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APPLICATION OF EXTRACTION AND OXIDATIVE PROCESSES OF MODEL MIXTURES WITH AIM TO DECREASING OF UNLIKELY COMPONENTS

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Abstract

All regulations agencies /EPA, EU/ have issued regulations for reducing the level of sulfur in gasoline and diesel fuel. In order to comply with these new regulations, essentially all domestic refineries are forced to install new fuel desulphurization processes. Well-known hydro treating processes are commercially available. These hydro treating processes operate at relatively high pressures and use significant amounts of hydrogen. Therefore, these processes require a significant capital investment and have high operating costs. In addition, most gasoline desulphurization processes based on hydrogenation degrade the quality of the gasoline.

In this paper is considered the possibility to use an extraction and oxidative methods as purifying methods from sulfur compounds and naphtalene from model mixtures.

Key words: purifying of motor fuel, model systems.

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1. Introduction

A process for the production of gasoline with a low sulfur content that comprises at least one selective hydrogenation of diolefins, optionally at least one stage for transformation, preferably to increase their weight, for light sulfur-containing compounds that are present in the gasoline, at least one fractionation of the gasoline that is obtained into at least two fractions: light gasoline and heavy gasoline, then optionally a stage for transformation, preferably for alkylation or adsorption, of sulfur-containing compounds and a treatment in a stage of at least a portion of the heavy fraction [1]. A process for the removal of organosulfur compounds from hydrocarbon materials is disclosed. The process includes contacting an ionic liquid with a hydrocarbon material to extract sulfur-containing compounds into the ionic liquid. The sulfur-containing compounds can be partially oxidized to sulfoxides and/or sulfones prior to or during the extraction step [2].

In order to reduce the overall cost of desulfurization, several new technologies are being developed which do not utilize conventional hydrotreating technology. Two of the most recognized non-conventional approaches are adsorption of sulfur compounds onto a solid adsorbent and extraction of sulfur compounds into a immiscible liquid phase. Phillips Petroleum has developed technology (U.S. Pat. No. 6,274,031) which utilizes a fluidized bed for adsorption of the sulfur compounds. Regeneration is in an oxygen environment requiring lock hoppers. The process has yet to be commercialized but the capital costs are believed to be higher than conventional hydrotreating. Other technologies based on adsorption such as Pritchard's process (U.S. Pat. No. 5,730,860), have failed to commercialize to date at least partially due to operational concerns and capital cost projections.

A desulfurization technology based on liquid/liquid extraction of the sulfur compounds would be attractive since generally mild conditions would result in lower capital and operating costs. However, a suitable solvent has been difficult to find since the organosulfur compounds in a hydrocarbon mixture generally have physical properties similar to the other organic compounds. One approach is to increase the polarity of the organosulfur compounds by partially oxidizing them and then extracting them into a polar solvent. Grossman, et al. proposed a process to oxidize the sulfur species to sulfoxides and/or sulfones using a microorganism in an aqueous based system. The sulfoxides and/or sulfones are subsequently reduced by a reducing agent in the aqueous phase. Some authors also proposed a step-wise process for oxidizing the sulfur compounds using an oxidizing agent such as peroxyacetic acid followed by extraction with a non-miscible solvent such as dimethyl sulfoxide. This process is further explained in a paper, AM-00-25, presented by Petro Star, Inc. at the National Petrochemical and Refiners Association 2000 annual meeting. UniPure Corporation presented an additional paper at the 2001 National Petrochemical and Refiners Association annual meeting, AM-01-10, proposing a similar approach based on an aqueous oxidation. All of these processes utilize a step-wise oxidation/extraction approach. Since the partially oxidized sulfur compounds are not fully extracted by the solvent, a fixed bed adsorption step is required downstream of the extraction step. In addition, these processes consume expensive chemical reagents [3].

2. Experimental

Applying to extraction process for establishing effectiveness of the one were compositing model systems, which are like as composition of middle distillated fractions. We were compositing three model systems as follow:
A – thiophene – n-hexadecane-naphthalene;
B – benzthiophene - n-hexadecane-naphthalene;
C – dibenzthiophene - n-hexadecane-naphthalene.

The content of thiophene, benzthiophene and dibenzthiophene was selected by way that the content of sulphur in the each model system to be 1000 ppm and the content of naphthalene – 20 % (m/m) in the each of the three model systems.

We choose this pure sulphur compounds on the base of literal data, according to which the tiophene, benzthiophene and dibenzthiophene are compounds that have hydro purified hard and have cracked and although the diesel fractions have been hydro purified the corresponding compounds put into the fractions. On the other hand benzthiophene and dibenzothiophene caused carcinogenic particles at the burning of fuels in motor engines.

The composite model systems were treated by process of extraction by the methodology given in [4-5].

The method of oxidative desulphurization process was the follow: mixture from 100 ml model systems, 100 ml oxidative mixture (H_2O_2 : $HCOOH/CH_3COOH$ in ratio 1:4 to 4:1) and 30 mg cobalt acetate were mixed at constant temperature and time of the contact – 30 min continuously. After the end of the reaction the model mixture is separated from the acid phase by usual funnel. The obtained model mixture is washed out with 5 % solution of $NaCO_3$ or with distillated water for elimination of acid products.

For establishing of optimum conditions of processes were made investigations at the follow parameters: temperature – 20 to 120 °C; time of the contact – 0,5 to 4,5 hour; ratio oxidative mixture : raw material /model mixture/ = 1:1 and 1:2.

The obtained raffinates were purifying after extraction of unlikely components by distillation processes. The quantity of sulphur compounds was measured on LAB-X 3000 by BDS EN ISO 20846 and BDS ISO 8754 and the quantity of arene compounds was checked though liquid chromatography by BDS ISO 12916.

3. Results and discussion

On the figures from 1 to 6 are given the results from the change of sulphur compounds and arene hydrocarbons content in model systems after extraction treatment at different conditions.

As you can see from the present data all selected from us solvents caused decreasing of sulfur compounds and arene contents in the model systems. The more effective solvent is furfural from used from us two solvents, though that the differences in the decreasing of sulphur compounds and arene hydrocarbons are in the frame of experimental error. It’s established experimentally that optimum conditions for purifying of model system are follows: temperature of extraction processes – 10-12 °C below critical temperature of solve, ratio model system: selective solvent = 1:1 and time contact – 4, 5 hour.

On figures 7 and 8 are given results from changing of sulphur and arene compounds after oxidative desulphurization at different temperatures. The oxidative mixtures led to decreasing of sulphur and arene contents in model mixtures. When we investigated the factor-temperature under oxidative process of purifying of model mixture from sulfur and arene compounds, we establish that increasing of temperature, the quantity of unlikely components decreased. The most decrease of unlikely components is obtained at maximum temperature of investigation 120 °C both ratio model systems: oxidative mixture. The obtained results and built dependences show that as better oxidative mixture from investigated from us oxidative mixtures is H_2O_2 : CH_3COOH in ratio 4 : 2, although at low temperatures decreasing of sulphur compounds haven't attitude clearly.

On figures 9 and 10 are shown the dependences of decreasing of sulphur and arene compounds from contact time. As you can see when contact time increases the change and decreasing of unlikely components increase, too.

It must be noticed that when we used oxidative mixture H_2O_2 : CH_3COOH the decreasing of sulphur compounds is more sharply. At investigation of oxidative desulphurization of used from us model systems we established that dibenzothiophene has oxidized the most easily, middle position is for benzothiophene and thiophene has removed from model system hardly. It was researched the effect and influence of quantity oxidative mixture used at processes of oxidative desuphurization. The obtained results are presented on fig. 11 and 12. The obtained data show that the influence of increasing of quantity of oxidative mixtures is minor for the all investigated model systems and respectively curves is each other too closely. It's proved that the optimum conditions for process of oxidative desulphurization on model systems are: temperature - 120 ºC, ratio model system: oxidative mixture = 1:2 and contact time – 4, 5 hour.

4. Conclusions

1. The corresponding processes for purifying of model systems are applying for the first time in our country.
2. It was established that the raffinates reached Bulgarian State Standard for sulphur content and arene hydrocarbons.
3. It's established that the process of extraction and oxidative desulphurization may apply for removal of unlikely compounds in model systems based on the petroleum products content.

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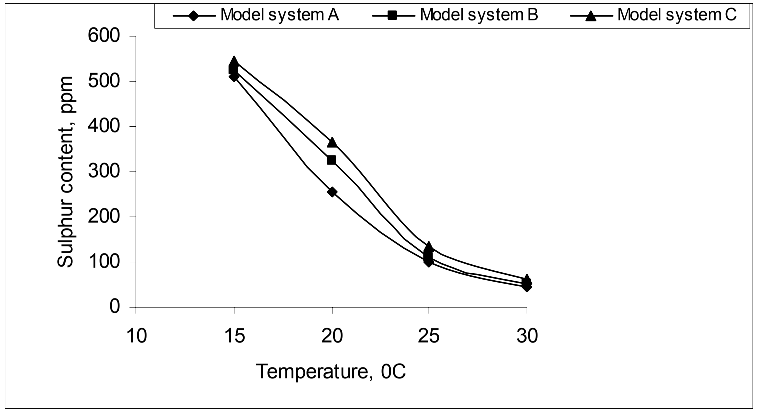

Fig. 1. Dependence of change of sulphur content in model systems A, B, C from temperature at solvent furfural

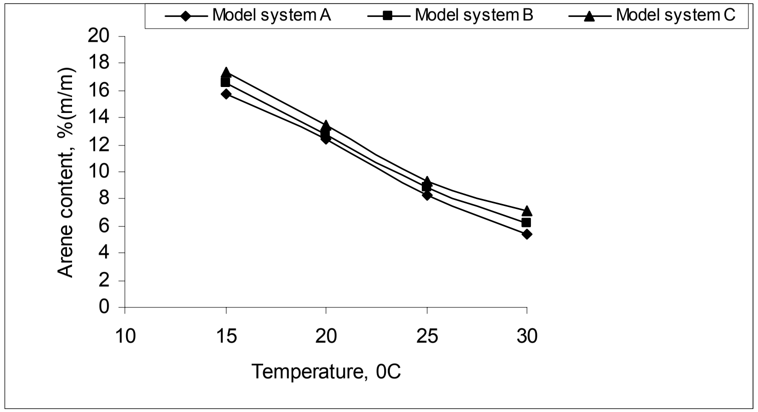

Fig. 2. Dependence of change of arene content in model systems A, B, C from temperature at solvent furfural

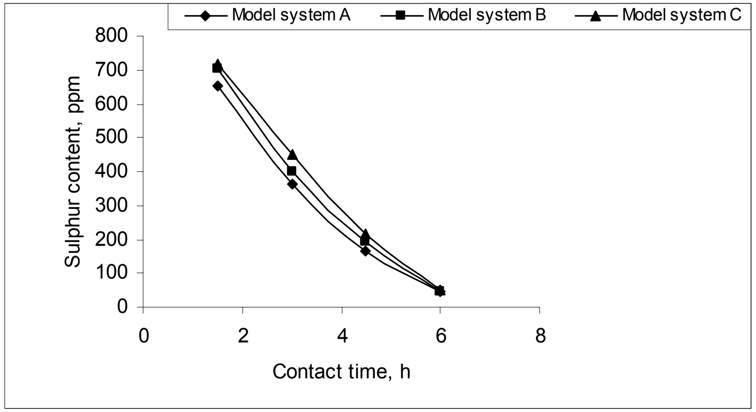

Fig. 3. Dependence of change of sulphur content in model systems A, B, C from contact time at solvent N-methyl pyrrolidone

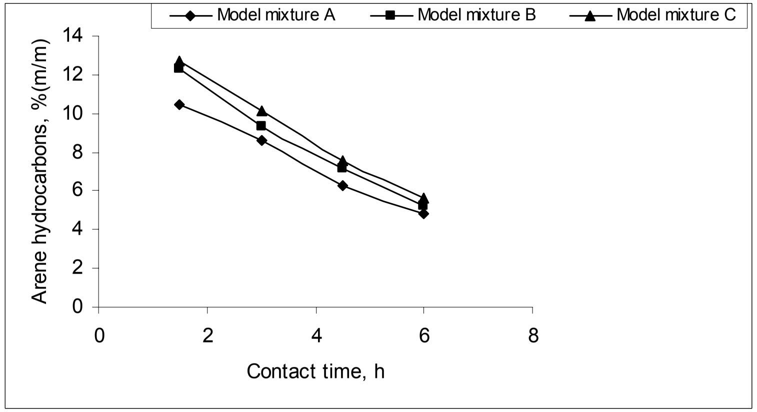

Fig. 4. Dependence of change of arene content in model systems A, B, C from contact time at solvent N-methyl pyrroliddone

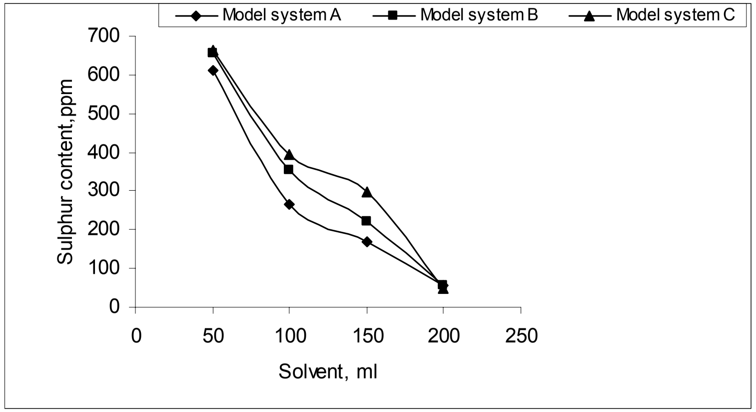

Fig.5. Dependence of change of sulfur content in model systems A, B, C from solvent quantity /used solvent - furfural/

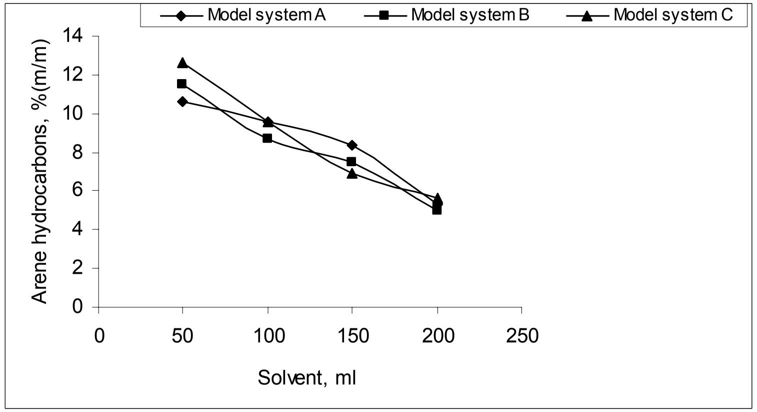

Fig.6. Dependence of change of arene content in model systems A, B, C from solvent quantity /used solvent - furfural/

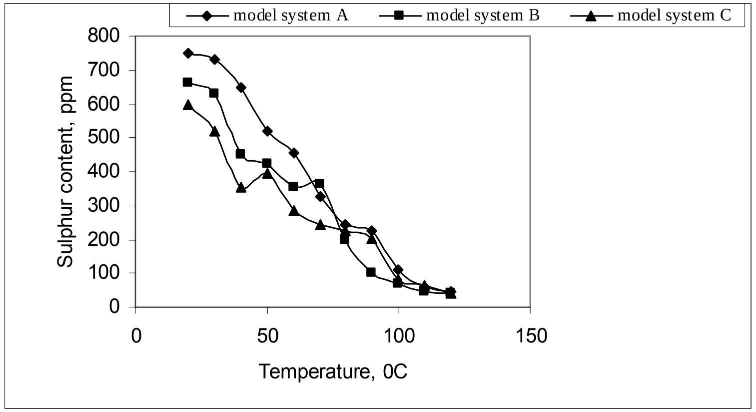

Fig. 7. Dependence of change of sulphur content from temperature /oxidative mixture H_2O_2: CHOOH/

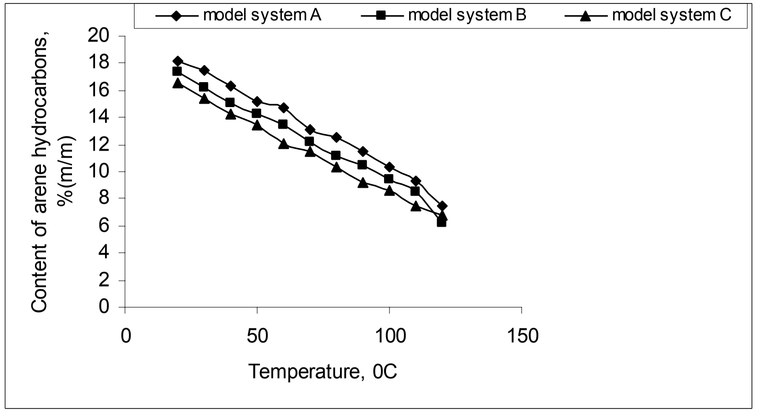

Fig. 8. Dependence of change of arene content from temperature /oxidative mixture H_2O_2: CHOOH/

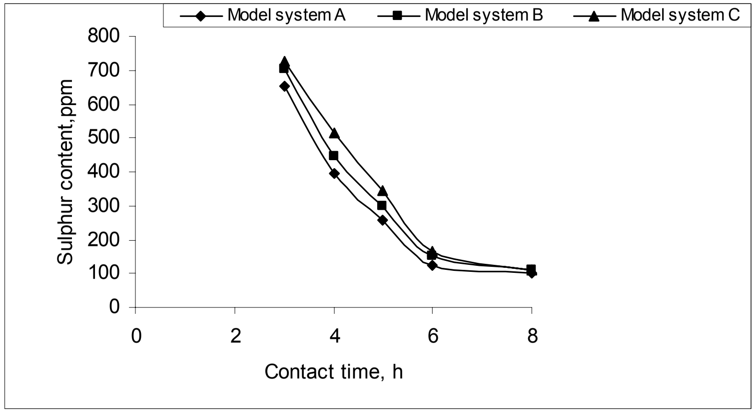

Fig. 9. Dependence of change of sulphur from contact time /oxidative mixture H_2O_2: CH_3COOH/

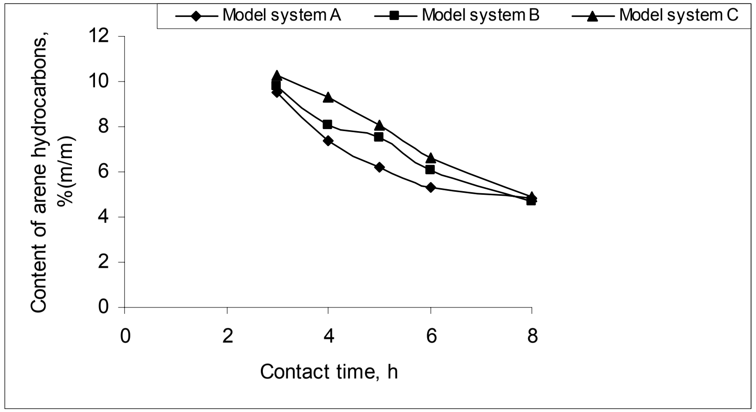

Fig. 10. Dependence of change of arene content from contact time /oxidative mixture H_2O_2: CH_3COOH/

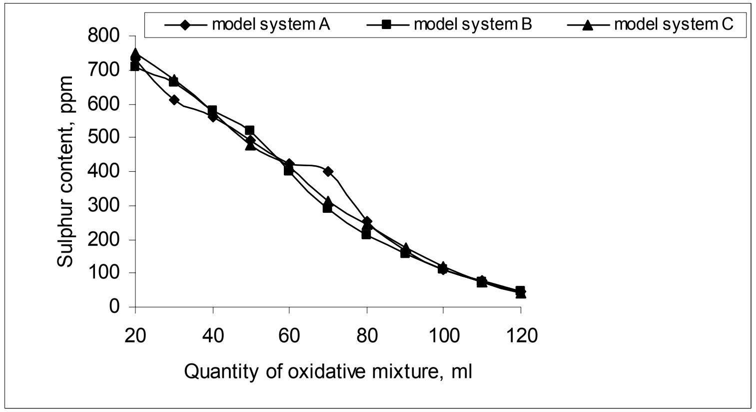

Fig. 11. Dependence of change of sulphur content from quantity oxidative mixture /oxidative mixture H_2O_2: CH_3COOH/

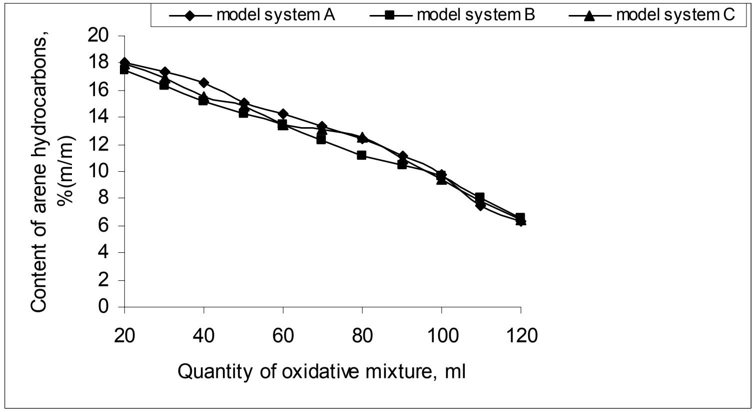

Fig. 12. Dependence of change of arene content from quantity oxidative mixture /oxidative mixture H_2O_2: CH_3COOH/