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Effects of organic nitrogen compounds on hydrotreating and hydrocracking reactions

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Abstract

A major issue encountered in hydrotreating and hydrocracking reactions, as in many others fixed bed catalytic processes, is the decrease of catalytic activity with time on stream. The organic nitrogen compounds act as temporary poisons in hydroprocessing catalysts besides being coke precursors. The inhibiting effects of nitrogen compounds present in crude oil have been studied on SRGO hydrotreating reactions and VGO hydrocracking reactions. The results show that selective removal of nitrogen by adsorption using silica and alumina in varying proportions, would not only increase the HDS catalyst activity by more than 60%, but would also reduce hydrogen consumption. This step of nitrogen removal can be installed additionally in the upstream of an existing SRGO HDS reactor to achieve higher desulphurization or can be designed with the grass roots units.

The inhibition effects of nitrogen on VGO hydrocracking have been studied at different temperatures and the reaction has been found to be highly non-linear in nature and the conversion rapidly drops and the slope becomes less steep as the nitrogen level increases. At higher reaction temperature, the drop in activity or conversion with feed nitrogen is less than that in lower temperatures due to the higher rate of desorption of nitrogen compounds at elevated temperatures. The drop in conversion with nitrogen compounds present in VGO indicates the presence of organo nitrogen compounds having higher basicity compared to the nitrogen compounds by pyridine doping. The hysteresis exists in adsorption/desorption of nitrogen compounds and it indicates that desorption is a very slow process. With the increase of nitrogen compounds in the feed, the conversion drops rapidly and it takes long time to reach an equilibrium value. Similarly, with the step increase in reactor temperature, nitrogen desorption takes place at a slow rate and the conversion level comes to an equilibrium value after ~8 days.

The observed effects of nitrogen inhibition on SRGO hydrotreating and VGO hydrocracking conversion are explained reasonably well by kinetic models.

Keywords: Nitrogen inhibition; Hydrotreating; Hydrocracking; SRGO; VGO; Hydrodesulphurization (HDS); Reaction kinetics; Organo nitrogen compounds

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1. Introduction

Environmentally driven regulations by various legislative bodies worldwide require significant improvement in the quality of fuels and lubes. Additionally, the worldwide petroleum reserves are becoming heavier and there is substantial increase in sulfur and nitrogen contents. To meet the growing requirement of improved quality of the products (fuels and lubes), hydroprocessing (hydrotreating and hydrocracking) has emerged as the pivotal secondary refining process in the modern petroleum refinery configuration and the global hydroprocessing capacity has become more than 50% of the crude throughput since the middle of last decade.

Hydroprocessing is a group of technologies where catalytic reactions take place in presence of hydrogen at elevated pressure to fulfill some or all of the following major objectives:

(i) Removal of hetero-atoms (e.g. S, N, metals, etc.) from hydrocarbon streams.
(ii) Saturation of unsaturated hydrocarbon compounds (e.g. olefins and aromatics).
(iii) Cracking of heavier hydrocarbon molecules to lighter ones for production of desired fuels and lubes.

Hydrotreating is used in the refinery for hydrodenitrogenation (HDN), hydrodesulphurization (HDS) and demetallation

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of various petroleum streams, while hydrocracking is practiced to convert heavy petroleum feedstocks into desirable lighter products. Hydrocracking process has the flexibility to handle variety of feedstocks.

Hydrotreating and hydrocracking reactions, as in many others fixed bed catalytic processes, encounter the problem of decrease of catalytic activity with time on stream. The organic nitrogen compounds present in the feed to hydrotreater and hydrocracker, act as temporary poisons as well as coke precursors for hydroprocessing catalysts, resulting in decrease in catalyst activity.

The nitrogen compounds present in a typical crude oil are indole, carbazole, pyridine, quinoline, acridine, phenenthridine, hydroxypyridine, hydroxyquinoline and their derivatives of alkyl, phenyl and naphthyl [1]. The nitrogen compounds are broadly classified into three categories namely, neutral organo N-compounds, basic organo N-compounds and weakly basic organo N-compounds.

Since hydrotreating and hydrocracking catalysts have acid sites, the basic organic nitrogen compound are characterized as strong HDS inhibitors and a fair amount of work have been devoted to thiophene and benzothiophene reaction networks [2–7]. Reported results on the inhibition of non-basic organic nitrogen compound are available [8,9]. Recently, Laredo et al. [9] reported that the inhibiting effect of the non-basic compounds, viz., carbazole, quinoline and indole, are very strong even at a concentration as low as 5 wppm.

Even though, the inhibiting behavior of various model nitrogen compounds on gas oil hydrotreating reactions, especially HDS, have been reported quite extensively, the concentration of nitrogen compounds and experimental conditions used do not have much relevance with respect to industrial gas oil hydrodesulphurization. As a result, there is a need to study the effect of actual nitrogen compounds present in industrial gas oil under the actual industrial condition.

In vacuum gas oil (VGO) hydrocracking, very little information is available in the open literature on the effects of nitrogen compounds on hydrocracking conversion. The information is closely guarded by the hydrocracking catalyst vendors and process licensors. As mentioned before, organo nitrogen compounds act as temporary poisons to the hydrocracking catalyst and these are precursors of coke formation and as a result, catalyst activity decreases with time. Different mechanisms of hydrocracking catalyst deactivation have been described quite extensively by Furimsky et al. [8].

In this paper, the effect of organic nitrogen compounds present in the feedstock on the catalyst activity has been studied in the gas oil hydrotreating, mainly for HDS reaction and vacuum gas oil (VGO) hydrocracking reactions.

2. Experiments

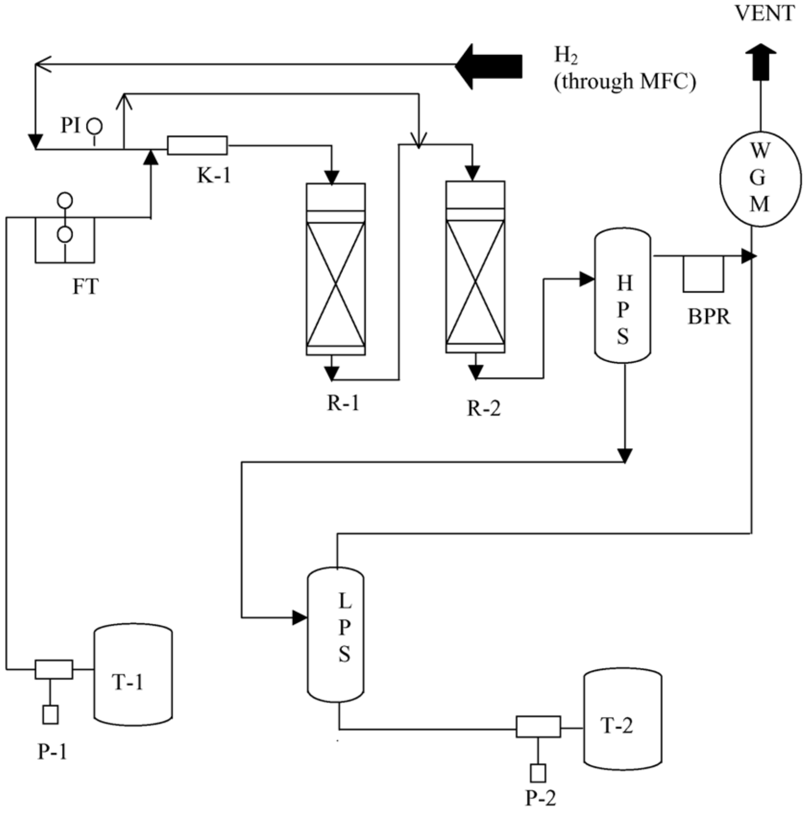
Experiments have been conducted for hydrotreating and hydrocracking reactions in hydroprocessing pilot plant reactors shown in Fig. 1. This pilot plant consists of two reactors in series and both are in downflow configuration. These reactors can be operated up to pressure of 200 kg/cm^2 and temperature of 450 °C. It can be seen from Fig. 1 that the feed is pumped to the first reactor (R1) by a piston type of pump (P) from feed tank (T1). The partially converted feed from the first reactor (ex-R1) goes to the second reactor (R2). The combination of products and unconverted feed is then routed to a high pressure separator (HPS). The liquid from HPS goes to low pressure separator (LPS). The gas from LPS joins with the gas from HPS (after pressure drop) and the combined gas is passed through a caustic scrubber and vented through metering by a weight gas meter (WGM). The liquid from LPS is collected into product tank (T2).

2.1. Experiments for gas oil hydrotreating

In gas oil hydrotreating, commercial catalyst with Ni–Mo formulation has been used. For studying the effect of presence of organo nitrogen compound on hydrotreating kinetics, specifically hydrodesulphurization (HDS), the SRGO feeds used in this study are referred as “Light feed” and “Full range SRGO feed”. The properties of both feeds are given in Table 1a. The catalyst used in this study is a Ni–Mo based HDS catalyst. The operating conditions used in the experiments are of typical conditions of commercial HDS reactors and the values are: pressure: 35–60 bar, temperature: 335–350 °C, LHSV: 1.0–1.75 h^{-1}; H_2/HC ratio: 267–400 Nm^3/m^3. Diluents such as silicon carbide have been used to have comparable kinetic data with that of commercial plant. For HDS experimentation, one reactor (R1) has been loaded with commercial catalysts, followed by pre-activation and sulfiding procedure as specified by vendor. The catalyst activities are monitored with respect to sulfur in the product for a particular feed with different organo nitrogen compounds. Total sulphur and total nitrogen have been analyzed in ANTEK analyzer.

2.2. Experiments for vacuum gas oil hydrocracking

Commercial hydrocrackers have two types of configuration, namely, once through configuration and two stage configuration [10]. In two stage configuration, the unconverted liquid stream from first stage is recycled for achieving 100% conversion (also called extinct cycle), while in once through single stage configuration, the unconverted feed is not recycled; the typical conversion for this configuration is 60–80%. The unconverted oil in once through configuration is considered to be an excellent feedstock for LOBS (lube oil base stock) production and fluid catalytic cracking (FCC). In our experiment for vacuum gas oil hydrocracking, commercial catalyst (zeolyte based) has been used in once through configuration. Hydrocracking catalysts are very sensitive to nitrogen compounds present in feed streams and therefore, feed to hydrocracker is first hydrotreated (by hydrotreating catalyst) to remove nitrogen to a prescribed level and subsequently, it reacts with hydrocracking catalyst. The properties of vacuum gas oil (VGO) used in the study are given in Table 1b. The operating conditions used in the experiments are typical of commercial hydrocracker units and the values are: pressure: 140–180 bar,



MFC: Mass flow controller, PI: Pressure indicator, T-1 and T-2: Feed and product tank, P-1 and P-2: Feed and product pump, FT: Flow transmitter, K-1: Knock out drum, R-1: Reactor 1, R-2: Reactor 2, HPS: High pressure separator, LPS: Low pressure separator, BRP: Back pressure regulator, WGM: Wet gas meter

Fig. 1. A schematic of the hydroprocessing pilot plant reactor system used for experimentation.

Table 1
Properties of (a) atmospheric gas oil, (b) vacuum gas oil and (c) hydrotreated vacuum gas oil (different nitrogen levels)

Description	Sulphur (wppm)	Nitrogen (wppm)	Distillation simulated TBP (ASTM D2887) (°C)		Density (kg/m^3)	Saturates (wt.%)	Aromatics (wt.%)
			IBP/5%	95%/FBP			
(a) Atmospheric gas oil (GO)							
Light feed	10700	64	125/205	360/436	845.8	75.0	25.0
Full range feed	11800	174	136/213	400/447	847.8	71.0	29.0

Distillation Simulated TBP (ASTM D2887) (°C)		Sulphur (wppm)	Nitrogen (wppm)	Density (kg/m^3)	Saturates (wt.%)	Aromatics (wt.%)	CCR (wt.%)	Ashphaltenes (wt.%)
IBP/5%pt	95%/FBP							
(b) Vacuum gas oil (VGO)								
250/320	520/540	6423	885	895.8	66.6	33.4	0.3	<0.05
(c) Hydrotreated vacuum gas oil (VGO) with different nitrogen levels								
242/310	514/536	36	5	883	87	13	<0.1	<0.05
245/315	515/538	148	21	884	82	18	<0.1	<0.05
250/318	513/535	612	80	886	79	21	<0.1	<0.05
248/320	520/538	1115	145	888	76	24	<0.1	<0.05
250/322	520/540	1548	200	890	74	26	<0.1	<0.05
245/320	519/539	3100	400	893	70	30	<0.1	<0.05
250/320	520/540	4650	600	894	68	32	<0.1	<0.05

temperature: 350–420 °C, LHSV: 1.0–1.3 h^{-1}, H_2/HC ratio: 1100–1500 Nm^3/m^3. Diluents such as silicon carbide have been used to ensure proper kinetics as in commercial plant. For hydrocracking experimentation, two reactors (R1 and R2) have been used in series after pre-activation and sulfiding as provided by the vendor. Reactor 1 (R1) has been used for hydrotreating of VGO and Reactor 2 (R2) has been used for hydrocracking of VGO with different level of nitrogen. Experiments have also been conducted in Reactor 2 (R2) by doping with basic nitrogen compound, i.e. pyridine, in hydrotreated VGO.

The catalyst activities in hydrocracking have been monitored with the conversion of VGO, defined as 370 °C(−), at the Reactor 2 (R2) exit with respect to Reactor 1 (R1) exit from the distillation data (D2887) carried out in simulated true boiling point (SIM TBP) apparatus.

3. Results and discussion

3.1. Effects of organo nitrogen compounds in straight run gas oil during hydrotreating reactions

The presence of nitrogen compounds acts as hindrance to hydrodesulphurization (HDS) of sulfur compounds, especially in the low ppm range, due to competitive adsorption. The nitrogen compounds can be selectively removed by means of adsorption, extraction, etc., prior to hydrodesulphurization, and the performance of HDS catalysts can be enhanced.

In this study, nitrogen compounds have been selectively removed from SRGO feed by adsorption using silica and alumina in varying ratios. The SRGO feedstocks having same sulphur and different nitrogen content have been subjected to pilot plant testing using SRGO HDS catalyst and the results are presented in Fig. 2. The typical operating conditions of commercial HDS reactor used for the experiments are: pressure = 49 bar, temperature = 345 °C, LHSV = 1.5 h^{-1} H_2/HC ratio = 267 Nm^3/m^3. It can be seen from Fig. 2 that removal of nitrogen compounds to the level of 15 wppm N prior to desulphurization can achieve 40–60% or even more desulphurization compared to that with untreated SRGO feed. This additional step of nitrogen removal can be installed additionally in the upstream of an existing SRGO HDS reactor to achieve more desulphurization or can be designed with the grass roots units. This, in addition, reduces the consumption of precious hydrogen due to reduced HDN requirement in HDS.

3.2. Application of model for prediction of diesel hydrotreating experimental data

For estimating the effect of nitrogen inhibition of HDS reactor, the model proposed by Laredo et al. [9] has been applied and tuned for the present system to explain the observed experimental data. The model, based on L–H kinetics, is of the following form:

$$r_{\mathrm{HDS}} = \frac{k_{\mathrm{HDS}} C_{\mathrm{S}}}{1 + k_{\mathrm{N}}^{n} C_{\mathrm{N}}^{n}}$$

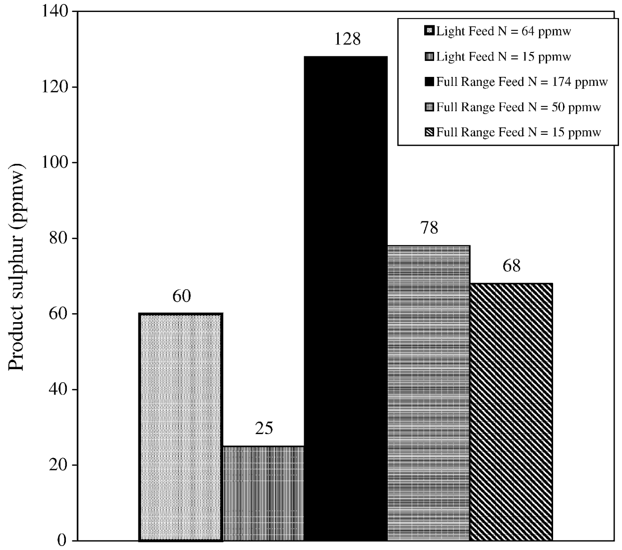


Fig. 2. Effects of organo nitrogen (N) compound on hydrodesulphurization are shown at liquid hourly space velocity (LHSV) = 1.5 h^{-1}, partial pressure of hydrogen (p_{H_2}) = 49 bar, temperature = 345 °C, and H_2/HC ratio = 267 Nm^3/m^3. Two types of feed and various level of total N were used.

where r_{HDS} is the rate of hydrodesulphurisation [wppm/min]; k_{HDS} the overall HDS apparent kinetic constant [1/min]; C_{S} the total sulphur concentration [wppm]; k_{N} is the apparent nitrogen compound equilibrium constant and represent the behaviour of all nitrogen compound present in gas oil fraction contributing to inhibition [L/mol]; C_{N} is the initial nitrogen compound concentration [mol/L]; and n is the fitting exponent whose value varies between 0.7 and 1.20.

The model tuning parameters for both the feed systems are in the following range:

k_{HDS} (min^{-1}): 0.13–0.15,
K_{N} (L/mol):250.0–255.0,
n: 0.70–1.20.

The match between experimental and model predicted product sulphur levels for various feed nitrogen is presented in Fig. 3. It can be observed that there is reasonable match between the values. Therefore, this type of model accurately depicts the inhibition effects of organo nitrogen compounds on HDS activity for different gas oil streams.

3.3. Effects of nitrogen compounds on hydrocracking of vacuum gas oil during reactions

For hydrocracking reactions of vacuum gas oil (VGO), the conversion is generally defined as formation of products up to SRGO range components, i.e. boiling point up to 370 °C(−). Since 370 °C(−) components are present in the VGO and hydrotreated VGO used for hydrocracking reactions in this study, the results are presented with net percent conversion, defined as, weight percent of 370 °C(−) in the product minus weight percent of 370 °C(−) in feed.

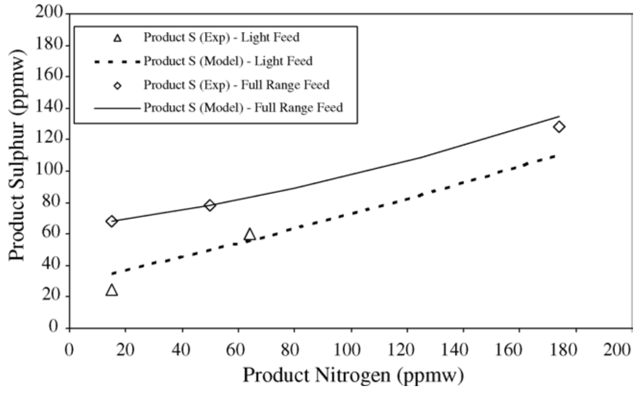


Fig. 3. Model performance for prediction of effect of product nitrogen on HDS activity (product sulphur) for light and full range DHDS feed.

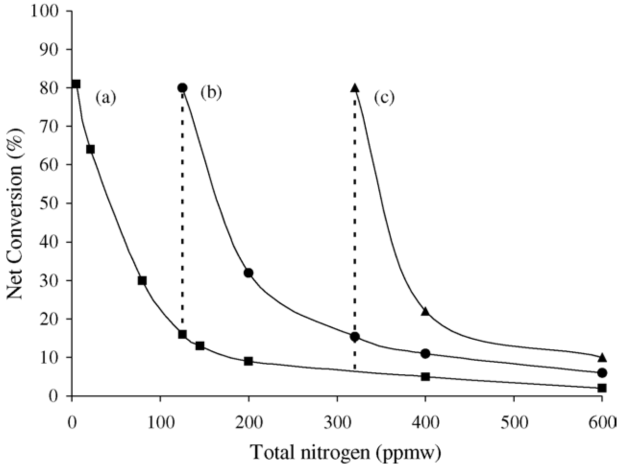


Fig. 4. Hydrocracking conversion [370 °C(−)] with increase in total nitrogen (N) content in feed. The reaction temperatures are (a) 370 °C, (b) 390 °C and (c) 405 °C. The other operating conditions are: pressure = 162 bar, LHSV = 1.0 h^{-1} and H_2/HC ratio = 1200 Nm^3/m^3.

3.3.1. *Effects with organo nitrogen compounds present in vacuum gas oils*

Vacuum gas oil (VGO) considered in this study has been obtained from an operating refinery in India and it contains 800 wppm organo nitrogen (N) compound. It is hydrotreated to different extents by conducting experiments at various severities in Reactor 1 (R1), so that the product, i.e., hydrotreated VGO contains 5, 21, 80, 125, 145, 200, 320, 400 and 600 wppm total N compound. The properties of the hydrotreated VGO with different nitrogen content is presented in Table 1c. The hydrocracking of hydrotreated VGO has been carried out in Reactor 2 (R2) at pressure = 162 bar, LHSV = 1.0 h^{-1} and H_2/HC ratio = 1200 Nm^3/m^3. The reaction temperature has been varied from 370 to 405 °C. The net conversions obtained with different hydrotreated VGO are presented in Fig. 4. In Fig. 4, the hydrocracking conversions at 370, 390 and 405 °C are presented with (a–c), respectively.

The inhibition effects of nitrogen on conversion at different temperatures are shown in Fig. 4(a–c) and these are highly non-linear in nature. The initial steep slope of these graphs show that as nitrogen level increases from zero value, the conversion rapidly drops and the slope becomes less steep as the nitrogen level increases. At higher reaction temperature, the drop in activity or conversion with feed nitrogen is less than that in lower temperatures. This is due to the higher rate of desorption of nitrogen compounds at elevated temperatures.

Considering the net conversion data (∼80%) at 370 °C as base case data, additional set of experiments have also been carried out for determining the temperature required to achieve base case conversion from 125 and 320 wppm total N present in feed. It was found that the required temperature change (ΔT) at 125 and 320 wppm N are +20 and +35 °C, respectively. Even though the required ΔTs are found for this typical VGO feed (properties in Table 1b), the information obtained from these experimental data is very important for hydrocracking reactions. For a commercial hydrocraker operation, the VGO properties would vary with respect to organo nitrogen compounds depending on the crude mix being processed and this type of information would be utilized for adjusting the catalyst average temperature (CAT) of the reactor bed for a targeted conversion.

3.3.2. *Effect of doped pyridine on hydrocracking conversion*

Pyridine is quite often used as doping agent for studying the impact of nitrogen compounds. VGO has been first hydrotreated to the total nitrogen (N) level of 5 wppm from 800 wppm N and then pyridine has been doped with this hydrotreated VGO at various levels such that the feedstock for hydrocracking reactions are of 100, 400 and 600 wppm. Hydrocracking reactions have been conducted in pilot plants at temperature = 370 °C, pressure = 162 bar, LHSV = 1.0 h^{-1} and H_2/HC ratio = 1200 Nm^3/m^3. The results of the hydrocracking net conversions for various feedstocks with increasing doped total N are presented in Fig. 5. In Fig. 5, the curves show a comparison between the impact of pyridine (a) vis-à-vis nitrogen compounds present in VGO stream (b). It may be noted that in the ranges of total nitrogen compared, i.e., 5–600 wppm, the net conversions with pyridine compounds are higher compared to the actual nitrogen present in feed. This higher drop in conversion with nitrogen compounds present in VGO indicates the presence of organo nitrogen compounds having higher basicity.

The trajectory of conversion, when nitrogen level in the feed is increased gradually from a low value, is different from that when nitrogen level is decreased from a higher value. This is shown in Fig. 6. This hyteresis indicates that while bringing down the nitrogen content from a high to a low value, the net conversion is lower at a particular nitrogen level in the path of increasing the nitrogen content from a low to a high value. This indicates that desorption is a very slow process and even though, apparent steady state was observed for each of the data point presented, there are some adsorbed nitrogen compounds which remain on the catalyst surface leading to reduction in conversion as shown in curve (b) in Fig. 6.

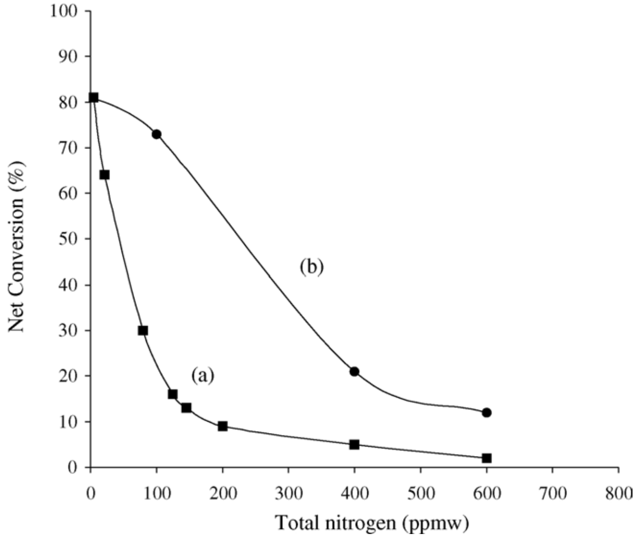


Fig. 5. Hydrocracking conversion [370 °C(−)] with increase in total nitrogen (N) content in feed. Case (a) represents nitrogen compound present in VGO and (b) represents nitrogen compound by pyridine doping. The reaction conditions are temperatures = 370 °C, pressure = 162 bar, LHSV = 1.0 h^{-1} and H_2/HC ratio = 1200 Nm^3/m^3.

3.3.3. Transient response of nitrogen compounds

The transient response of nitrogen compounds on hydrocracking conversion have been studied for two cases: (1) increasing total feed nitrogen from 5 to 125 ppmw at a reaction temperature of 370 °C, and (2) increasing reaction temperature from 370 to 390 °C at a total feed nitrogen of 320 wppm. The other operating parameters are: pressure = 162 bar, LHSV = 1.0 h^{-1} and H_2/HC ratio = 1200 Nm^3/m^3. The feed N used in these experiments are actual N compounds present in VGO. In both cases, the transient responses observed by monitoring conversion with time on streams (TOS) are presented in Figs. 7 and 8. It is illustrated in Fig. 7 that with the increase in nitrogen compounds in the feed, the conversion drop rapidly, but it takes a long time to reach an equilibrium value. While the major drop in activity takes place within 2–3 days, it has taken ∼8 days to come to an equilibrium value. Similarly, with the step increase in reactor temperature, nitrogen desorption takes place at a slow rate as presented in Fig. 8. Here also, the conversion level comes to an equilibrium value after ∼8 days.

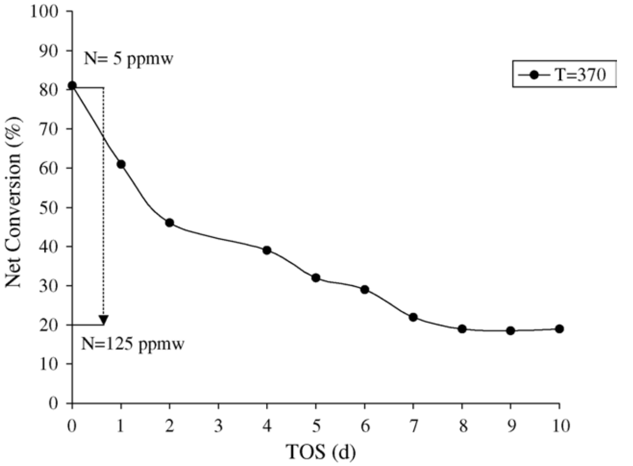


Fig. 7. Transient response of hydrocracking conversion [370 °C(−)] with increases in concentration of organo nitrogen compound in feed (VGO). Net conversion is plotted against times on stream in days for temperatures = 370 °C, pressure = 162 bar, LHSV = 1.0 h^{-1} and H_2/HC ratio = 1200 Nm^3/m^3.

When there is a step change in concentration of nitrogen compounds in the feed, the concentration of adsorbed nitrogen on the active sites of the catalyst follows a first order response curve (uptake curve for adsorption) of the following form (Ruthven [10]):

$$1-\frac{(C_N)_t}{(C_N)_\infty}=k_1\exp(-\bar{p}\times \mathrm{TOS})$$

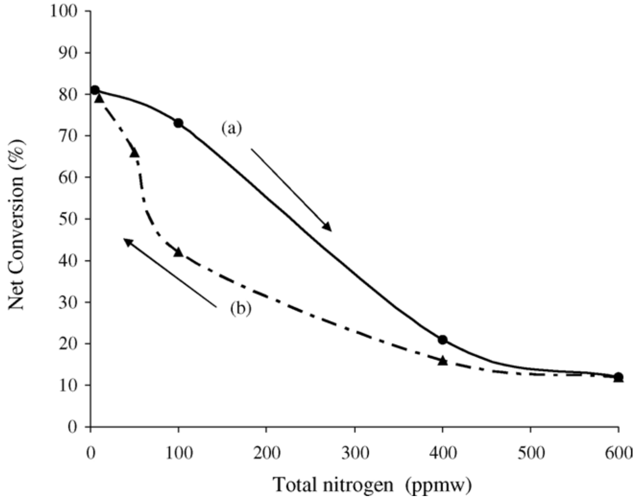


Fig. 6. Hydrocracking conversion [370 °C(−)] with (a) adsorption and (b) desorption of pyridine dopped in hydrotreated VGO at various level. The reaction conditions are temperatures = 370 °C, pressure = 162 bar, LHSV = 1.0 h^{-1} and H_2/HC ratio = 1200 Nm^3/m^3.

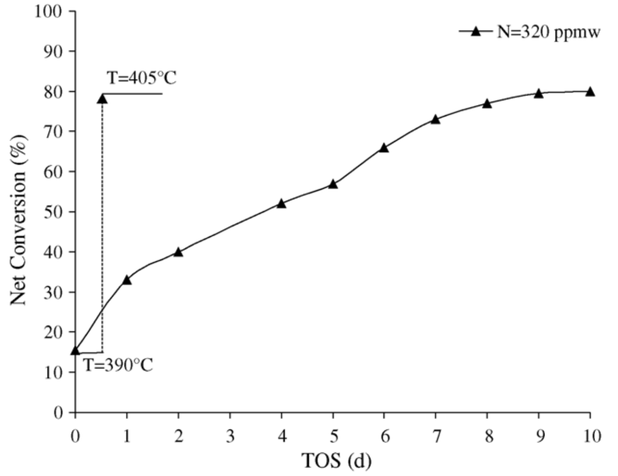


Fig. 8. Transient response of hydrocracking conversion [370 °C(−)] with increases in temperature from 390 to 405 °C at 320 wppm concentration of organo nitrogen compound in feed (VGO). Net conversion is plotted against times on stream at pressure = 162 bar, LHSV = 1.0 h^{-1} and H_2/HC ratio = 1200 Nm^3/m^3.

where C_N denotes nitrogen concentration (subscripts t and ∞ denote time of "t" and time approaching infinity, respectively), k_1 is adsorption constant, $\bar{p}$ is a function of pressure and TOS denotes time on stream.

In this case, as there is a step jump in the feed nitrogen concentration, the nitrogen adsorbed on the catalyst active sites asymptotically comes to an equilibrium value in a period of about 8 days (as already mentioned). This is reflected in the transient conversion behaviour. Similar response with respect to desorption is observed in case of step increase in reaction temperature and the equilibrium conversion is achieved in about 8 days.

In hydrocracker reactors, since hydrocracking catalyst faces changes in nitrogen environment during its life cycle, these transient responses are very much useful for commercial operation of a hydrocracker unit.

3.4. Application of model for prediction of VGO hydrocracking experimental data

A VGO hydrocracker model has been developed earlier based on continuum theory of lumping approach in which the reaction mixture is classified into continuous boiling mixtures of paraffinic, naphthenic and aromatic compounds. The individual component material balance and the intricacies of the modeling are described in one of our earlier publications (Narasimhan et al. [11]). The yield distribution function, $P(k, K)$, during cracking reaction determines the yields of species with reactivity k from hydrocracking of components with reactivity K. It follows a skewed Gaussian type distribution function. The 1D model is a set of coupled integro-differential equations and has six skewed Gaussian functions to describe the primary yield distribution of hydro- cracking of paraffins to lower paraffins, hydrocracking of naphthenes to lower naphthenes and lower paraffins and hydrocracking of aromatics to lower aromatics, naphthenes and paraffins. The skewed Gaussian function is formulated as follows:

$$P(k,K) = \frac{1}{s\sqrt{2\pi}} \exp^{[(k/K)^{a_0} - 0.5]^2/a_1} - A + B$$

$$A = \exp\left(-\left(\frac{0.5}{a_1}\right)^2\right)$$

$$B = a_2\left[1 - \left(\frac{k}{K}\right)\right]$$

where a_0, a_1, a_2 are the parameters to be estimated for each yield distribution function. As there are six yield distribution functions, 18 parameters to be estimated through regression of experimental data. "s" is estimated from material balance constraints imposed on yield distribution functions. In addition to the above parameters three more parameters need to be estimated from species type distribution functions, $D(k)$. In all there are 21 parameters for this model. Parameter estimation is carried out using the conversion data as responses applying Levenberg–Marquardt algorithm, which is a non-linear least square regression technique with multiple responses. The parameters have been found to be feed invariant for VGO range feedstocks. However, these are catalyst dependent. The methodology for estimation has already been published (Basak et al. [12]). The model tuning parameters for the present study is given in Table 2.

Table 2
Model prediction of effect of feed nitrogen on hydrocracking conversion (T: 370 °C; P: 162 bar; LHSV: 1.0 h^{-1}; H_2/Oil Ratio: 1200 Nm^3/m^3)

Serial number	Feed nitrogen (wppm)	Conversion (wt.%)	
		Experimental	Model
1	5	81	78
2	21	64	64
3	80	30	35
4	400	5	8
Model tuning parameters	a_0: 12.65; a_1: 259.0; a_2: 1.05e-07; s: 2.0; K: 1.33		

Model tuning parameters: a_0, 12.65; a_1, 259.0; a_2, 1.05e−07; s, 2.0; K, 1.33. Operating conditions: temperature, 370 °C; pressure, 162 bar; LHSV, 1.0 h^{-1}; H_2/oil ratio, 1200 Nm^3/m^3.

In the model, the effect of temporary deactivation (through nitrogen) has been accounted through preliminary deactivation model, developed through (i) in-house correlation based on long duration pilot plant testing (processing feedstocks containing nitrogen at different levels) and (ii) catalyst specific data (given by catalyst vendors). Due to presence of nitrogen, the concentration of acid sites of dual function hydrocracking catalyst (containing metal function for hydrogenation and acid function for cracking activity), get reduced as a result of which the conversion decreases. To obtain the same level of conversion, it is required to increase the catalyst average temperature, which is estimated through various correlations. In the present study, the effect of nitrogen deactivation in terms of change in catalyst temperature (T, in °C) with increase in nitrogen concentration (C_N, in wppm) has been considered through a simplistic relation of the following form:

$$T = 2.2e - 09 \times C_N^3 + 9.35e - 07 \times C_N^2 - 0.0206 \times C_N + 4.91$$

Through a conjunction of this type of correlation and the hydrocracker kinetic model, the change in conversion with change in nitrogen concentration has been estimated. The typical match between pilot plant results and model predictions is presented in Table 2 and there has been satisfactory match between the values.

Further research work is being pursued for development of rigorous deactivation model, which includes kinetics for actual number of acid sites and the effect of nitrogen on the blocking of the sites, leading to non-availability of acid sites for hydrocracking. Some work for development of kinetic model with pure compound like pyridine, piperdine, etc. has been reported in the literature (Hadjiloizou et al. [13]); however, rigorous deactivation kinetic model for VGO hydrocracking is not available. The formulation and performance of our rigorous deactivation model will be reported later.

4. Conclusions

The inhibiting effects of nitrogen compounds present in crude oil were studied on SRGO hydrotreating reactions and VGO hydrocracking reactions. Results show that selectively removal of nitrogen by adsorption using silica and alumina in varying proportions, would not only increase the HDS catalyst activity by more than 60%, but also would reduce the hydrogen consumption. This step of nitrogen removal can be installed additionally in the upstream of an existing SRGO HDS reactor to achieve more desulphurization or can be designed with the grass roots units.

The inhibition effects of nitrogen on hydrocracking conversion at different temperatures are highly non-linear in nature and the conversion rapidly drops and the slope becomes less steep as the nitrogen level increases. At higher reaction temperature, the drop in activity or conversion with feed nitrogen is less than that in lower temperatures due to the higher rate of desorption of nitrogen compounds at elevated temperatures. The drop in conversion with nitrogen compounds present in VGO indicates the presence of organo nitrogen compounds having higher basicity compared to the nitrogen content by pyridine doping. The hyteresis exists in adsorption/desorption of nitrogen compounds and it indicates that desorption is a very slow process. With the increase in nitrogen compounds in the feed, the conversion drops rapidly, but it takes a long time (∼8 days) to reach an equilibrium value. Similarly, with the step increase in reactor temperature, nitrogen desorption also takes place at a slow rate and the conversion level comes to an equilibrium value after ∼8 days. In both the cases of adsorption/desorption of nitrogen compound, the nature of the response suggests first order kinetics. In hydrocracker reactors, since hydrocracking catalyst faces changes in nitrogen environment during its life cycle, these transient responses are very much useful for commercial operation of a hydrocracker unit. The observed effects of nitrogen inhibition on SRGO hydrotreating and VGO hydrocracking conversion are explained reasonably well by kinetic models.

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