

Chemistry and Technology of Fuels and Oils

4⁽⁵⁹⁶⁾'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

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: html@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

D. P. Savitskii, Ya. M. Stanishevskii, D. Yu. Sadovskii, and A. S. Makarov. 3
Effect of Fusel Oils on Rheological Properties of Suspensions
of Coals at Different Stages of Metamorphism

*Wittawat Ratanathavorn, Chonlawit Borwornwongpitak,
Chanatip Samart, Prasert Reubroycharoen.* 7
Bio-Oil Production from Giant Leucaena Wood by Liquid Phase Pyrolysis

CHEMOTOLOGY

T. A. Zaimovskaya, E. G. Bordubanova, A. S. L'yadov, and O. P. Parenago. 12
Tribological Properties of Plastic Lubricants Infused
with Molybdenum-Containing Additives

*Yu. V. Popov, S. M. Ledenev, N. Yu. Tokmacheva,
O. V. Anishchenko, S. A. Spirichev, and K. Yu. Eistfel'd.* 16
Antiscoring Additives for Transmission Oils Based on C₁₀ α-Olefin Fraction

RESEARCH

V. G. Surkov, A. K. Golovko, and M. V. Mozhaikaya. 18
Mechanochemical Conversions of High-Molecular Oil Components
in Presence of Quartz

Gu Shaonan, Li Wenjun, Luo Wenli, Chang Zhidong. 21
A Novel Application of Silica Sol to Improve Stability of Sodium
Dodecyl Sulfate Foam Used for Enhancing Oil Recovery

K. E. Pankin. 27
Estimation of Combustion Heat of Biofuels Based
on Wood and Wood Waste Pyrolysis Products

N. N. Rokosova, V. Yu. Rokosova, and Yu. V. Rokosov. 31
Hydrocarbons in Products of Oxidative-Hydrolytic
Transformation of Sapropelites

*M. N. Dadashev, D. G. Filenko, N. M. Bulaeva,
V. A. Vinokurov, and R. R. Mursalov.* 35
Dependence of Oil Extraction Factor
on Thermodynamic Parameters of Solvent

*L. A. Gulyaeva, N. Ya. Vinogradova, V. A. Khavkin,
A. E. Gorlov, A. V. Shumovskii, and G. V. Bitiev.* 38
Preparation of Oil Shale and Oil Residue Blend for Gasification

N. M. Likhterova, K. V. Shatalov, V. V. Suzikov, and I. M. Nikitin. 42
Influence of Test Parameters on Corrosive Effect of Aviation Fuels
on Nonferrous Metals under Dynamic Conditions

Zhang Hao, Lu Yuan, Li Kai. 47
Research on Temporary Sealing of Fractured Reservoirs Using Scaling Agents

REVIEWS

I. G. Yashchenko and Yu. M. Polishchuk. 50
Classification of Poorly Recoverable Oils and Analysis
of Their Quality Characteristics

INNOVATIVE TECHNOLOGIES OF OIL AND GAS

Li Hui, Wang Yan, Luo Zhongming, Liu Jie. 57
Calculation of Water Injection Response Time
for Low-Permeability Anisotropic Reservoir

Ma Tian-shou, Chen Ping. 60
A New Method for Calculating Wellbore Collapse Pressure in Shale Formations

Sun Qiji, Wang Chunsheng, Wang Xiaohu, Dong Bin. 66
Development of a New High-Temperature-Resistant Plugging Agent
for Heavy Oil Recovery by Steam Flooding of Reservoirs

Effect of Fusel Oils on Rheological Properties of Suspensions of Coals at Different Stages of Metamorphism

D. P. Savitskii, Ya. M. Stanishevskii, D. Yu. Sadovskii, and A. S. Makarov

E-mail: den.83@mail.ru

The salient technological properties of coal suspension are studied using fusel oil as the dispersion medium. The distinctive features of the rheological behavior and flow pattern of coal suspensions as a function of the nature of coal are ascertained. It is shown that the effective viscosity of coal suspensions decreases as the coal passes from the lignite to the anthracite stage. The calorific value and degree of combustion of coal suspensions produced by using fusel oil are higher than those of the original coal.

Key words: coal suspension, fusel oil, rheological properties.

Bio-Oil Production from Giant Leucaena Wood by Liquid Phase Pyrolysis

Wittawat Ratanathavorn, Chonlawit Borwornwongpitak, Chantip Samart, Prasert Reubroycharoen

E-mail: prasert.r@chula.ac.th

Bio-oil production from giant leucaena wood by liquid phase pyrolysis in an autoclave in the presence of decane as the solvent and ZSM-5, NiMo/Al₂O₃, Pt/Al₂O₃ and their mixtures as the catalysts at 350°C and 1 MPa initial hydrogen (H₂) pressure was investigated. Catalyst type had no significant effect on the yield, but carbon-hydrogen-nitrogen (CHN) analysis revealed that NiMo/Al₂O₃ is the optimal catalyst as it yielded bio-oil having the lowest oxygen content (10.0 wt. %) with an oil yield of 4.3 wt. %. Optimization of the reaction temperature in the 250–400°C range and the initial H₂ pressure in the 0.5–3 MPa range by sequential univariate analysis revealed that the reaction temperature is the most influential parameter for oil yield and oxygen content, reaching the highest oil yield of 8.60 wt. % with the lowest oxygen content of 5.50 wt. % at 400°C in the presence of NiMo/Al₂O₃ catalyst. Elevation of the initial H₂ pressure had no significant effect on the bio-oil and char yields, although the bio-oil yield fell slightly from 5.40 to 3.90 wt. % as the pressure was elevated from 0.5 to 3 MPa. However, elevation of initial H₂ pressure significantly reduced gas yield: CO₂ and CO yields dropped respectively by 1.8 and 3.2 times at 1 MPa and by 5.25 and 12 times at 3 MPa compared to the yields at 0.5 MPa.

Key words: bio-oil, giant leucaena, biomass pyrolysis, liquid phase pyrolysis, catalyst, depolymerization.

Tribological Properties of Plastic Lubricants Infused with Molybdenum-Containing Additives

T. A. Zaimovskaya, E. G. Bordubanova, A. S. L'yadov, and O. P. Parenago

E-mail: lyadov@ips.ac.ru

Wear and score resistance properties of different types of plastic lubricants infused with additives based on sulfur-containing molybdenum compounds are studied. It is shown that the tribological properties of all the studied lubricants improve upon infusion of 2–8 wt. % of molybdenum dithiocarbamate and that the additives are most active in the lubricants containing polyurea thickener.

Key words: plastic lubricants, polyurea thickener, Aerosil, mineral oils, poly- α -olefin, diameter of wear spots, critical load

Antiscoring Additives for Transmission Oils Based on C₁₀ α -Olefin Fraction

Yu. V. Popov, S. M. Ledenev, N. Yu. Tokmacheva, O. V. Anishchenko, S. A. Spirichev, and K. Yu. Eisel'd

E-mail: ledenev@vstu.ru

Sulfur- and chlorine-containing products are obtained by reacting C₁₀ α -olefins with sulfur monochloride and then sulfidized with saturated aqueous sodium sulfide solution to synthesize sulfur-containing products. The optimum conditions are determined for synthesizing these products, which can be recommended as additives that improve tribological properties of lubricants. It is shown that specimens of mineral oils prepared by using the synthesized additives correspond in key performance properties to transformer oil quality group TM-4, SAE, 80W-90, and API of the GL-4 type with improved antiscoring properties.

Key words: olefin fraction, sulfur-containing additives, antiscoring properties, transmission oil.

Mechanochemical Conversions of High-Molecular Oil Components in Presence of Quartz

V. G. Surkov, A. K. Golovko, and M. V. Mozhaiskaya

E-mail: sur@ipc.tsc.ru

It is demonstrated by mechanochemical conversions of high-molecular oil components that degradation of oil hydrocarbons by mechanical treatment in the presence of quartz is accompanied by formation of gaseous hydrocarbons. Upon mechanochemical treatment in the presence of quartz, the asphaltene content decreases in Zuunbayan oil, but increases in Stolbovoi oil. Mechanical treatment reduces solid paraffin content in Stolbovoi oil, but increases it in Zuunbayan oil. Mechanochemical treatment of oil in the presence of quartz causes accumulation on the solid phase particles of poorly soluble organic substances consisting essentially of heteroatomic compounds. The obtained data can be used to develop mechanochemical oil treatment flow chart.

Key words: mechanochemical treatment, mechanochemistry, quartz, solid paraffins.

A Novel Application of Silica Sol to Improve Stability of Sodium Dodecyl Sulfate Foam Used for Enhancing Oil Recovery

Gu Shaonan, Li Wenjun, Luo Wenli, Chang Zhidong

E-mail: wjli_ustb@163.com

Use of silica sol is proposed for stabilizing sodium dodecyl sulfate (SDS) foam used for enhancing oil recovery. For a comparison of the SDS foam stabilizing performances of silica sol and silica

nanoparticles, the stability, rheological properties, and viscoelasticity of these two stabilizers were studied by using Waring blender, R/S Plus Rheometer, and Extensional Viscometer. After addition of 0.05 wt. % of silica sol and silica nanoparticles to the foam, the foam half-life increased by 29.3 and 21.1%, respectively. Thus, silica sol is more effective in increasing foam stability than silica nanoparticles. It also increases the viscosity and elasticity modulus of liquid film to a greater extent than silica nanoparticles. The main reason for the obtained results seems to be better dispersity of silica sol than silica nanoparticles.

Key words: silica sol, silica nanoparticles, foam stability, viscoelastic properties, air-liquid interface.

Estimation of Combustion Heat of Biofuels Based on Wood and Wood Waste Pyrolysis Products

K. E. Pankin

E-mail: texmexium@mail.ru

An attempt has been made to theoretically estimate the combustion heat of the proposed liquid fuel based on products of high-temperature treatment of plant materials. The most complete qualitative and quantitative composition of the biofuel has been established, and the lowest heat of combustion of its components and the specific air consumption for combustion of the mix has been calculated. The obtained data are compared with the combustion heat of conventional oil fuels.

Key words: wood pyrolysis, biofuel, calorific value.

Hydrocarbons in Products of Oxidative-Hydrolytic Transformation of Sapropelites

N. N. Rokosova, V. Yu. Rokosova, and Yu. V. Rokosov

E-mail: chemgeo@rambler.ru

The qualitative and quantitative composition of hydrocarbons formed upon oxidative-hydrolytic treatment of Kuzbas and Mongolian sapropelic oil shales under hydrous pyrolysis conditions is disclosed by chromato-mass spectrometry. It is shown that oxidative-hydrolytic transformation of the organic mass of these sapropelites at 400°C in aqueous-alkaline solution is associated to the extent of 30-40% with formation of paraffinic-naphthenic hydrocarbons, primarily normal C₁₀–C₃₁ alkanes and normal C₁₄–C₂₈ alkenes. It is indicated that, in contrast to anhydrous pyrolysis products, destructive oxidation-hydrolysis products contain more monounsaturated olefins with a different double bond position. The composition of the hydrocarbon biomarkers confirms marine origin of the original biomass of the studied oil shales.

Key words: sapropelites, oil shales, oxidative-hydrolytic transformation, biomarkers, hydrous pyrolysis.

Dependence of Oil Extraction Factor on Thermodynamic Parameters of Solvent

M. N. Dadashev, D. G. Filenko, N. M. Bulaeva, V. A. Vinokurov, and R. R. Mursalov

E-mail: jnus@mail.ru

The process of oil expulsion from a solid porous medium by supercritical CO₂ is studied in a wide range of state parameters. The dependence of oil expulsion factor on the temperature in the 40–80°C range and the pressure in the 9–13 MPa range is investigated. It is shown that elevation of CO₂ temperature to 55–80°C leads to a decrease in extraction factor. It is indicated that there is a definite pressure threshold above which it is impossible to reduce consumption of expelling agent and to increase oil expulsion factor and that the optimum volume of discharge lies within two pore volumes in the whole studied temperature and pressure range.

Key words: oil extraction factor, oil expulsion, supercritical fluid, critical point, carbon dioxide.

Preparation of Oil Shale and Oil Residue Blend for Gasification

L. A. Gulyaeva, N. Ya. Vinogradova, V. A. Khavkin, A. E. Gorlov, A. V. Shumovskii, and G. V. Bitiev

E-mail: gulyaeva@vniinp.ru

The results of experimental studies on preparation of oil shale and oil residue blend for gasification to produce synthesis gas of the desired composition are reported. The feasibility of preparation of stable oil shale suspension in aqueous emulsion of high-viscosity residual fuel oil having structural-rheological characteristics that ensure unhindered pumping of gasification feedstock through the gas generator nozzle and uniform distribution in the combustion chamber is shown.

Key words: oil shale, high-viscosity oil, heavy oil residue, residual fuel oil, structural-rheological characteristics, gasification

Influence of Test Parameters on Corrosive Effect of Aviation Fuels on Nonferrous Metals under Dynamic Conditions

N. M. Likhterova, K. V. Shatalov, V. V. Suzikov, and I. M. Nikitin

E-mail: alyamurashkina@gmail.com

Experimental data are obtained to show the influence of parameters of aviation fuel test by a TsITI-M device on the corrosive effect of the fuels on copper and VB-23-NTs bronze. It is shown that corrosivity of fuels increases under dynamic conditions. Reduced fuel flow rate reduces the corrosive effect of the fuel on nonferrous metals. Presence of nonferrous metals reduces thermo-oxidative stability of the fuel threefold. It is indicated that the corrosion loss of copper is maximum at 150°C. Elevation of fuel temperature from 130 to 170°C reduces the corrosive effect of the fuel on VB-23 NTs bronze.

Key words: corrosion, copper, bronze, thermo-oxidative stability, aviation fuel, dynamic conditions.

Research on Temporary Sealing of Fractured Reservoirs Using Scaling Agents

Zhang Hao, Lu Yuan, Li Kai

E-mail: cdutzhh08@163.com

Loss of drilling fluid in fractured reservoirs impedes drilling operation and may cause great damage to reservoirs. A new technique has been developed for temporary scaling (sediment forming) sealing protection of fractured reservoirs that combines the advantages of chemical, bridge, and shield sealing methods. Laboratory results indicated that plugging effect of scale forming agent is excellent with an average scaling rate of 96.14%, bridging fiber materials have good capacity for absorption on scaling products, which facilitates aggregation of scaling products, plugging zone can withstand up to 6 MPa pressure, and sealing product erosion rate is great, averaging 95.48%, which can reduce the damaging effect of plug removing agents on reservoirs.

Key words: fractured formation, temporary sealing, chemical sealing, bridge sealing, shield sealing, temporary sealing by scaling.

Classification of Poorly Recoverable Oils and Analysis of Their Quality Characteristics

I. G. Yashchenko and Yu. M. Polishchuk

E-mail: sric@ipc.tsc.ru

Poorly recoverable oils are typified on the basis of analysis and generalization of the published data. An oil quality index that allows investigation of the characteristics of poorly recoverable oil reserves is proposed. Types of poorly recoverable oils are classified in terms of quality index into three classes, namely, low-, medium-, and high-quality oils. The peculiarities of physicochemical properties of poorly recoverable low-, medium-, and high-quality oils are determined by analyzing data on 18,000 specimens of oils having anomalous properties and 9000 specimens of oils bedded under complex conditions. A comprehensive classification of oils based on physicochemical properties is proposed, taking account of the density, viscosity, sulfur, resin, asphaltene, solid paraffin, vanadium, nickel, and light fraction content, gas saturation of the oil, etc. The investigation results can be used for optimizing the routes of transporting oils having anomalous physicochemical properties through pipelines.

Key words: poorly recoverable oils, oil quality index, oil classification, oil quality classes, oils anomalous properties.

Calculation of Water Injection Response Time for Low-Permeability Anisotropic Reservoir

Li Hui, Wang Yan, Luo Zhongming, Liu Jie

E-mail: wangyanwangwang@126.com

A model is proposed for predicting the time of response of an oil well to change in pressure in injection well while developing lowpermeability oil reservoir. The principal equation is deduced on the basis of nonlinear seepage law and of the method of gradual change in steady states and takes account of the

anisotropy of the oil formation. It is shown that, in comparison with the conventionally used model, this model allows calculation with greater accuracy.

Key words: anisotropy, nonlinear seepage, low-permeability reservoir, response time.

A New Method for Calculating Wellbore Collapse Pressure in Shale Formations

Ma Tian-shou, Chen Ping

E-mail: matianshou@126.com

A new simple and accurate method is developed for calculating the equivalent density of wellbore collapse pressure in shale formations with bedding planes, which can be used for well path optimization. The calculation takes account of in-situ stresses, occurrence of bedding planes (direction, dip), strength of bedding planes, rock strength, wellbore trajectory (deviation, azimuth), and attached stresses caused by mud filtrate invasion. The influence of bedding planes on the equivalent density of wellbore collapse pressure is discussed.

Key words: shale gas, bedding plane, horizontal well, wellbore stability, weak plane, collapse pressure

Development of a New High-Temperature-Resistant Plugging Agent for Heavy Oil Recovery by Steam Flooding of Reservoirs

Sun Qiji, Wang Chunsheng, Wang Xiaohu, Dong Bin

E-mail: sunqiji422@126.com

The process of development of a gel plugging agent usable in heterogeneous formations at high temperatures is discussed. The variation method is used to determine the static and dynamic properties of the agent and its optimal concentration. To optimize the plugging process, the experimental data are integrated with the numerical modeling data obtained by CMG software. The plugging agent contains 0.03% coagulant, 2.75% cross-linking agent I, 2.1% cross-linking agent II, and 8% main heat-resistant agent. Gel viscosity 2000-5000 mPa·sec, pH 6-8, plugging rate >90.39%, working temperature >280°C. The optimum injection control profile radius at which oil recovery increases and flooding decreases is 20 m.

Key words: thermal recovery, steam injection into oil formation, plugging agent, injection control profile, single fluid process.