

Chemistry and Technology of Fuels and Oils

1 (593) '2016

Head Editor

A. I. Vladimirov – Cand. Eng. Sci., prof.

Associate Editor

B. P. Tumanyan – Dr. Eng. Sci., prof.

Editorial Board

S. N. Volgin – Dr. Eng. Sci., prof.

I. B. Grudnikov – Dr. Eng. Sci., prof.

Yu. L. Ishchuk – Dr. Eng. Sci., prof.
(Ukraine)

I. P. Karlin – Dr. Chem. Sci., prof.

V. L. Lashkhi – Dr. Eng. Sci., prof.

A. Luksa – Dr. Eng. Sci., prof. (Poland)

A. M. Mazgarov – Dr. Eng. Sci., prof.

E. D. Radchenko – Dr. Eng. Sci., prof.

V. A. Ryabov – Director General of the Oil Refiners and Petrochemists Association

E. P. Seregin – Dr. Eng. Sci., prof.

Publisher— ICST «TUMA Group» LLC

Редактор

В. С. Дмитриева

Ответственный секретарь

О. В. Любименко

Графика и верстка

В. В. Земсков

Подготовка материалов

Н. Н. Петрухина,

С. О. Бороздин

Адрес редакции:

119991, ГСП-1, Москва, В-296,
Ленинский просп., 65. РГУ нефти и газа
им. И. М. Губкина, редакция «ХТТМ»

Телефон/факс: (499) 507-80-45

e-mail: htm@list.ru

Материалы авторов не возвращаются.

Редакция не несет ответственности
за достоверность информации
в материалах, в том числе
рекламных, предоставленных
авторами для публикации.

Формат 60 84 1/8.

Печать офсетная.

Усл. печ. л. 7.

Тираж 1000 экз.

Отпечатано ООО «Стринг»

E-mail: String_25@mail.ru

Contents

CURRENT PROBLEMS

Alternative Feedstock

O. I. Krivonos, E. N. Terekhova, G. V. Plaksin, and A. V. Lavrenov. Catalytic Hydroliquefaction of Spropels 3

O. Yu. Poletaeva, D. Zh. Latypova, and E. M. Movsum-zade. Hydrocarbon Fuels from Oil Shale Gasification Synthesis Gas 9

CHEMICAL ENGINEERING AND EQUIPMENT

N. A. Samoilov and S. K. Churakova. Effect of Diffusion on Efficiency of Fractionating Tower Contact Devices 13

PETROCHEMISTRY

N. A. Salimova, S. G. Amirov, and S. S. Ismailova. Dearomatization of Motor Oils by Alkylation over Zeolite Catalyst 19

RESEARCH

A. A. Kazakov, G. V. Tarakanov, and N. G. Ionov. Mechanisms of Oxidative Desulfurization of Straight-Run Residual Fuel Oil Using Ozonized Air 23

O. M. Gorelova and L. F. Komarova. Appraisal of Feasibility of Use Of Various Types of Hydrocarbon Stocks for Producing Benzene Rubber Solvent 26

A. P. Semenov, V. I. Medvedev, P. A. Gushchin, V. S. Yakushev, and V. A. Vinokurov. Inhibiting Gas Hydrate Formation by Polymer–Monoethylene Glycol Mixture 29

V. A. Vinokurov, I. M. Kolesnikov, V. I. Frolov, V. A. Lyubimenko, S. V. Lesin, and S. I. Kolesnikov. Effect of Electromagnetic Radiation on Thermal Cracking of Activated Oil Sludge 34

Shi Yan, Sun Zhaolin, Wang Haiyan, and Song Lijuan. Effect of Polyethylene Glycol on Preparation And Performance of Ni-Mo Hydrodesulfurization Catalysts 39

Lin Tiejun, Wei Chenxing, Zhang Qiang, and Sun Tengfei. Calculation of Equivalent Circulation Density in Reaming-Hole Section in Deepwater Drilling 43

METHODS OF ANALYSIS

B. P. Tonkonogov, V. A. Dorogochinskaya, L. N. Bagdasarov, and E. V. Mozhaikaya. Development of a Proximate Ir Spectrometric Base Oil Viscosity, Viscosity Index, and Pour Point Determination Method 46

ECOLOGY

Du Kun, He Man, Lian Minglei, and Li Yu. Catalytic Wet Air Oxidation Treatment of Oily Wastewaters 51

Yu. V. Golubkov, N. V. Ermolaeva, and L. E. Shwarzburg. Nitrogen-Bearing Organic Components of Industrial Oils 54

INNOVATIVE TECHNOLOGIES OF OIL AND GAS

Liu Fan, Jiang Hanqiao, and Wu Xuelin. An Improved Approach to Evaluation of Polymer Hydrodynamics at Early Polymer Flooding Stage 57

Yang Hao. A Composite Material for In-Situ Heating of Oil Shale with High Temperature and Pressure Resistance and Low Elasticity 61

Li Jiwei, Liu Gonghui, and Li Jun. Mathematical Modeling of Unsteady Flow in Controlled Mud-Cap Drilling 66

Catalytic hydroliquefaction of sapropels

O. I. Krivonos, E. N. Terekhova, G. V. Plaksin, and A. V. Lavrenov

E-mail: oksana@ihcp.ru

Catalytic hydroliquefaction of sapropels differing in organic matter and heteroatom contents in the presence of $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$, $\text{Co/MoAl}_2\text{O}_3$, and $\text{Fe/NiAl}_2\text{O}_3$ catalysts is studied. The process conditions ($\text{Co/MoAl}_2\text{O}_3$ catalyst, temperature 450°C , reaction time 1 h, and partial hydrogen pressure 6 MPa) that yield maximum liquid products (53%) and convert organic matter of sapropels maximally (74%) are determined. It is shown that liquid products of sapropel organic matter degradation contain essentially $\text{C}_8\text{-C}_{29}$ saturated hydrocarbons and aromatic, naphthenic, and oxygen- and nitrogen-bearing compounds in much smaller quantities. A scheme is proposed for catalytic hydroliquefaction of the organic matter of sapropels.

Keywords: hydroliquefaction, sapropel, bio-oil, alternative feedstock.

Hydrocarbon fuels from oil shale gasification synthesis gas

O. Yu. Poletaeva, D. Zh. Latypova, and É. M. Movsum-zade

E-mail: ol612@mail.ru

Fischer-Tropsch synthesis is carried out over cobalt catalysts using model oil shale gasification gas. It is demonstrated by example of model mixtures ($\text{CO} + \text{CO}_2 + \text{H}_2 + \text{N}_2$) of Leningrad and Kashpir oil shale gasification products that a wide hydrocarbon fraction can be obtained over cobalt catalyst. The effect of synthesis gas composition, carrier and promoter type, temperature, pressure, and volume stock feed rate on the catalyst efficiency, carbon monoxide conversion, and selectivity and yield of liquid products is studied. A liquid hydrocarbon selectivity of up to 88.7% is achieved at low methane selectivity (3.3%). The obtained hydrocarbons are characterized by a chain growth probability of up to 0.87.

Keywords: synthesis gas, Fischer-Tropsch synthesis, promoter, oil shale.

Effect of diffusion on efficiency of fractionating tower contact devices

N. A. Samoilov and S. K. Churakova

E-mail: naum.samoilov@yandex.ru

A study has been made of 13 industrial fractionating towers having a variety of plate contact devices (S-valve, straight-through valve, rectangular cap, and valve devices made by Glitsch) and 11 industrial fractionating towers having a variety of cross-flow packing contact devices. It is demonstrated that the efficiency of contact devices of various designs is less in the stripping sections of the fractionating towers than in the concentrating sections. Analysis of the mechanisms of diffusion of fractionated components in vapor and liquid phases in contact devices shows that the diffusion coefficient in the vapor phase decreases from the top to the bottom of the tower as the concentration of high-boiling components increases. This reduces mass transfer from one phase to another in the contact device in the stripping section of the tower and, as a result, reduces the efficiency of the contact device in this section of the tower. It is shown that elevation of pressure in the tower and increased temperature gradient across the tower height cause further decline of the contact device efficiency in the stripping section of the tower.

Keywords: Fractionation, diffusion in gases, diffusion in liquids, contact device, efficiency.

Dearomatization of motor oils by alkylation over zeolite catalysts

N. A. Salimova, S. G. Amirov, and S. S. Ismailova

E-mail: sabir.54@mail.ru

Gasoline dearomatization by alkylation in the presence of zeolites and subsequent fractionation of the alkylate into dearomatized gasoline and aromatic hydrocarbon concentrate is studied. It is shown that acid centers of the catalyst play a part in the alkylation reactions. At 1:1 feedstock aromatic hydrocarbon:styrene weight ratio the aromatic hydrocarbon content in the gasoline falls from 22.58 to 6.51 wt. % upon complete conversion of styrene. As a result, environment-friendly gasoline component and the alkylation products phenyl arylethanes, which can be used as dielectric liquids, are obtained.

Keywords: zeolite, gasoline, dearomatization, n-decene, styrene.

Mechanisms of oxidative desulfurization of straight-run residual fuel oil using ozonized air

A. A. Kazakov, G. V. Tarakanov, and N. G. Ionov

E-mail: g.tarakanov@astu.org

The possibility of reducing sulfur content of Astrakhan gas condensate in residual fuel oil by oxidative desulfurization using ozonized air is examined. The optimal conditions for oxidizing with ozone and for thermal decomposition of oxidized sulfur compounds are determined. The sulfur content in residual fuel oil can be reduced from 2.86 to 0.48 wt. %, whereupon hydrogen sulfide is removed completely from the residual fuel oil and the combustion heat increases.

Keywords: ozonized air, sulfoxides, sulfones, oxidative desulfurization.

Appraisal of feasibility of use of various types of hydrocarbon stocks for producing benzine rubber solvent

O. M. Gorelova and L. F. Komarova

E-mail: osgor777@mail.ru

This paper reports the results of study of composition of gas condensates of Urengoi field and liquid products of pyrolysis of Muna brown coal of the Altai Region for selecting a feedstock for producing rubber solvent (Nefras C2 80/120, Kalosha rubber solvent) with maximum yield. The studied feedstock is fractionated in a laboratory distillation column. For the fraction corresponding to the Nefras CS2 80/120 boiling point range, the hydrocarbon composition is determined in compliance with TU 38.401-67-108–92 specifications. A method is proposed for removing unsaturated and aromatic hydrocarbons from the Nefras C2 80/120 fraction, which consists in dynamic adsorption on silica gel.

Keywords: gas condensate, brown coal, synthetic liquid fuel, Kalosha rubber solvent, Nefras C2 80/120.

Inhibiting gas hydrate formation by polymer–monoethylene glycol mixture

A. P. Semenov, V. I. Medvedev, P. A. Gushchin, V. S. Yakushev, and V. A. Vinokurov

E-mail: semyonovanton@mail.ru

Inhibition of formation of methane hydrate with cubic structure CS-I and methane-propane (95.66 CH₄ + 4.34 C₃H₈ mole %) hydrate with cubic structure CS-II by isothermal method and method of cooling at the constant rate of 2°C/h, using 0.5% of a kinetic inhibitor (KIH) + 20.8% of the thermodynamic inhibitor (TIH) monoethylene glycol (MEG) is studied. It is shown that the synergic effect of increase in inhibiting capacity of a polymeric kinetic inhibitor (KIH) in the

presence of 20.8% of MEG (TIH) is observed in the case of both methane hydrate and methane-propane hydrate inhibition. The synergy manifests itself in the form of increase in supercooling degree by 2.5–3°C that is attained in the KIH + TIH system before the initiation of hydrate formation as compared to a system that contains no TIH (MEG). The induction time is shown to depend on the degree of supercooling in the system while inhibiting CS-I and CS-II hydrates with 0.5% KIH + 20.8% MEG. The obtained data indicate that KIH + MEG antihydrate reagents can be used to inhibit formation of technogenous gas hydrates at < 0°C temperatures.

Keywords: kinetic hydrate formation inhibitors, thermodynamic hydrate formation inhibitors, ethylene glycol, methane hydrate, methane-propane hydrate, supercooling degree.

Effect of electromagnetic radiation on thermal cracking of activated oil sludge

V. A. Vinokurov, I. M. Kolesnikov, V. I. Frolov, V. A. Lyubimenko, S. V. Lesin, and S. I. Kolesnikov

E-mail: fvi209@mail.ru

The wave parameters for correlating differing nature and potential of ionization, which allow determination of the minimum time for activating hydrocarbons with specific bonds, are calculated. The results of study of the effect of electromagnetic radiation parameters on the products of thermal cracking of nonhydrofined oil sludge are reported. These results are used to build for the first time mathematical models that allow both interpolation and extrapolation of the parameters of the oil sludge thermal cracking process.

Keywords: thermal cracking, electromagnetic radiation, activated carbon, vacuum gas oil, oil sludge, mathematical modeling.

Effect of polyethylene glycol on preparation and performance of Ni-Mo hydrodesulfurization catalysts

Yan Shi, Zhaolin Sun, Haiyan Wang, and Lijuan Song

E-mail: shiyan1816@163.com

Ni-Mo catalyst precursors were prepared by precipitation method. Ni-Mo bulk hydrodesulfurization catalysts were obtained from these precursors after proper drying, molding, and calcination. The effect of polyethylene glycol (PEG) with different molecular weights and

in various dosages on the structure and catalytic properties of these catalysts was investigated applying X-ray diffraction, low-temperature BET N₂ adsorption analysis, and scanning electron microscopic methods. It is shown that the structure, surface properties, and activity of the catalysts can be improved by adding PEG. The pore volume, specific surface area, and pore size of the catalysts increase gradually with increasing PEG dosage, and the dispersion of the active ingredient increases initially and then decreases.

Keywords: bulk catalyst, polyethylene glycol, hydrodesulfurization, activity evaluation.

Calculation of equivalent circulation density in reaming-hole section in deepwater drilling

Lin Tiejun, Wei Chenxing, Zhang Qiang, Sun Tengfei

E-mail: suntengfei7@sina.com

A method is proposed for calculating and analyzing solid concentration in annular space and equivalent circulation density (ECD) in a pilot hole and in the reaming section in deepwater drilling. It is shown that drilling of a slim pilot hole first and broadening it by reaming later is better than without drilling a pilot hole because the former technology keeps the hole cleaner and reduces solid concentration in the annular space and equivalent circulation density.

Keywords: deepwater drilling, pilot hole, solid concentration, reaming, equivalent circulation density.

Development of a proximate ir spectrometric base oil viscosity, viscosity index, and pour point determination method

B. P. Tonkonogov, V. A. Dorogochinskaya, L. N. Bagdasarov, and E. V. Mozhayskaya

E-mail: kmozhayskaya@gmail.com

It is proved by example of individual hydrocarbons that IR spectrometry can be applied to analyze properties of base oils. A proximate viscosity, viscosity index, and pour point determination method is developed based on quantitative IR spectrometry using areas of two characteristic peaks and regressive analysis for API-classified group 3 and 4 oils. This method can be used for quality control and real-time study of base oils.

Keywords: base oils, viscosity, viscosity index, pour point, IR spectrometry.

Catalytic wet air oxidation treatment of oily wastewaters

Kun Du, Man He, Minglei Lian, and Yu Li

E-mail: xuchunhua2015@hotmail.com

The effect of reaction temperature, reaction time, initial chemical oxygen demand (COD), excess O₂ (EO), and catalyst concentration on the efficiency of catalytic wet air oxidation (CWAO) treatment of refinery wastewaters consisting of various oily wastes, water, heavy metals, toxic compounds, etc. was studied. In general, COD decreases substantially with temperature, EO, and oxidation time. Addition of homogeneous Co²⁺-based catalysts reduces COD by as much as 98.7%.

Keywords: catalytic wet air oxidation, oily wastes, chemical oxygen demand, wastewater treatment, cobalt catalyst.

Nitrogen-bearing organic components of industrial oils

Yu. V. Golubkov, N. V. Ermolaeva, and L. E. Shwarzburg

E-mail: ermolaeva_n_v@mail.ru

The chemical composition of I-20A and I-40A industrial oils produced by various companies is studied by chromatomass spectrometry. These oils are found to have more than 20 nitrogen-bearing organic compounds, including ones that are hazardous to human health. It is shown that the composition of organic nitro-compounds of various batches of oils differs markedly. Steps for protecting the environment and health of workers from the identified compounds are proposed.

Keywords: industrial oil, nitrogen-bearing organic compounds, chromatomass spectrometry, lubricating-cooling technological fluids.

An improved approach to evaluation of polymer hydrodynamics at early polymer flooding stage

Fan Liu, Hanqiao Jiang, and Xuelin Wu

E-mail: liufan.sv@gmail.com

An improved approach based on steady fluid flow power-law with due account of threshold pressure is proposed to analyze polymer behavior underground at early polymer flooding (EPF)

stage with reference to Bohai offshore field, China. In this approach, practical injection well and geological data are used to obtain various important parameters, such as flow behavior index, average effective viscosity within polymer-swept portion, in-situ resistance factor, etc. The reliability of the approach is proved by comparing the results with flowback and ECLIPSE-simulation data. It allows monitoring of polymer performance changes in reservoirs over time and can be applied for reservoir development at subsequent stages.

Keywords: early polymer flooding stage, polymer performance evaluation, threshold pressure, polymer viscosity in formation conditions, in-situ resistance.

A composite material for in-situ heating of oil shale with high temperature and pressure resistance and low elasticity

Yang Hao

E-mail: yanghao@cugb.edu.cn

High-temperature resistant cementing material is required for wells drilled for heavy and shale oil production by steam injection and in-situ combustion and for deep geothermal wells. Current cementing materials do not meet these requirements. The authors have developed a cementing material with a heat resistance of up to 600°C, compressive strength exceeding 60 MPa, and an elasticity of as low as 12 GPa. This material can be used for cementing both oil and gas wells. It can strongly cement formation rocks and well casings.

Keywords: cementing, high temperature, high pressure, low elasticity, oil shale, electric well heating, well cementing, mortar, in-situ combustion, composites.

Mathematical modeling of unsteady flow in controlled mud-cap drilling

Jiwei Li, Gonghui Liu, and Jun Li

E-mail: lijawei2009@live.com

Controlled mud-cap (CMD) drilling is an advanced deepwater drilling technology. When the surface pump is shut down, the CMD system causes unsteady flow that may create control problems. A new mathematical model has been developed to simulate unsteady flow in CMD systems. The model predicts the transient flow, the equilibrium time, and the change in bottomhole pressure during the unsteady flow. The simulation results show that the flow parameters change rapidly during the first 10 min and unsteady flow causes fluctuation in

bottomhole pressure. In combination with measured data, the transient flow behavior computed by the model can be used for early detection of well kick after shutdown of the mud pump.

Keywords: deepwater drilling, mud-cap drilling, unsteady flow, mathematical model, kick detection.