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HYDRODESULFURIZATION OF LIGHT GAS OIL – Kinetic determination in a batch reactor

The performed investigations were directed toward the analysis of the performance and activity of the fresh and regenerated Cyanamid HDS 20C catalyst in a laboratory batch reactor (2 dm³) for the HDS of the diesel fraction (light gas oil, LGO). Testing of the regenerated catalyst was performed with light gas oil (LGO) of different characteristics.

The determined values of the reaction rate constant were compared to some published data in the literature for the HDS of specific sulfur compounds, as well as the values of the activation energy.

The rates of deactivation of the fresh and regenerated catalyst actually existed compared to some other results recently published in the literature. However, such an observed differences were not sufficient to derive a relation which could be used for the determination of the rate of catalyst deactivation.

In the period 1990–1994 the content of sulfur in LGO (diesel fraction) was limited to 0.05mass% (USA) while in some other countries (EU and Japan) it was 0.2 mass%. However, in 1995 in many countries this limit was decreased to 0.05 mass% (in Europe, in gasoline and in diesel) and also in gas oil (0.2 mass%) and jet fuel (0.3 mass%). EU regulations are now at the level of 0.035 mass% (350 ppm) as a upper limit in diesel and only 0.015 mass% in gasoline (150 ppm). They will be further decreased in the next few years (till 2005 to 50 ppm and less in LGO and gasoline). This facts requires improvement of some of the older technologies of sulfur conversion present in different hydrocarbon mixtures, and the development a new catalyst type and reactor design.

The hydrodesulfurization (HDS) of different crude oil fractions which contain sulfur compounds has for a many years been one of the basic catalytic processes in a modern refinery. This process enables the transformation of sulfur compounds from the complex hydrocarbon mixture, via many different reaction of double bond and aromatic ring saturation (hydrogenation) and very important breaking of the C–S and C–H bonds. Hydrogen sulfide (H₂S) and other hydrocarbons (C_nH_{2n-x}) with a lower molar mass than the starting compound are the main product of the HDS process.

The problem of the conversion of sulfur compounds (by using hydrogen in the process of hydrodesulfurization – HDS), particularly heterocyclic sulfur compounds, from the gasoline and middle fractions of crude oil (kerozine, light gas gas oil – LGO or heavy gas oil – HGO) is nowadays as noted one of the most important processes in a refinery. Published data in the literature, covering the conversion of different

model compounds (sulphide, thiophene, benzothiophene and dibenzothiophene), as well as those dealing with the actual feeds (LGO or LCO – light cyclic oil), were analysed in great detail presenting enough information for making good strategy and a final decision how to realize the HDS process in an industrial unit. However, such information is usually only the initial one, and must be followed by the analysis of the specific type of catalyst which is planned to be used, as well as by testing the chosen industrial conditions (temperature, pressure, space velocity, ratio of hydrogen to hydrocarbon fraction) for obtaining optimal conditions for the conversion of specific sulfur compounds in some industrial unit.

The main focus in the present investigation was oriented to the analysis of the HDS of LGO. Namely, as known LGO is a very complex mixture including many S compounds, especially polyaromatic sulfur compounds such as: benzothiophene, dibenzothiophene and their substituted alkyl derivatives (4-methyldibenzothiophene (4-MDBT); 4,6-dimethyl-dibenzothiophene (4,6-DMDBT)) which are very stable and can not be hydrogenated at moderate pressure and temperature. New standards indicate that a deep HDS process must be performed for removing such types of refractory compounds [1–5].

The Co–Mo catalyst activity for the HDS of LGO was tested in a batch autoclave in this study, not only with fresh, but also using regenerated catalyst of this type. The main task in these investigations was oriented toward finding optimal conditions for the HDS of LGO. Two types of LGO fractions were tested; more experiments were performed with LGO having a larger amount of sulfur compounds (Table 1).

EXPERIMENTAL

The main goal of the performed investigation was directed toward the analysis of the activity of regenerated Cyanamid HDS 20C catalyst and to find possible effects with such a catalyst in industrial application. At the beginning of the experimental testing,

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Table 1. Characteristics of the LGO used in the experimental investigation

Characteristics	LGO (URAL REB)	LGO (KIKINDA)
density 15°C, g/cm ³	0.8414	0.8227
sulfur, mass%	0.92	0.092
viscosity 20°C, mm ² /s	4.74	3.96
Ash, mass%	<0.001	<0.001
Coke, mass%	0.09	0.02
Distillation °C, initial	201	167
5 vol%	228	209
10	236	217
50	276	252
60	279	263
90	320	305
95	331	316
End	345/98	320/98
P+N, v/v%	75.5	89.8
O, v/v%	0	0
A, v/v%	24.5	10.2

two types of different raw materials (LGO from different crude oil) were chosen (type A from URAL REB and type B from the crude oil Kikinda). However, the preliminary testing of the main characteristics of both LGO and the obtained results indicated that the LGO from Kikinda had only a small content of sulfur compounds (0.1 mass% S, Table 1), so most of the experiments were performed using only the LGO from Ural REB with almost 1 mass% S.

The HDS of LGO was tested in 2 dm³ autoclave at 300–350°C under a pressure of 43 bar by using a stirrer rotation of 400 and 600 rpm and always with the same ratio of hydrogen:LGO (180–190 Nm³/m³) at the beginning of the reaction. By determining the change of sulfur content in the LGO with time, the kinetics of the pseudo-first order HDS process were confirmed and the reaction rate constant and activation energy were calculated from the corresponding Arrhenius plot ($\ln(k) - (1/T)$).

The experimental results are presented in Table 2 (characteristic of the sulfur content) determined by using a standard method of S determination in a hydrocarbons mixture, as well as by using a specially derived "fast" method for sulfur determination based on analysis of the refraction index and a previously prepared corresponding calibration diagram. The so-called "indirect" or fast method of sulfur content determination was derived using the results of many investigation of both characteristics (refraction index and sulfur content) of LGO (type A), as well as by using artificial standards containing only small amount of sulfur compounds

Table 2. Experimental results of the HDS of LGO performed in an autoclave

	Cat., g N-new; R-reg.	t, °C	P, bar	%S (direct)	%S (indirect)	Com- ments
LGO	–	–	–	0.92*	0.92*	
1	(N), 14	278–330	40–42	0.151	–	Ural REB
2	(N), 14	298–336	40	0.138	–	
3	(N), 2.8	300–301	40	0.461	0.55	
4	(N), 2.8	320–322	40–43	0.286	0.38	
5	(N), 2.8	350	45	0.072*	0.072*	
6	(N), 2.8	294–300	45	0.517	0.53	Kikinda
7	(N), 2.8	300	45–47	0.027	–	
8	(N), 2.8	350–380	48	0.008	–	
9	(N), 2.8	350	46	0.021	–	
10	(N), 2.8	300	41	0.025	–	
11	(R), 2.8	300	41	0.525	0.53	Ural REB
12	(R), 2.8	325	42	0.431	0.50	
13	(R), 2.8	350	45	0.21	0.16	
14	(R), 2.8	300	43–45	0.583	0.63	
15**	(R), 2.8	300	45	0.588	0.65	

*Samples used for preparation of the calibration diagram (Figure 1)

**Experiments performed at 600 rpm (mixing intensity); in experiments 1–15 the mixing intensity was 400 rpm.

Experiments 1, 2 and 8 were performed under non-isothermal conditions.

prepared by mixing known amounts of LGO (A) with lower and higher amounts of sulfur compounds (Figure 1).

The calibration curve was made by using mixtures of different portions of LGO (A) and products obtained in experiment 5 (Table 2). The sulfur content in all the samples collected during each HDS experiment was determined on the basis of the measured refraction index (n_D^{20}) and calibration plot (Figure 1).

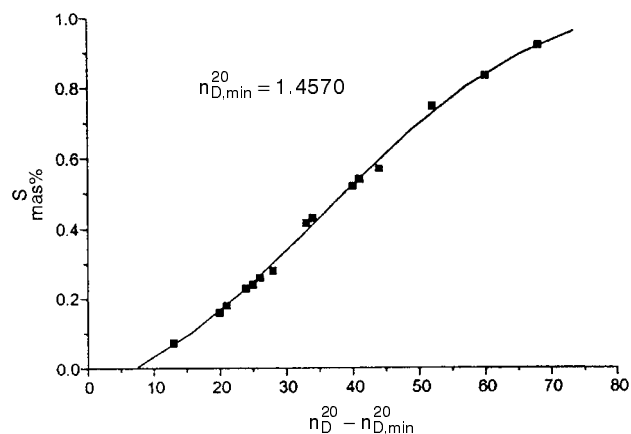


Figure 1. Calibration plot used for determining the sulfur content in the product of the HDS of LGO.

Determination of the reaction rate constant (HDS LGO-A)

On the basis of data from an autoclave and from the corresponding mole balance, the apparent reaction rate constant (k_{ap}) of the HDS of LGO was determined knowing the reaction time and temperature at which the HDS was performed. For this purpose, a first order reaction rate was assumed:

$$(-r_{HDS}) = k \cdot a \cdot C_S \quad \text{gS/cm}^3_{oil} \cdot h = k_{ap} C_S \quad (1)$$

where: a – is catalyst activity; $k_{ap} = k \cdot a$ – apparant reaction rate contant which also includes catalyst activity and temperature influence.

The mole balance for the process realized in a batch reactor is:

$$(-r_{HDS}) \cdot V_{oil} \cdot dt = -dm_s \quad (2)$$

where, after replacing equation (1) of the reaction rate into the mole balance (2):

$$k_{ap} \cdot C_{S0} (1 - X_S) \cdot V_{oil} = m_{S0} \cdot (dX_S/dt) \quad (3)$$

because: $C_{S0} = m_{S0}/V_{oil}$; $X_S = (C_{S0} - C_S) / C_{S0}$

After integratiling equation (3) from $t=0$ where $X_{S0} = 0$ to some time, t , where the sulfur conversion is X_S , one can obtain the integral equation for determining the apparent reaction rate constant on the basis of the catalyst mass:

$$k = k_{ap}/(m_{cat}) = -\ln(1-X_S) / m_{cat} \cdot t, \quad 1/\text{g}_{cat} \cdot \text{s} \quad (4)$$

Figure 2 represents the reaction rate constant determined by applying the integral equation (4) by using the results of sulphur determination in the experiments performed with regenerated and fresh catalyst at different reaction temperatures, while Figure 3 shows the Arrhenius plot [$\ln(k)$ vs. $(1/T)$] used for calculation of the activation energy of the HDS reaction of the LGO (type A).

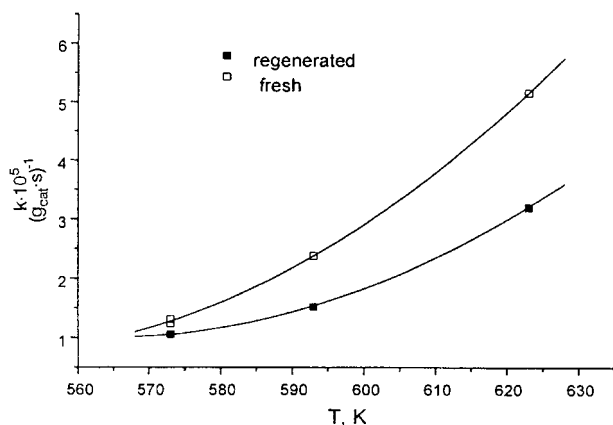


Figure 2. Dependence of the reaction rate constant on temperature

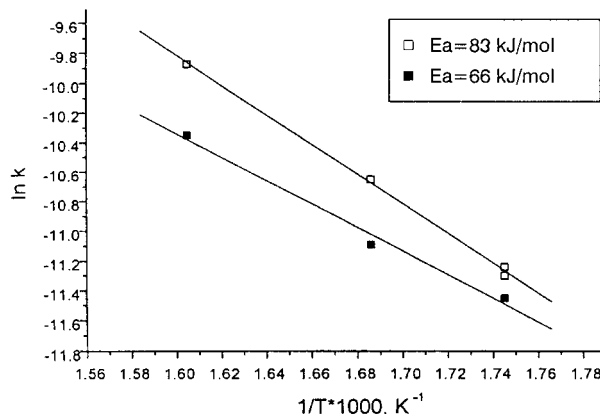


Figure 3. Arrhenius plot for determination the activation energy of the HDS process; \square – fresh catalyst, \blacksquare – regenerated catalyst.

The calculated value of the reaction rate constant agrees fairly with some data from the literature for similar type of catalyst which for specific sulfur compounds are:

Thiophene	$1.38 \cdot 10^{-3}$ (1/g _{cat} ·s)
Benzothiophene	$8.11 \cdot 10^{-4}$ (1/g _{cat} ·s)
Dibenzothiophene	$6.11 \cdot 10^{-5}$ (1/g _{cat} ·s)
Benzo(b)naphtho(2,3-d) thiophene	$1.61 \cdot 10^{-4}$ (1/g _{cat} ·s)

And results of this study:

LGO (regenerated catalyst)	$1 \cdot 10^{-5}$ – $3 \cdot 10^{-5}$ (1/g _{cat} ·s)
LGO (fresh catalyst)	$1 \cdot 10^{-5}$ – $5 \cdot 10^{-5}$ (1/g _{cat} ·s)

Calculated values of the activation energy are also of the same order as those published in the literature for some model compounds and hydrocarbon fractions similar to LGO. Obviously, this is not the true activation energy, because the complex HDS process takes into account not only resistance to the chemical (surface) reaction but also other resistances, at first those corresponding to the internal diffusion of sulfur compounds into the catalyst pores. Very interesting results from this study are that small difference exists between the reaction rate constant of fresh and regenerated catalyst at 300°C, while at a higher temperature (350°C) it is much more expressed. This is reasonable, because at 300°C regenerated catalyst has sufficient activity to be effective for some HDS reactions which are very fast at this temperature (the HDS of sulphides, disulphides and thiophenes). Only at higher temperatures, where the HDS process of some heterocyclic S compounds might be observed (dimethyl substituted dibenzothiophenes such as 4,6 dimethyl-dibenzothiophene), the initial activity of the catalyst (fresh or regenerated) becomes very important.

Experiments 3, 6, 11, 14 and 15 indicated the extent of catalyst deactivation after several uses in the same experiments performed under the same reaction conditions. It was not possible to calculate the rate of catalyst deactivation from this experiments, but it is obvious that deactivation existed. For example, usage of the fresh catalyst (twice) showed decreases of sulfur

conversion in the second run by about 10% (from 0.59 in the first to 0.52 in the second), and in the case of regenerated catalyst also by app. 10% (from 0.52 to 0.46). After each experiment performed in a batch autoclave for about 5 to 6 hours, a small amount of the catalyst was also lost from the initial mass ($m_0 = 2.8$ g), so this effect must also be taken into account for making correct conclusions regarding the rate of catalyst deactivation.

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IZVOD

HIDRODESULFURIZACIJA LAKOG GASNOG ULJA

– Ispitivanje kinetike HDS u šaržnom reaktoru

(Naučni rad)

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Ispitivanja aktivnosti novog (svežeg) i regenerisanog katalizatora tipa Cyanamid HDS 20C je realizovano u ovom radu u laboratorijskom šaržnom reaktoru (2 dm³). Smanjena aktivnost regenerisanog u odnosu na svež katalizator povezana je promenom izračunate konstante brzine reakcije desulfurizacije lakog gasnog ulja. U cilju određivanja konstante brzine merena je konverzija sumpornih jedinjenja i određivana kinetika procesa HDS primenom integralne metode. Lako gasno ulje različitog porekla (iz nafte Ural REB sa 0,92 mas% sumpora i nafte "Kikinda" sa vojvodanskih izvora sa 0,092 mas%) je korišćeno u ovim ispitivanjima.

Određena je konstanta brzine i energija aktivacije procesa HDS pod pretpostavkom da je u pitanju pseudo reakcija I reda. Dobljene brojne vrednosti su upoređene sa objavljenim rezultatima u literaturi koji se odnose na HDS čistih model jedinjenja (tiofen, benzotiofen, dibenzotiofen i supstituisani derivati ovih jedinjenja).

Utvrđeno je da postoji samo mala razlika u određenoj prividnoj konstanti brzine (tj. i aktivnosti) za sveži i regenerisan katalizator na 300°C, koja postaje sve veća kako se proces izvodi na višim temperaturama (350°C).

Ovako ponašanje regenerisanog katalizatora može se objasniti činjenicom da LGU u svom sastavu ima pored slabije reaktivnih sumpornih jedinjenja aromatskog tipa (benzo i dibenzotiofeni) i izvestan udeo jedinjenja tipa sulfida, disulfida i tiofena koji su mnogo reaktivniji. Takav odnos manje i više reaktivnih jedinjenja sumpora utiče na ukupan efekat HDS i potrebu da katalizator poseduje potrebnu aktivnost kako bi se tek na višim temperaturama ostvarila željena konverzija sumpornih jedinjenja aromatskog tipa.

Ponovljeni eksperimenti pod istim uslovima ukazuju da postoji razlika između brzina deaktivacije svežeg i regenerisanog katalizatora kao i da se brzina deaktivacije može dovesti u vezu sa objavljenim rezultatima iz literature. Međutim, uočeni efekti deaktivacije katalizatora i podaci koji se mogu iskoristiti nisu bili dovoljni da se detaljno prouči i definiše brzina deaktivacije katalizatora.

Key words: HDS • LGO • Diesel fraction • Kinetics • Catalyst activity •

Ključne reči: HDS • Lako gasno ulje • Kinetika • Aktivnost katalizatora •

- Ea=82 kJ/mol
- Ea=66 kJ/mol