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Study on single-stage hydrocracking of vacuum residue in the suspension of Ni–Mo catalyst

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Abstract

Activity of the Ni–Mo/Al_2O_3 catalyst was studied in a single-stage hydrocracking process of vacuum residue (VR) of Ural crude. The process was carried out in a continuous flow reactor, at the temperature of 410–450 °C, at the pressure of 12–20 MPa, at the liquid space velocity of 0.25–0.75 h^{-1} and at the gas space velocity of 2500 h^{-1}, and a suspension of the catalyst tested was used. The catalyst was found efficient for the hydrogenation processes, inclusive of hydrodesulphurisation processes, but its cracking activity was moderate. The catalyst concentration and hydrogen pressure did not affect significantly the VR hydrocracking process over the studied scope of parameters, and only some small effect was noticed on hydrodesulphurisation of the cracking products. On the other hand, the reaction temperature and LHSV were found to strongly affect the VR hydrocracking process and to reduce the contents of asphaltenes and CCR, while the impact on hydrodesulphurisation was lower. The reaction rates and activation energy values were determined for those reactions. The conversion figure for VR to distillates (bp < 538 °C) reached 61.6–88.7 wt.% at 430 °C, and sulphur was converted at 70–85 wt.%.

Keywords: Vacuum residue; Hydrocracking; Hydrodesulphurisation; Ni–Mo catalyst; Asphaltenes

1. Introduction

Vacuum residue (VR) makes the heaviest fraction obtained from vacuum distillation of crude oil. That contains predominantly hydrocarbons with boiling points over 520 °C, and also about 3% sulphur and 0.5% nitrogen in the form of heteroorganic compounds. Moreover, minor amounts of organometallic compounds, predominantly nickel and vanadium compounds can be found in VR. As heavy grades of crude take higher and higher shares in the crude oil pool available for processing, the refiners have to cope with the problem of increasing volumes of VR—nowadays, these volumes amount to 25 wt.% of the feed on average. When the vacuum residue is utilised as heavy fuel oil, it is responsible for considerable environmental pollution and that outlet violates the existing environmental legislation. Hence, the efficiency of present-day refineries is highly dependent on their processes for further conversion of VR. Vacuum residue can be converted into low-boiling materials in coking, visbreaking, cracking or hydrocracking processes. The dominating share of visbreaking and coking process results now from their lower investment and operating costs [1]. Hydrocracking of vacuum residue has the potential of offering better yields of high-quality motor fuels as referred to the volume of crude processed. Hence, the research work is focused on improving that process further [2–22].

Hydrocracking of vacuum residue is far more difficult than hydrocracking of crude oil distillates since VR includes considerable shares of asphaltic and resinous components. These are thermally unstable and they undergo cracking reactions readily. The obtained chemical compounds are cokes forming product [23]. Most contaminating components present in crude oil (compounds of sulphur, nitrogen and heavy metals) are derived from asphaltic and resinous substances, and in particular with asphaltenes. Asphaltenes are the compounds with the most complex chemical structures and highest molecular weights. That a group incorporates condensed polycyclic aromatics, inclusive of

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heterocyclic compounds [24]. Asphaltenes contained in VR are well soluble in that residue despite their high molecular weights. The cracking process carried out at the temperature of about 420 °C results in dealkylation and dehydrogenation of asphaltenes what is favourable for coke formation. The parameter, which reflects the propensity of oil products to coking is Conradson Carbon Residue (CCR). In order to reduce the volume of by-product coke formed the VR cracking process is run in the presence of hydrogen and a hydrocracking catalyst.

The objective of hydrocracking is conversion of vacuum residue to lower boiling hydrocarbon products with removing simultaneously sulphur and nitrogen compounds and heavy metals from the hydrocracking products, and with reducing the amount of coke formed in the process. The heavy metals removed from the feed and the produced coke will be deposited on the catalyst to lower its catalytic activity. Hence, the catalyst needs to be replaced continuously and so the process is usually carried out in ebullated or fluidised catalytic bed reactors. The principal task for the hydrocracking catalysts is to suppress the coke formation [5,6]. Usually, metals like Mo, Ni, Fe and Co, or their combinations like Ni–Mo are employed for that purpose. Improved cracking and hydrogenating activity of the Ni–Mo catalyst can be obtained by modifying its support material, e.g. by impregnation of Al_2O_3 with a fluoride [3]. The vacuum residue hydrocracking process usually involves the use of heterogeneous catalysts but it is also possible to use a dispersed catalyst precursor which is converted into a specific catalyst in the process itself, e.g. MoS_2 from molybdenum naphthenate. Hydrocracking of VR is usually organised as a one-step or two-step process. The two-step process frequently employs individual reactors operated at different temperatures. And the product can be recycled to improve conversion of VR.

The VR hydrocracking process is always accompanied by the hydrodesulphurisation, hydrodenitrogenation and hydrodemetallization reactions. That results from the fact that the major part of sulphur and nitrogen, and nearly all organic compounds of heavy metals can be found in thermally unstable resins and asphaltenes. These would crack at the temperatures employed for the VR hydrocracking process.

Vacuum residue hydrocracking is a very difficult process. It was implemented in the industry only after many years of research and after solving numerous process-related problems and developing new process equipment [13–22]. The most popular and well-established commercial VR hydrocracking processes it: H-Oil, LC-finning and BOC Unibo [25,26].

This paper presents the activity for the suspension of the Ni–Mo/Al_2O_3 catalyst employed in the vacuum residue hydrocracking process. In particular, the effect was studied from the process parameters on the conversion of VR to light products and on the reduced sulphur, asphaltenes and CCR contents in the obtained hydrocracking products. The selected catalyst was expected to convert efficiently VR and yield considerable volumes of light cuts (gasoline and diesel oil) with simultaneous hydrodesulphurisation.

2. Experimental

2.1. Materials

The hydrocracking experiments involved the vacuum residue of Ural crude (initial boiling point: 405 °C; content of: 538 °C+ residue 88.4 wt.%, sulphur 2.54 wt.%, nitrogen 0.53 wt.%, asphaltenes 5.24 wt.%, CCR 15.8 wt.% and heavy metals: V 150 ppm, Ni 45 ppm).

Ni–Mo/Al_2O_3 was employed as a catalyst; it was crushed and sieved, and its <0.06 mm fraction was used in tests. Its specification has been presented below: specific volume 0.64 $cm^3 g^{-1}$, specific surface area 260 $m^2 g^{-1}$, average pore radius 3.7 nm, porosity 67%, bulk density 1.047 g dm^{-3}.

The surface area (BET) and the porous structure of the catalyst was investigated by means of the nitrogen adsorption and desorption method at the temperature of −196 °C, with the use of the NOVA 2200 Quantachrom equipment. The porous structure and porosity were studied with the use of the mercury porosimetry method and Pascal 440 tester.

The tested Ni–Mo/Al_2O_3 catalyst was expected not only to catalyse the VR hydrocracking process but to catalyse the hydrogenation processes as well, i.e. first of all to prevent coking [5] and to desulphurise the hydrocracking products.

2.2. Hydrocracking of vacuum residue

The flow-through test stand, made of stainless steel, was employed for the investigations of the VR hydrocracking process. The arrangement of that equipment was shown in Fig. 1. The flow experimental reactor makes the principal element of the stand. Its volume is 0.6 dm^3 and its design makes the liquid circulate. That is a flow reactor with internal circulating pipe [23,27], and hydrogen is both a reacting substance and a mixing agent at the same time.

The VR hydrocracking process was studied at the temperature of 410–450 °C, under the pressure of 12–20 MPa, in the presence of the Ni–Mo/Al_2O_3 catalyst, which had been ground to reduce its grain size down to below 0.06 mm. The vacuum residue was mixed with 1–10 wt.% of catalyst at 150 °C. That mixture was then fed from the mixer (1), by means of the pump (2), to the reactor (4), at the liquid hourly space velocity (LHSV) of 0.25–0.75 h^{-1}. The compressor (3) was employed to force hydrogen to the reactor (4), at the pressure of 12–20 MPa and at the gas hourly space velocity of 2500 h^{-1}. The reaction mixture was then transferred to the separator (5) wherefrom the liquid products with catalyst in it were drained periodically. The gaseous products and unconverted hydrogen were released to atmosphere through the cooler (6) and the flow control

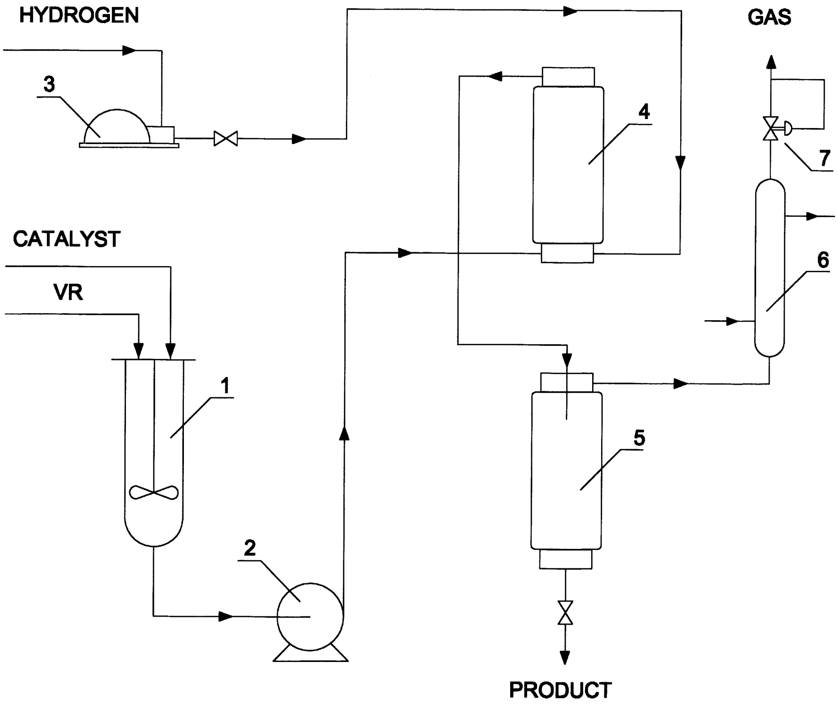

Fig. 1. A schematic diagram of the reactor used for hydrocracking of vacuum residue (for explanation see main text).

valve (7). The product gases were periodically sampled for analysis.

The liquid product was subjected to filtration at 50 °C in order to separate the catalyst. The product with no catalyst in it was then subjected to fractional distillation to produce the following fractions: gasoline, diesel oil, vacuum gas oil (VGO) and final VR. The distillation cuts were analysed for their sulphur contents, while asphaltenes and CCR were determined in VGO and VR. In order to calculate the amount of C_1–C_4 hydrocarbons formed in the process, the volume of the reactor outlet gas was measured and the concentration of gaseous VR cracking products was analysed in the gas stream.

It is most advantageous from the viewpoint of thermodynamics and kinetics to operate the VR hydrocracking process under isothermal conditions. Those conditions can be provided in a laboratory model of VR hydrocracking bubbler-type reactor with internal circulation, where the temperature difference between the reactor bottom and top is below 1 °C. That reactor operates in a similar way as the H-Oil reactor with the ebullated bed does [23].

2.3. Determination of physical–chemical properties of obtained products

- The liquid products obtained from the VR hydrocracking process were subjected to atmospheric distillation, according to the Polish Standard PN-81/C-04012. That treatment yielded the gasoline fraction with the boiling point below 180 °C. The atmospheric distillation residue was subjected to further distillation under vacuum as per the method presented in ASTM D 1160-95. The diesel oil fraction with the boiling range of 180–370 °C was subjected to further distillation under 10 mmHg vacuum, and the vacuum gas oil (VGO) fraction with the boiling range of 370–538 °C was subjected to further distillation under 1 mmHg vacuum, and 538 °C+ vacuum residue (VR) streams were produced.
- The content of C_1–C_4 hydrocarbons in gaseous products was determined by the chromatographic method: Perkin-Elmer gas chromatograph, FID detector, Chromosorb P + 25% dimethylsulfolane, 6 m × 3 mm i.d. column. Nitrogen was used as a carrier gas, and the temperature was programmed from 30 to 100 °C.
- The Fisons Instruments EA-1108 analyser (acc. to ASTM D 1552-1990) was employed for elemental analysis CHNS-O of the raw material and the liquid products obtained from the hydrocracking process. The content of Conradson Carbon Residue (CCR) was found in accordance with ASTM D 189-88. The content of asphaltenes was determined with the use of the UOP 614-80 method (extraction with n-heptane and toluene at 80 °C). Asphaltenes are defined as materials which are heptane insoluble–toluene soluble.

Conversion figures for VR as well as sulphur, asphaltenes and CCR were calculated by balancing the contents of those components in the feed and in the hydrocracking products in the following equation:

$$C_i = 100\frac{(m_{\text{feed}}x_{i\,\text{feed}} - \sum m_i x_i)}{m_{\text{feed}}x_{i\,\text{feed}}}$$

where C_i is the conversion for component "i"; m_{feed} the weight of feed (VR), $x_{i\ \text{feed}}$ the weight fraction of component "i" in feed, m_i the weight of component "i", and x_i the weight fraction of component "i".

3. Results and discussion

The influence of the vacuum residue hydrocracking process parameters on the conversion figures for the raw material as well as for sulphur compounds, asphaltenes and CCR contained in the feed has been presented graphically in Figs. 2–5. The variable parameters were as follows: catalyst concentration, reaction temperature, hydrogen pressure and liquid hourly space velocity. Fig. 6 provides the effects of reaction temperature, hydrogen pressure and liquid hourly space velocity on the yields of hydrocarbon fractions obtained from fractional distillation of the VR hydrocracking liquid product. Table 1 provides rate constant and activation energy values for the analysed reactions, while Table 2 shows sulphur contents in hydrocarbon fractions obtained from distillative separation of the hydrocracking products.

3.1. Effect of catalyst concentration

The employed Ni–Mo/Al_2O_3 catalyst is a bi-functional catalyst; it is active in the cracking and hydrogenation reactions at the same time. The support material, i.e. Al_2O_3, provides the cleavage function. Its cleavage activity is dependent on acidity of its acid centres which catalyse the reactions proceeding via the ionic mechanism, inclusive of cracking of C–C bonds. The support material employed in that catalyst is a weak acid and hence its cleavage performance is moderate. The hydrogenation function in the catalyst is provided by the system of transition metals Ni–Mo deposited on the support surface. The hydrogenation reactions catalysed by that system follow the radical mechanism.

The basic function of the hydrocracking catalyst in the discussed process is to eliminate the condensation reactions of highly unsaturated compounds that yield from the cracking process. Said condensation reactions are responsible for the formation of coke in the reactor or in the downstream equipment, hence for process disturbances. Another important function of the hydrocracking catalysts is boosting the hydrofining reactions of the VR hydrocracking products, inclusive of hydrodesulphurisation.

Fig. 2 presents the relations between the catalyst concentration and conversion figures for VR, sulphur, asphaltenes and CCR. Experiments were carried out for the catalyst concentration range of 1–10 wt.%, for the reaction temperature of 430 °C, for LHSV of 0.5 h^{-1} and at pressure of 16 MPa. As can be seen from the presented profiles, VR conversion is in practice constant and it amounts to about 62%. It is dependent on catalyst activity and/or catalyst concentration to a limited extent only. That fact proves that the cracking reactions result from thermal cleavage of C–C bonds. The effect of catalyst concentration on the conversion of asphaltenes and CCR contained in VR is also low, and the increase of catalyst concentration from 1 to 10% improves the conversion of asphaltenes and CCR by 4%.

The effect of catalyst concentration on the VR hydrodesulphurisation process is more sharply outlined since hydrodesulphurisation is a catalytic process and it is strongly controlled by the catalyst activity. The increase of catalyst concentration from 1 to 10% improves the conversion of sulphur from 70 to 88%. It is known from literature reports that any reduced activity of the hydrocracking catalyst results in increased volumes of coke produced in the cracking process. In laboratory tests, lowering the catalyst concentrations from 10 to 1 wt.% did not result in increased

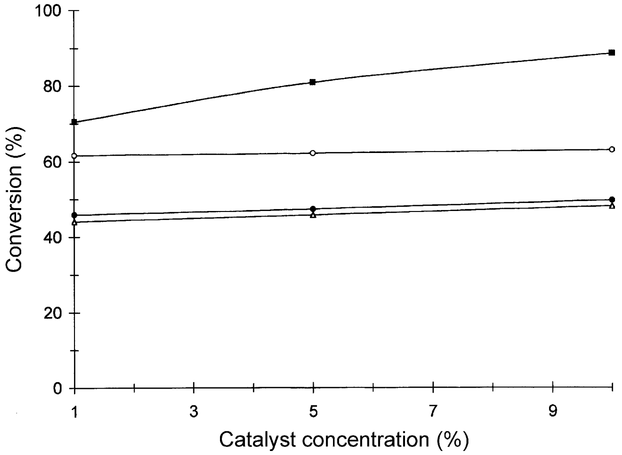

Fig. 2. Influence of catalyst concentration on VR, sulphur, asphaltenes, and CCR conversion: (T = 430 °C, P = 16 MPa, $V_{\text{feed}} = 0.5\ h^{-1}$). (○) VR, (■) Sulphur, (△) Asphaltenes and (●) CCR.

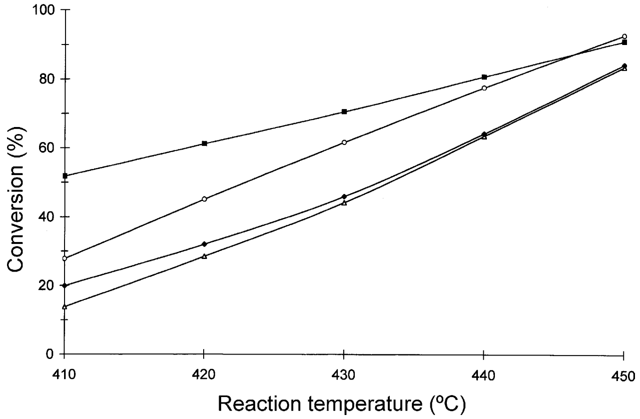

Fig. 3. Influence of reaction temperature on VR, sulphur, asphaltenes, and CCR conversion: (P = 16 MPa, $V_{\text{feed}} = 0.5\ h^{-1}$, C_{CAT} = 1%). (○) VR, (■) Sulphur, (△) Asphaltenes and (●) CCR.

volumes of coke. The catalyst residence time in the reaction zone was too short in the tests to significantly lower the catalyst activity. Any increased production of coke was also too small to be detected. Since the catalyst concentration affects the conversion of VR and improves the quality of products slightly only, the catalyst concentration of 1 wt.% was selected for further investigations on the VR hydrocracking process.

3.2. *Effect of reaction temperature*

The temperature effects on the conversion of vacuum residue, sulphur, asphaltenes and CCR have been presented in Fig. 3. The experiments were carried out at the catalyst concentration of 1 wt.%, under hydrogen pressure of 16 MPa, and at LHSV = 0.5 h^{-1}. Increasing process temperature results in nearly linear growth of VR conversion over the whole temperature range studied. The conversion figure climbs up from 27.8% at 410 °C to 92.7% at 450 °C. Reaction temperature effect on the hydrodesulphurisation process is much lower what results from the specific properties of the catalyst employed in the study. Sulphur conversion at 410 °C amounts to about 52% while the temperature increase to 450 °C brings it up to 91%. That confirms high catalytic activity in the desulphurisation process over a wide range of temperatures. Conversion of asphaltenes and CCR changes with the increasing temperature according to a model that is similar to that for VR, but the conversion figures for asphaltenes and CCR are by ~10% lower. The investigation programme revealed that the higher conversion can be expected for sulphur, then the conversion of VR follows (especially at low temperatures), and asphaltenes and CCR will offer the poorest conversion over the studied scope of process parameters.

The temperature effect is represented in the kinetic equation by the rate constant which is characteristic for the reaction rate and catalyst activity. The obtained findings were utilised to determine average rate constants for the hydrocracking reactions of VR and asphaltenes contained therein, and also for the simultaneous hydrocracking products hydrodesulphurisation reactions and for the reactions which reduce their CCR content by way of hydrogenation. One should understand averaged apparent values here since the desulphurisation, hydrocracking and hydrogenation processes cover a number of chemical reactions and not single and specific reactions. Hence, the kinetic calculations were referred to a model representing the whole group of chemical transformations of the same type, e.g. hydrodesulphurisation. For the first-order reactions, the rate constants can be found from Eq. (1), where t is the reaction time, and c_0 and c_t the concentrations of the studied substances in the feed and in the hydrocracking product, respectively, after the reaction time t. The reaction time was assumed at 120 min, i.e. the average VR residence time in the reactor at LHSV = 0.5 h^{-1}. When the rate constant values have been found for a few temperatures, the activation energy E_a can be calculated from the Arrhenius equation (2), where T is the absolute temperature, R the gas constant equal to 8.3134 J/(°C mol), and A a constant value.

$$k = \frac{1}{t} \ln \frac{c_0}{c_t} \tag{1}$$

$$\log k = -\frac{E_a}{2.303R}\frac{1}{T} + \log A \tag{2}$$

The average rate constant values k were calculated from Eq. (1) for three temperatures within 410–430 °C and plotted as log k versus 1/T. Straight lines were obtained which were utilised to determine the activation energy values. The average values for the rate constants k and for the activation energy for individual reactions were presented in Table 1. The activation energy value found for the hydrodesulphurisation reaction is relatively low and it amounts to 37.4 kJ/mol. That proves a high activity of the catalyst in the hydrodesulphurisation reaction, and for a relatively low influence from temperature on the reaction. The VR hydrocracking reaction has a much higher activation energy value, and even higher value is specific for the reactions that are responsible for the reduction of asphaltene and CCR contents in the hydrocracking products. That evidences lower catalyst activity in those reactions and lower rates of those reactions. Hence, lower conversion of VR, asphaltenes and CCR can be obtained under mild temperature, and the temperature effects are stronger for those reactions, what can be observed in plots (Fig. 3).

3.3. *Effect of liquid space velocity*

In order to study the effect of space velocity of the feed on the VR hydrocracking process, the following conditions were adopted for the experiments: reaction temperature 430 °C, pressure 16 MPa, catalyst concentration 1 wt.%. As can be seen from the profiles presented in Fig. 4, the reduced liquid space velocity (i.e. longer average residence time for the liquid in the reactor) improves conversions of VR, sulphur, asphaltenes and CCR. What is observed is a sharp rise in the conversion figures for asphaltenes and CCR while general conversion of VR is not affected so severely. Any changes in the liquid hourly space velocity affect the conversion of sulphur in a more mild way. Thus, the conversion figure for sulphur amounts to 61% at the liquid space velocity = 0.75 h^{-1}, and for LHSV = 0.25 h^{-1} it climbs up to 85%. For the same process conditions, the reduction in LHSV from 0.75 to 0.25 h^{-1} improves the VR conversion from 41 to 83%, that of asphaltenes from 19 to 83%, and that of CCR from 17 to 81%.

When the reaction temperature effects within 410–450 °C (for LHSV = 0.5 h^{-1}, Fig. 3) are compared to those of LHSV within 0.75–0.25 h^{-1} (for temperature of 430 °C, Fig. 4), those parameters are seen to have much similar influence on the conversion of asphaltenes and CCR. As regards the conversion figure for VR and sulphur, the effect from temperature is much stronger than that from LHSV.

3.4. *Effect of hydrogen pressure*

Fig. 5 makes the graphical presentation for the effect of hydrogen pressure on the vacuum residue hydrocracking process for the experiments which have been carried out under the following conditions: reaction temperature 430 °C, liquid hourly space velocity 0.5 h^{-1}, catalyst concentration 1 wt.%. When the hydrogen pressure is increased from 12 to 20 MPa, conversion of asphaltenes and CCR rises by about 10%. The effect of hydrogen pressure on the conversion of sulphur and VR is not so well marked. Over the pressure range studied, sulphur conversion improves by 3% with the rising pressure, and conversion of VR declines at the same time by 3%. That is a surprise since hydrodesulphurisation is a catalytic process that is strongly affected by both catalytic activity and hydrogen pressure.

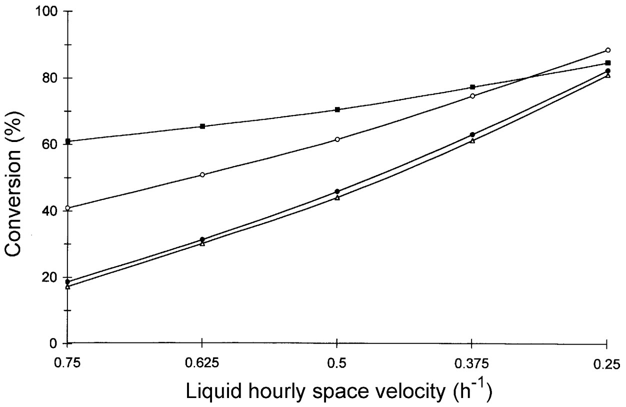

Fig. 4. Influence of liquid hourly space velocity in the reactor on VR, sulphur, asphaltenes, and CCR conversion: (T = 430 °C, P = 16 MPa, C_{CAT} = 1%). (○) VR, (■) Sulphur, (△) Asphaltenes and (●) CCR.

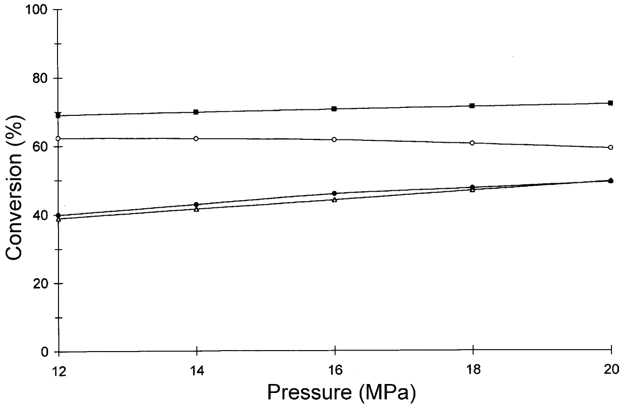

Fig. 5. Pressure effect on VR, sulphur, asphaltenes, and CCR conversion: (T = 430 °C, V_{feed} = 0.5 h^{-1}, C_{CAT} = 1%). (○) VR, (■) Sulphur, (△) Asphaltenes and (●) CCR.

Table 1
Reaction rate constants and activation energies for studied reactions that make up hydrocracking of vacuum residue

	Rate constant values k (min^{-1})			Activation energy value E_a (kJ/mol)
	410 °C	420 °C	430 °C	410–430 °C
VR	0.0277	0.0317	0.0343	86.9
Sulphur	0.0329	0.0343	0.0355	37.4
CCR	0.0249	0.0289	0.0319	109.4
Asphaltenes	0.0219	0.0279	0.0316	135.4

The moderate impact from the hydrogen pressure on the VR hydrocracking process and on hydrocracking products desulphurisation process can be accounted for by the fact that the experiments were carried out at a huge excess of hydrogen to provide good mixing conditions for the suspension in the reactor employed for laboratory tests. The hydrogen flow was 50 times higher than the stoichiometrically calculated amount to be consumed in the hydrogenation reactions.

3.5. *Influence of process parameter on product composition*

Fig. 6 presents the effects of process parameters on the composition of the vacuum residue hydrocracking products. The effects were defined by the volumes of fractions obtained from fractional distillation of the reaction products. Higher reaction temperatures clearly reduce the volume of the heaviest fraction—VR. That fraction, despite the same initial boiling point as for the feed, is characterised by a different chemical composition and somewhat different physical–chemical properties than the feedstock. For example, asphaltenes contained in the starting VR are well soluble in that residue, and asphaltenes contained in the final VR do not dissolve readily in that material. The reason is dealkylation of hydrocarbon substituent groups from condensed aromatic rings, hence increased aromaticity of asphaltenes [6] and their inferior solubility in paraffin hydrocarbons present in the hydrocracking products.

For higher reaction temperatures, the yields of the lightest fractions: gases and gasoline, are a bit higher—the higher the temperature, the higher the yield is. The shares of methane, ethane, propane and butane in the gas fraction are nearly equimolar, and any change in the parameters does not change the ratio of components in the gas fraction. The cracking and hydrocracking processes catalysed by carbonate ions produce much less methane and ethane than propane and butane. The catalytic mechanism for carbonate ions generates high shares of iso-compounds both in C_4 fraction and in gasoline. The hydrocarbons C_1–C_4 are formed in equimolar amounts in the studied process, and the content of C_4 hydrocarbons is low. Hence, apparently the cracking process is not catalysed by carbonate ions but it is a thermal process.

The weight share of gasoline fraction in the gas products is comparable to that of gas fraction, and that ratio is slightly

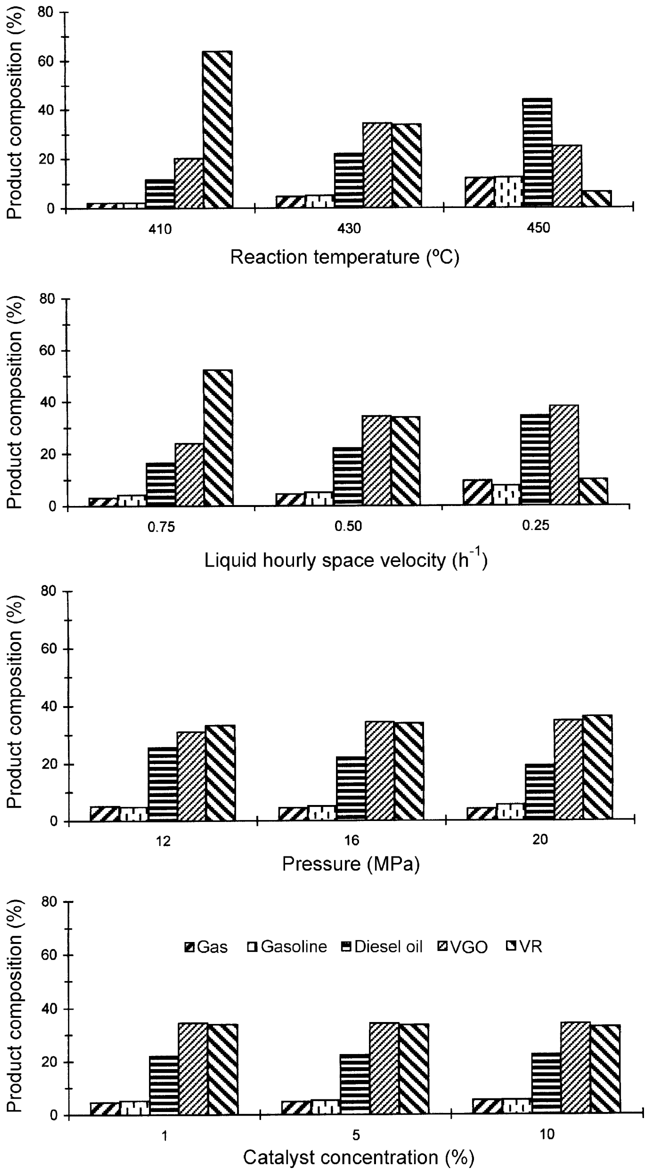

Fig. 6. Influence of process parameter on product composition. (○) Gas, (■) Gasoline, (△) Diesel oil, (●) VGO and (□) VR.

only influenced by any change in parameters. The temperature effect is much higher in case of diesel oil fraction. Its yield amounts to 11.5% at 410 °C and it goes as much high as to 44.2% at 450 °C. The yield of VGO reaches its peak value of 34.3% at 430 °C, and when the temperature is further increased to 450 °C, its value drops down back to 25%. The reason is that above 430 °C any further increase in temperature consumes more VGO (in its cracking to lighter cuts) than is formed from VR cracking. The VGO fraction is not any less valuable than motor fuel cuts. It makes a feed to the catalytic cracking process to produce motor fuels, and it also makes a good quality oil pool for the production of lube oils, or it can be used as fuel oil.

Lowering liquid hourly space velocity from 0.75 to 0.25 h^{-1} clearly increases the conversion degree of VR what is reflected by higher yields of all hydrocarbon fractions, which are lighter than VR. Higher temperatures and expanded mean residence times for raw material in the reactor improve the yields of the most valuable fractions, i.e. gasoline, diesel oil and vacuum gas oil. The volume of less demanded gas fraction rises as well. The effect of residence time on the conversion of the cuts lighter than VR is similar within the studied range of parameters to the temperature effect but it is less intensive.

The shares of hydrogen fractions in the hydrocracking products were slightly affected by the hydrogen pressure within 12–20 MPa. Some small increase for higher-boiling fractions was observed for higher hydrogen pressures. That can testify that the hydrogenation reactions became prevailing over the cracking reactions when the pressure was raised. The catalyst concentration in the studied range of 1–10 wt.% does not affect strongly the shares of hydrocarbon fractions in the hydrocracking products, but the production of lighter fractions increases somewhat with the increasing catalyst concentration.

3.6. *Influence of process parameters on reaction product hydrodesulphurisation*

The VR hydrocracking process is accompanied by hydrodesulphurisation reactions. In order to characterise the scope of hydrodesulphurisation for the obtained hydrocracking products, Table 2 presents the sulphur contents in hydrocarbon fractions obtained from the distillation of the VR hydrocracking products versus process temperature, pressure, feed LHSV and catalyst concentration. The sulphur content in any fraction obtained from the process is much lower than that in the feed (2.54 wt.%). The lighter the product fraction, the lower its sulphur content is. The gasoline fraction has the sulphur content of 0.014–0.095 wt.%, while the sulphur content in the diesel oil fraction increases to 0.17–0.40 wt.%. These values are close to sulphur contents in gasoline and diesel oil fractions obtained by distillation of crude oil. Hence, the fractions obtained from distillation of VR hydrocracking products can be subjected to hydrofining jointly with the crude oil distillation cuts.

The sulphur content in VGO fractions amounts to 0.32–0.77 wt.%. These fractions can thus make feeds to the catalytic cracking plants to be converted into fuel cuts. The highest sulphur content has been met in the vacuum distillation residue from the VR hydrocracking products (1.11–1.60 wt.%) but it is by 40% lower than the sulphur level in the feedstock. Hence, VR hydrocracking can yield additional volumes of valuable light hydrocarbon fractions and it can remove considerable shares of sulphur at the same time. In order to show the level of hydrodesulphurisation versus the process parameters studied, Table 2 provides participation figures for sulphur in individual fractions separated from VR hydrocracking products in relation to the sulphur levels in the hydrocracking feed. As can be seen, the motor fuel fractions contain small shares only of sulphur left

Table 2
Influence of process parameters on sulphur content in products obtained from VR hydrocracking

Process parameters				Sulphur content in products of VR hydrocracking (wt.%)				Sulphur participation from VR in products of hydrocracking (%)				
Temperature (°C)	LHSV (h^{-1})	Pressure (MPa)	Catalyst content (%)	Gasoline	Gas oil	VGO	VR	Gasoline	Gas oil	VGO	VR	Σ
Vacuum residue—raw material				–	–	–	2.54	–	–	–	100	
Effect of reaction temperature												
410	0.5	16	1	0.07	0.40	0.77	1.60	0.05	1.81	6.12	40.19	48.17
430	0.5	16	1	0.05	0.31	0.54	1.46	0.09	2.69	7.29	19.48	29.55
450	0.5	16	1	0.03	0.17	0.32	1.11	0.12	2.96	3.15	2.80	9.03
Effect of liquid hourly space velocity												
430	0.25	16	1	0.01	0.30	0.40	1.28	0.03	4.09	6.00	5.04	15.16
430	0.50	16	1	0.05	0.31	0.54	1.46	0.09	2.69	7.29	19.48	29.55
430	0.75	16	1	0.10	0.33	0.63	1.50	0.14	2.13	5.93	30.83	39.02
Effect of hydrogen pressure												
430	0.5	12	1	0.06	0.32	0.68	1.49	0.09	3.23	8.30	19.48	31.09
430	0.5	16	1	0.05	0.31	0.54	1.46	0.09	2.69	7.29	19.48	29.55
430	0.5	20	1	0.04	0.25	0.47	1.27	0.08	1.89	6.42	18.10	26.49
Effect of catalyst concentration												
430	0.5	16	1	0.05	0.31	0.54	1.46	0.09	2.69	7.29	19.48	29.55
430	0.5	16	5	0.03	0.22	0.38	0.92	0.06	1.92	5.10	12.12	19.20
430	0.5	16	10	0.01	0.12	0.21	0.60	0.02	1.06	2.81	7.71	11.60

in the hydrocracking products. Light hydrocarbons produced in VR hydrocracking, equivalent to the gasoline cut, contain only 0.02–0.14 wt.%, and those equivalent to the diesel oil cut contain 1.06–4.09 wt.% of sulphur introduced with the feed. The VGO fraction contains 2.81–8.30 wt.%, and secondary VR contains 5.04–40.19 wt.% of sulphur contained in the primary VR material. That proves high activity of the Ni–Mo/Al_2O_3 hydrocracking catalyst in the desulphurisation processes.

When the effect of the studied hydrocracking parameters on the conversion of desulphurisation of the VR hydrocracking products (Figs. 2–5) is compared to the sulphur contents in those products (Table 2), one can notice that the hydrocracking products hydrodesulphurisation level is chiefly affected by the reaction temperature, LHSV (i.e. reaction time) and catalyst concentration. The effect from the hydrogen pressure is low. That is unusual since the literature reports declare the hydrodesulphurisation level to be predominantly influenced by the catalyst activity and hydrogen pressure. That low impact from the hydrogen pressure on hydrodesulphurisation of the hydrocracking products can be explained by the fact that, under adopted process conditions, hydrocracking and hydrodesulphurisation take place at a huge excess of hydrogen. Hence, diffusion of hydrogen to the catalyst, within 12–20 MPa, is not a conversion-limiting factor. So, any change in the hydrogen pressure hardly affects the rates of hydrogenation processes. The excessive volume of hydrogen is necessary to maintain hydraulics of the process, in particular to provide the fluidised bed conditions.

The reactor model with internal circulation, as adopted for our laboratory tests, assures high internal circulation at high hydrogen flow-rates, so the reacting substances are perfectly mixed. And that results in high diffusion to the catalyst surface and improved reaction rate (in particular for hydrogenation reactions). The hydrogenation reactions are exothermic reactions. The exothermic balance of the VR hydrocracking process results predominantly from the hydrodesulphurisation reaction. The advantage of the reactor model adopted for the study is its nearly isothermal regime what is especially needed in the VR hydrocracking process since higher temperatures are responsible for excessive and unwanted cracking of VR, and hence for excessive coking inside the reactor.

4. Conclusions

The catalytic performance was studied for the difunctional Ni–Mo/Al_2O_3 catalyst in the single-stage VR hydrocracking process, with a suspended catalyst bed. The Ni–Mo/Al_2O_3 catalyst employed in the tests was found to be efficient in hydrogenation processes, inclusive of hydrodesulphurisation processes, while its cracking potential is moderate.

Within the VR hydrocracking parameters, the catalyst concentration in the reaction mixture influences hydrodesulphurisation of the VR cracking products only, while the effect on the VR conversion to lighter products and/or on lowering the asphaltene and CCR contents in those products is none in practice. That results from the properties of the catalyst employed, where the support material—Al_2O_3—is weak acidic, so it has some minor cracking performance. The hydrogen pressure has no effect on VR hydrocracking over the studied scope. It slightly affects the hydrodesulphurisation process only and is responsible for reduction of asphaltene and CCR contents. The reason can be a high excess of hydrogen adopted in experiments, what was required for efficient fluidisation of the reaction mixture and catalyst, but what was far above the hydrogenation stoichiometry.

High effects on VR hydrocracking were observed from the reaction temperature and LHSV (reaction time). Any increase in temperature or contact time strongly improves VR conversion to lighter products and reduces asphaltene and CCR shares in those products. That can be explained by the thermal nature of the VR and asphaltenes cracking processes. The reaction time and temperature affect the VR hydrocracking products hydrodesulphurisation processes to a lower degree—hydrodesulphurisation processes are catalytic processes. The activation energy values found for those reactions confirm the above statements since hydrodesulphurisation has the lowest activation energy, hence it is the least susceptible to temperature effects.

The studied catalyst makes it possible to convert VR into considerable volumes of valuable lighter fractions; their quality makes them useful in motor fuel blending. At 430 °C, conversion of VR to distillates (bp < 538 °C) reached 61–88.7 wt.%, with sulphur conversion amounting to 70–85 wt.%.

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