whereas, the conversion is ~73 wt % for nonbasic compounds. Thus, the product, obtained by the hydrotreatment of the feed for a long reaction time (of 2 h), contains mainly nonbasic nitrogen (~82 wt % of the total nitrogen in the product). However, as the reaction time is reduced, the conversion of both basic and nonbasic nitrogen compounds decrease. But in the region of higher space time (about 1.5–2 h), some differences in the change in the rate of basic and nonbasic nitrogen compounds conversions are observed. In this range of space time, the conversion of nonbasic nitrogen compound increases at a sharp rate as compared to that of basic nitrogen compounds. This may be possibly due to the generation of more basic compound from the nonbasic compounds. This also indicates that the nonbasic nitrogen compounds require more reaction time for their conversion.

Kinetics of Removal of Total, Basic, and Nonbasic Nitrogen Compounds. As mentioned earlier, it is well-known that nonbasic nitrogen compounds are hydrogenated first to basic nitrogen compounds, which undergo further reactions to eliminate the nitrogen atom from the molecule. Thus, a consecutive reaction scheme as shown below can be proposed for the HDN reaction:



where, k_1 is the apparent rate constant for the conversion of nonbasic nitrogen compounds to basic nitrogen compounds and k_2 is the apparent rate constant for the conversion of basic nitrogen compounds to ammonia and nitrogen free hydrocarbons.

Besides this scheme of consecutive reactions, a simplified reaction scheme (eq 2) considering the removal of only total nitrogen from the feed is also generally proposed for the HDN of heavy gas oil:

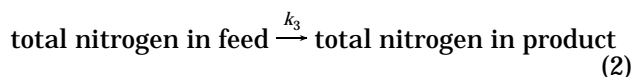


Table 3. Values of R -squared for Different Models Having Different Values of Order of Reaction

for HDN of	values of R -squared for different values of order of reaction, n		
	$n = 1.0$	$n = 1.5$	$n = 2.0$
total nitrogen	0.934	0.995	0.979
nonbasic nitrogen	0.904	0.989	0.972

where k_3 is the apparent rate constant for the removal of total nitrogen from the heavy gas oil.

The conversion of nonbasic nitrogen compounds to basic ones (i.e., first part of eq 1) as well as the removal of total nitrogen compounds from heavy gas oil can be described by a simple power law model and the values of the rate constants can be calculated from the following equation:

$$k = \frac{1}{n-1} \left[\frac{1}{N_p^{n-1}} - \frac{1}{N_f^{n-1}} \right] \text{LHSV} \quad (3)$$

where k = apparent rate constant for conversion of total or nonbasic nitrogen present in heavy gas oil, $\text{h}^{-1}(\text{wt} \%)^{1-n}$, n = order of reaction, N_p = total or nonbasic nitrogen present in product (wt %), N_f = total or nonbasic nitrogen present in feed (wt %), and LHSV = liquid hourly space velocity (h^{-1}).

The value of order of reaction, n , depends on the boiling range of the petroleum fraction as well as on the types of nitrogen compounds present in the fraction. We have attempted to determine the value of n from the best fit of the experimental data. In the present work, the removal rates of total and nonbasic nitrogen compounds were tested for three values of reaction order (i.e., $n = 1.0, 1.5, 2.0$). In this context, it may be noted that when the order of reaction is 1.0, then the following equation (eq 4) is applicable:

$$\ln(N_f/N_p) = k/\text{LHSV} \quad (4)$$

The results of fitting different orders of reactions are shown in Table 3, in which the value of R -squared has been tabulated for all these three orders of reaction. The R -squared is generally treated as a statistical measure of the fitness; the closer the value to 1.0, the better is the fitness. It is clear from the results of Table 3 that our experimental data show the best fit for a reaction order of $n = 1.5$. The fit of experimental data for $n = 1.5$ is shown in Figure 6. As mentioned earlier that Kwak et al.⁹ have reported the value of n to be 1.7 for the HDN of a bitumen-derived liquid. Hence, the values of k_1 and k_3 have been calculated from eq 3 using $n = 1.5$. The values of k_1 and k_3 for four different temperatures (365, 385, 400, and 415 °C) are given in Table 4.

For calculating the value of k_2 , apparent rate constant for the removal of basic nitrogen compounds, the series reaction scheme as shown in eq 1 has been considered. It can be represented symbolically as follows (eq 5):



where A and B represent, respectively, nonbasic and basic nitrogen compounds, and C represents the hydrocarbon molecule after elimination of the nitrogen atom.

For a consecutive reaction like eq 5, the rate of disappearance of the intermediate product (B) can be

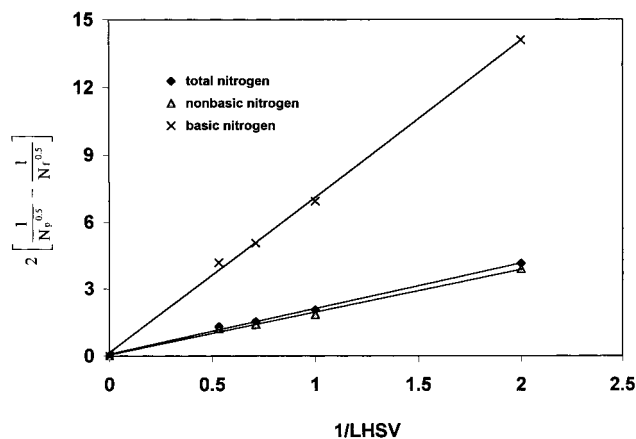


Figure 6. Fit of experimental data generated at 385 °C, 88 bar, LHSV of 1.0 h⁻¹, and a hydrogen/heavy gas oil of 600 mL/mL to the power law model for an order of reaction equals to 1.5 ($n = 1.5$).

Table 4. Values of Apparent Rate Constants for the Conversion of Nonbasic and Basic Nitrogen Compounds at Different Temperatures

apparent rate constants, h ⁻¹ (wt %) ^{-0.5}	temperature, °C			
	365	385	400	415
k_1	1.16	1.84	2.64	3.41
k_2	2.98	4.58	6.53	8.15
k_3	1.26	2.06	2.92	3.75

calculated using the following equation (eq 6):

$$-dN_B/dt = k_1 N_A^{1.5} - k_2 N_B^{1.5} \quad (6)$$

where N_A and N_B are the concentrations of A and B, respectively, at a time t . It has been assumed here that the removal of basic nitrogen compounds also follow a 1.5th order reaction kinetics.

The value of k_2 was calculated by numerically solving eq 6 and using known values of k_1 (from Table 4) and experimentally determined values of N_A and N_B for various levels of LHSV. The values of k_2 for four different temperatures (365, 385, 400, and 415 °C) are given in Table 4.

It is evident from the values of Table 4 that the values of apparent rate constant for the conversion of nonbasic nitrogen compounds to the basic ones are much lower than that of the subsequent reaction of the basic compounds leading to the elimination of the nitrogen atom. It is also interesting to note that the values of apparent rate constant for the conversion of nonbasic to basic nitrogen are mostly equal to those for the removal of total nitrogen. Therefore, the rate of initial hydrogenation of the nonbasic nitrogen compounds producing the basic ones is the controlling step in the removal of nonbasic nitrogen compounds from heavy gas oil.

The activation energies were then calculated from the Arrhenius plot (see Figure 7). The values of activation energies for the conversion of nonbasic to basic compounds and HDN of basic compounds are 80 and 74 kJ/mol, respectively. The activation energy for the removal of total nitrogen from the heavy gas oil is 80 kJ/mol.

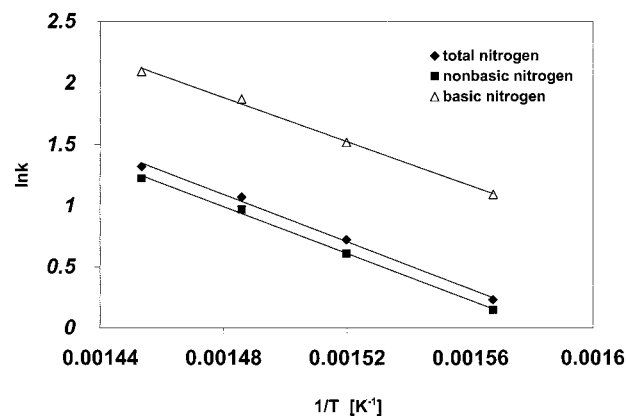


Figure 7. Arrhenius plots of rate data.

Kwak et al.⁹ have reported an activation energy of 94 kJ/mol for the HDN of a bitumen-derived liquid. Yui and Sanford²⁷ have reported the values of activation of activation energy to be 98 and 76 kJ/mol, respectively, for the HDN of coker and hydrocracker gas oil.

Implication of the Findings on Catalyst Development. The results of the present study provide useful information for the development of better catalyst for the efficient HDN of oil sands-derived heavy gas oil. It is observed from the results of the kinetic analysis that it is the prehydrogenation of the nonbasic nitrogen compounds, which controls the overall HDN of the heavy gas oil. This is an important finding, which needs to be considered for the development of better catalysts for the HDN of heavy gas oil. Therefore, the improvement in the HDN rate of heavy gas oil could possibly be achieved by increasing the hydrogenation activity of the catalyst.

Another important aspect, which also needs to be taken into account, is that the nonbasic nitrogen compounds having very low rate of initial hydrogenation are present in predominant proportion in the fed heavy gas oil (see Table 1). In addition, the results also indicate that carrying out the hydrotreatment of heavy gas oil at higher pressure and higher volumetric ratio of hydrogen/heavy gas oil favors the efficient conversion of the nonbasic nitrogen compounds.

Conclusion

The present study indicates that during the HDN of heavy gas oil, the rate of removal of nonbasic nitrogen compounds is much lower than that of basic nitrogen compounds. As a result, the product obtained even after the hydrotreatment of heavy gas oil at a very high temperature or high space time contained mainly nonbasic nitrogen compounds. It is also observed that the hydrogenation of nonbasic nitrogen compounds producing basic nitrogen compounds is the limiting step in the HDN of heavy gas oil. Therefore, the development of efficient catalyst systems for HDN of heavy gas oil should aim at providing more activity for the initial hydrogenation of the nonbasic nitrogen compounds.

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