

The Use of Supercritical Solvents in Polyaromatic Conversion

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Nowadays, the processes aimed at the deep conversion of heavy oil are of great interest. **Polyaromatic and sulfur-containing compounds (such as anthracene and dibenzothiophene) are one of the main components of heavy oil fractions which are hard to process.** Catalytic hydrotreatment of heavy petroleum fractions (vacuum gas oil, light gas oil, etc.) is widely used to improve the quality of the resulting products. As the hydrotreatment of oil fractions often requires the use of harsh process conditions and consumes a high amount of molecular hydrogen, the researchers' interest is focused on the development of novel approaches including the use of supercritical fluids. In this work, the influence of solvent in the supercritical state on the conversion and product composition of cracking and desulfurization of **polyaromatic and sulfur-containing compounds is described.** The experimental results showed that the use of **a supercritical solvent mixture composed of n-hexane and methanol** allows the polyaromatic compounds to be effectively converted into monoaromatics providing a high conversion degree (up to 95 %).

1. Introduction

Oil is a complex mixture of highly hydrophobic hydrocarbons. The molecules can also contain some other elements such as oxygen, nitrogen, sulfur, or phosphorus. Crude oil mainly consists of linear hydrocarbons with the number of carbon atoms from 4 to 30, as well as aromatic and naphthenic compounds. Gasoline is a mixture of short-chain hydrocarbons (4-8 atoms), while diesel consists of higher-molecular carbon chains (12-20 atoms). Mineral fuel is a complex specific mixture of hydrocarbons, in fact, a mixture of linear, isomeric alkanes, cycloalkanes, and aromatic compounds.

Catalytic hydrotreatment of petroleum fractions is an established and widely used purification technology, usually **applied** to improve the quality of oil fractions. There are two types of hydroconversion technologies: catalytic hydrotreatment and catalytic hydrocracking. The hydrotreatment process aims at the removal of undesirable heteroatoms such as sulfur, nitrogen, and oxygen as well as metals, and partial reduction of aromatics (Biswas and Maxwell, 1990). Catalytic hydrocracking is a conversion process that primarily aims at a decrease in the boiling point of petroleum fractions. It is used for processing heavy oil fractions, gas oil, vacuum gas oil, etc. Liquid-phase catalytic cracking is the technology most commonly used for converting heavy oil fractions to produce gasoline and propane (Primo and Garcia, 2014).

Currently, the developments in oil hydroconversion are aimed at a decrease in the cost of processes. The modern tendencies include the search for new catalysts and process conditions. One of these approaches is the use of supercritical and subcritical fluids (SCF) as solvents for hydrocracking and hydrodesulfurization processes (Ates *et al.*, 2014). Water is the most often used solvent in the hydroprocessing of heavy oil fractions. In the supercritical state, water is non-polar and perfectly dissolves hydrocarbons (Hosseinpour *et al.*, 2018). The use of supercritical water (SCW) in desulfurization is prospective due to water oxidative capacity, which leads to the removal of both sulfur atoms and other heteroatoms (nitrogen, metals, oxygen) (Timko *et al.*, 2015). Hydrocracking processes in SCW are characterized by both high conversion (Reina *et al.*, 2016) and yield of light fractions (gasoline, kerosene) (Tan *et al.*, 2017) due to the hydrothermal destruction of heavy hydrocarbons (Yeletsky *et al.*, 2019). Besides, water in the supercritical state serves as a

hydrogen donor, which allows processes to be carried out in an inert atmosphere (Gai *et al.*, 2016). As water has a respectively high critical point ($T_c = 374.15\text{ }^\circ\text{C}$, $P_c = 22.13\text{ MPa}$), the researchers try to find the alternative solvent characterized by the lower critical temperature. Supercritical hydrocarbon solvents such as tetralin (Kim *et al.*, 2018), hexane, and dodecane (Viet *et al.*, 2012) can also serve as hydrogen donors. All studies indicate that the use of supercritical solvents, in addition to the complete removal of heteroatoms and high conversion of raw materials, leads to a decrease in the viscosity and density of the resulting product, and also prevents coking of the catalyst, providing a longer lifetime (Kim *et al.*, 2018).

The second direction of the development of hydroprocessing is the use of oxide catalysts. The activity of oxide catalysts in hydrodesulfurization and hydrocracking processes directly depends on the dispersion of the active phase and the presence of hydroxyl groups on the surface of the catalyst (Dhar *et al.*, 2003). High dispersion of the active phase can be achieved by special methods of catalyst synthesis, in particular, the use of a hydrothermal deposition. Work on hydrotreatment of heavy oil fractions in the presence of catalysts obtained using supercritical fluids has shown that the high surface area of catalysts, the presence of a large number of hydroxyl groups, and the unique morphology (high dispersion, uniformity of distribution, the small size of active phase particles) of such catalysts leads to an increase in the efficiency of hydroconversion processes of petroleum feedstock (Alibour *et al.*, 2009), providing both a high degree of sulfur removal (Haji *et al.*, 2010) and highly selective cracking of petroleum hydrocarbons (Quilfen *et al.*, 2018). Besides, such catalysts are highly active without prior sulfidation (Haji *et al.*, 2010).

The current work is aimed at the choice of supercritical solvent for cracking and desulfurization processes in the presence of metal oxide-containing catalysts that allows high conversion of heavy oil component to be reached. The results obtained in this research will be the basis for developing modern approaches for deep oil processing.

2. Experimental

2.1 Catalyst preparation

The catalysts were synthesized according to the following procedure. Polymeric support – hypercrosslinked polystyrene with tert-amino groups Macronet (MN-100, Purolight Inc., UK) was modified with silicon oxide to provide strong acid sites. The polymer surface modification was performed by hydrolysis of (3-aminopropyl)triethoxysilane (APTES, 99.9 %, Sigma Aldrich, USA) in preheated water. In a typical experiment, 3 g of MN-100, and 10 mL of distilled water were placed into the reactor (PARR 4307, Parr Instrument Ltd., USA). The reactor was sealed, purged with nitrogen, and heated up to $150 \pm 5\text{ }^\circ\text{C}$ under a nitrogen pressure of 6.0 MPa. Then, 1.17 mL of APTES (calculated as 10 wt % of SiO_2 on the 1 g of MN-100) were added dropwise into the reactor through the burette. The mixture was held at the indicated conditions for 60 min, cooled down to room temperature, and filtered. The resulting sample was heated under the nitrogen at $250 \pm 5\text{ }^\circ\text{C}$ for 4 h to form the silica phase.

The catalyst was prepared by hydrothermal deposition (Stepacheva *et al.*, 2019). 3 g of the modified polymer, 1.5 g of nickel nitrate hexahydrate and 1.43 g cobalt nitrate hexahydrate (calculated as 10 wt % of Ni and 10 wt. % of Co on 1 g of the support), and 15 mL of distilled water were placed into the reactor (PARR 4307, Parr Instrument Ltd., USA). The reactor was sealed, purged with nitrogen, heated up to $200 \pm 5\text{ }^\circ\text{C}$ under a nitrogen pressure of 6.0 MPa, and held for 15 min. Then, the reaction mixture was cooled down to room temperature and filtered. The resulting catalyst was washed with 10 mL of distilled water to remove nitrates and dried in the air at $105 \pm 5\text{ }^\circ\text{C}$ for 1 h. The catalyst samples were reduced in the hydrogen flow (flow rate of 10 mL/min) at $300 \pm 5\text{ }^\circ\text{C}$ for 5 h.

2.2 Anthracene and dibenzothiophene conversion procedure

The experiments were performed in a six-cell Parr Series 5000 Multiple Reactor System (Parr Instrument, USA) with a cell volume of 50 mL. In a typical experiment, 1 g of model heavy-oil compound (anthracene or dibenzothiophene), 0.1 g of catalyst, and 30 mL of solvent were placed into the reactor cell. The reactor was sealed and purged three times with nitrogen to remove air. Then the nitrogen pressure was set to 3.0 MPa, and the reactor was heated up to $300\text{ }^\circ\text{C}$. These process conditions were chosen according to the critical points of the solvents. After reaching the reaction temperature, the pressure increased up to 12 MPa depending on the solvent. Experiments were performed with varying process time (from 10 min to 3 h) to maintain phase equilibrium. Methanol ($T_c = 240\text{ }^\circ\text{C}$, $P_c = 7.95\text{ MPa}$), propanol-2 ($T_c = 235.6\text{ }^\circ\text{C}$, $P_c = 5.37\text{ MPa}$), n-hexane ($T_c = 234.7\text{ }^\circ\text{C}$, $P_c = 3.03\text{ MPa}$), and benzene ($T_c = 289.41\text{ }^\circ\text{C}$, $P_c = 4.92\text{ MPa}$) were used as solvents.

2.3 Reaction mixture analysis

The liquid phase was analyzed by GCMS using gas chromatograph GC-2010 and mass-spectrometer GCMS-QP2010S (SHIMADZU, Japan) equipped with chromatographic column HP-1MS with 30 m length, 0.25 mm diameter, and 0.25 μm film thickness. The column temperature program was set as follows: initial temperature 120 $^{\circ}\text{C}$ was maintained for 5 min then the column was heated up to 250 $^{\circ}\text{C}$ with the rate of 5 $^{\circ}\text{C}/\text{min}$ and maintained at 250 $^{\circ}\text{C}$ for 5 min. Helium (volumetric velocity of 20.8 cm^3/s , the pressure of 253.5 kPa) was used as a gas-carrier. The injector temperature was 280 $^{\circ}\text{C}$, ion source temperature was 260 $^{\circ}\text{C}$; interface temperature – 280 $^{\circ}\text{C}$.

3. Results and discussion

3.1 Catalyst characterization

As the textural properties, as well as the composition of the active phase, strongly affect the heavy oil hydroprocessing the synthesized catalyst was characterized by different techniques. The catalyst porosity was studied performed using the low-temperature nitrogen physisorption (Beckman Coulter SA 3100 analyzer, Coulter Corporation, USA). Fig. 1 presents the adsorption-desorption isotherms for the initial polymer, modified polymer, and the resulting catalyst. The surface modification leads to a slight decrease in the surface area in comparison with the initial MN-100. However, the surface area of macropores increases **with the consequent decrease in micropore surface area** indicating the pore reorganization (see Table 1). This was confirmed by both the changes in the isotherm and hysteresis loop forms (Fig. 1a) as well as the pore size distribution (Fig. 1b). The deposition of the metal phase on the surface of the modified polymer did not show any changes in the porous structure in comparison with the support. Besides, neither the surface area nor pore volume practically decreased during the metal incorporation (see Table 1).

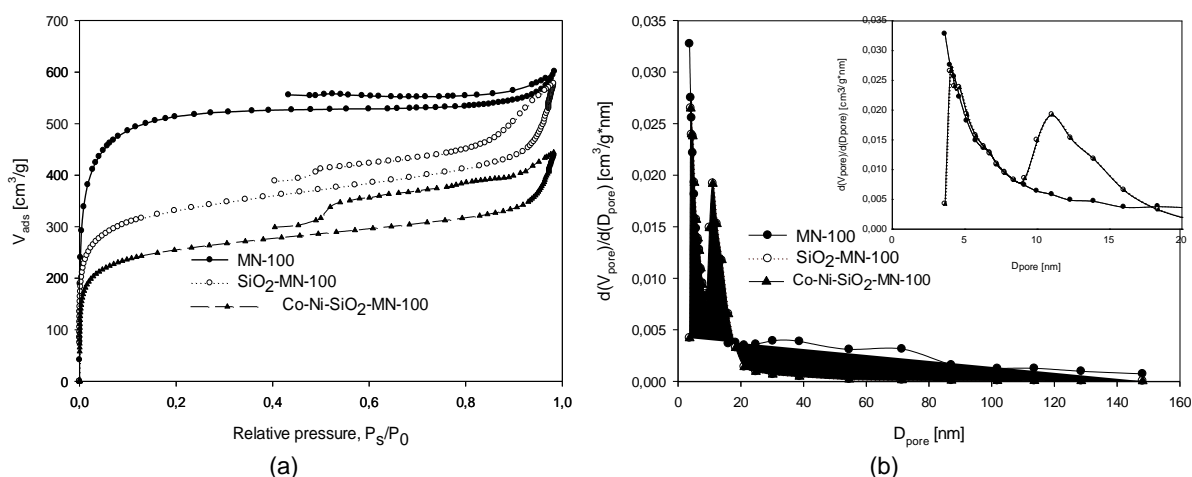


Figure 1: Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) for the synthesized catalyst

Table 1: Results of catalyst studies

Sample	S_{BET} , m^2/g	$S_{\text{t-plot}}$, m^2/g	V_{pore} , cm^3/g	Element concentration, wt. %			Total acidity, $\mu\text{mol}/\text{g}$
				Si	Co	Ni	
MN-100	840	200* 590**	0.52	-	-	-	-
SiO ₂ -MN-100	780	320* 390**	0.55	9.7	-	-	843
Co-Ni-SiO ₂ -MN-100	740	350* 320**	0.57	9.6	9.8	9.8	814

*macropore surface area, ** micropore surface area

The distribution of the silica- and metal-containing phase on the surface of polymeric support was studied by transmission electron microscopy (JEOL JEM1010, JEOL Ltd., Japan). Fig. 2 presents the TEM images for

the synthesized samples of the modified support (Fig. 2a) and the resulting catalyst (Fig. 2b). It is well seen that the deposition method used allows the SiO₂ and metal oxide particles to be distributed uniformly on the polymer surface. Moreover, the silica-containing phase seems to be precipitated on both internal and external surfaces of MN-100. The mean silica particle diameter was found to be 30±5 nm. The metal-containing phase particle size of about 2.5 nm was estimated. As the surface area decreases insignificantly, it can be proposed that the particles of the nickel-containing phase were well dispersed on the outer and inner surface of the supports.

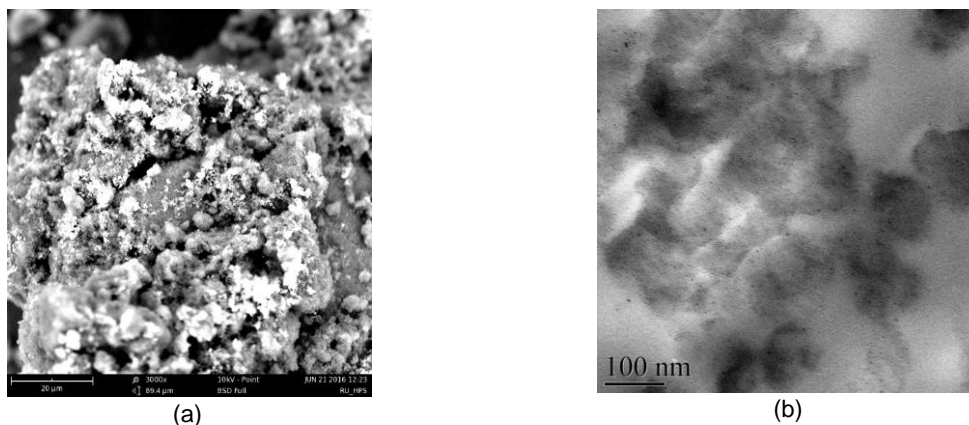


Figure 2: TEM images of modified polymer (a) and resulting catalyst (b)

Analysis of the active phase composition was performed using the X-Ray photoelectron spectroscopy (ES-2403 spectrometer equipped with PHOIBOS-100-MCD energy analyzer, Specs GmbH, Germany). The high-resolution XP spectra of Si 2p sublevel for Co-Ni-SiO₂-MN-100 shows the formation of silicon oxide and hydrated silica (Si-OH) on the MN-100 surface during the synthesis. Noteworthy, the formation of hydroxyl groups on the surface of the support leads to the recharge of the surface and facilitates the deposition of metal ions. Spectra analysis on Ni 2p sublevel showed that nickel in the catalyst is presented by the mixture of nickel (II) and nickel (III) oxyhydroxides. Analysis of the high-resolution XP spectra of Co 2p sublevel showed the formation of Co₃O₄ and Co(OH)₂ on the catalyst surface.

The measurements of catalyst acidity were carried out by the ammonia chemisorption using Micromeritics AutoChem 2910 analyzer (Micromeritics, USA). The ammonia desorption curves were typical for SiO₂ containing the peak with the activation energy of desorption less than 130 kJ/mol attributed to the weak acid sites and two peaks with the activation energy of desorption 130-180 and >180 kJ/mol characteristic for the strong acid sites. The deposition of the metal-containing phase did not decrease significantly the total catalyst acidity (see Table 1).

3.2 Solvent influence on anthracene cracking

The analysis of the liquid phase after the anthracene cracking showed the predominant formation of monoaromatics such as benzene, toluene, xylenes. Besides, the formation of some amount of dihydroanthracene, tetrahydro anthracene, and diphenylmethane was observed. Moreover, when methanol and propanol-2 were used as a solvent, the formation of *i*-propylbenzene and toluene was observed **due to the condensation**. In general, the following scheme of anthracene conversion in a supercritical solvent can be proposed (see Fig. 3).

The conversion degree seemed to be higher (up to 85 wt. %) in the polar solvent (in particular, in propanol-2). **This can be attributed to the high dehydration degree of the solvent with the following hydrogenation of the substrate**. But the higher yield of monoaromatics (up to 70 wt. %) was obtained while using *n*-hexane as a solvent **indicating the predominant behavior of C-C bond cracking**. Methanol provides the predominant formation of dihydroanthracene (over 42 wt. %), and tetrahydro anthracene (ca. 16 wt. %), while the conversion degree was about 65 wt. %. This can be explained by the higher degree of methanol dehydration in the supercritical state in comparison with the other solvents used. The lowest conversion degree (about 46 wt. %), and hence, the lowest yield of monoaromatics (34 wt. %) was found to observe when using benzene in the supercritical state, but this solvent provides the highest solubility of anthracene at the room temperature due to the similar nature.

When the solvent mixture (hexane-methanol and hexane-propanol-2) was used, the conversion degree significantly increased up to 90 and 95 wt. % respectively. In this regard, the yield of monoaromatics also

increased up to 85 wt. %. This can be attributed to the synergetic effect of the solvents resulting in the acceleration of cracking reactions with the hydrogenation of the radicals formed.

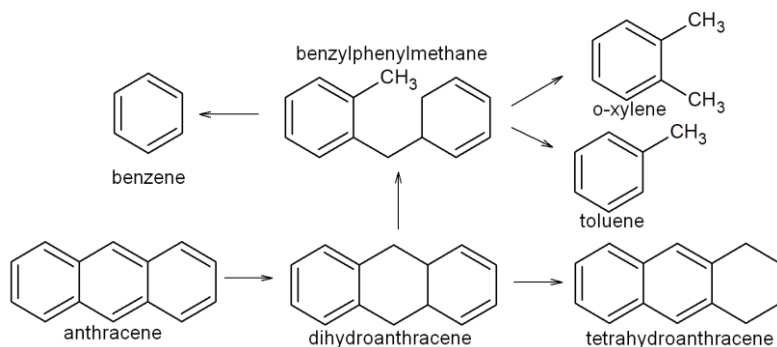


Figure 3: Possible ways for anthracene cracking in supercritical solvent

3.3 Solvent influence on dibenzothiophene desulfurization

The analysis of the liquid phase after the dibenzothiophene conversion showed the formation of monoaromatics (benzene, toluene, and biphenyl) as well as the corresponding cyclic compounds. It is interesting, that in contrast to the typical desulfurization, the formation of aliphatic hydrocarbons (heptens, methylhexene, methyl-ethyl hexane, etc.) was observed indicating the cracking reaction to have a place. In general, the following scheme of dibenzothiophene conversion in a supercritical solvent can be proposed (see Fig. 4).

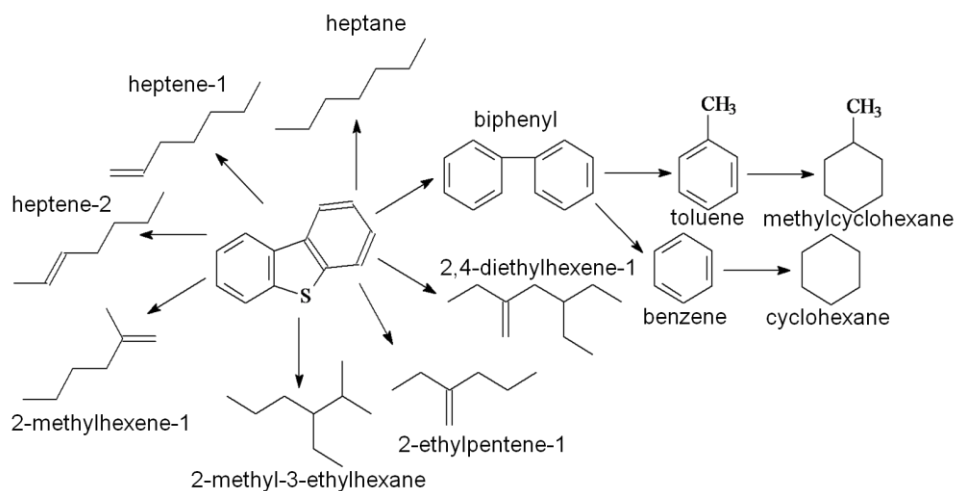


Figure 4: Possible ways for dibenzothiophene conversion in supercritical solvent

As dibenzothiophene is the oil compound which conversion is complicated, the use of supercritical solvents seems to be an effective alternative. The experimental results on the influence of solvent on dibenzothiophene desulfurization and cracking showed that in the individual solvent the conversion degree did not exceed 50 wt. %. In methanol, however, the conversion was reached up to 72 wt. % providing the formation of monoaromatics and cyclic compound with a yield of 65 wt. % in total. The lowest conversion was observed when using benzene and propanol-2 as solvents (17 and 23 wt. % respectively) that can be explained by their lower hydrogen formation activity. In this case, the predominant formation of biphenyl was observed. However, the cracking was observed in benzene. This can be explained by the fact that benzene can not be the hydrogen donor in the supercritical state.

In the solvent mixture (hexane-methanol and hexane-propanol-2) the synergetic effect was also observed (as in the case of anthracene cracking). The conversion degree increased up to 97 and 64 wt. % for hexane-methanol and hexane-propanol-2 respectively. Interestingly that in the hexane-methanol mixture the total yield of cyclic and alkene compounds was about 80 wt. %.

4. Conclusions

In the current work, the influence of supercritical solvent on the heavy oil model compound (anthracene and dibenzothiophene) conversion was studied. Four compounds (n-hexane, benzene, methanol, and propanol-2) at the conditions above the critical point were used as solvents. It was shown that the use of supercritical fluids for the conversion of polyaromatic compounds (i.e. anthracene), including the sulfur-containing (dibenzothiophene), allows the aromatics and light aliphatic products to be obtained. Moreover, the reaction pathways in supercritical fluids significantly change from those observed in the typical conversion conditions. The highest conversion degree (over 95 wt. %) was observed for both anthracene and dibenzothiophene cracking when using n-hexane-methanol (1:1 by volume).

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