### Chemistry and Technology of Fuels and Oils

# **3**(595) **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: httm@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

Alternative Feedstock	
<i>M. A. Ershov, E. V. Grigor'eva, I. F. Khabibullin, and V. E. Emel'yanov.</i> Development of E30 Bioethanol Fuel Composition Based on Low-Octane Fractions of Exhaustive Hydrocarbon Feedstock Processing	3
R. Maceiras, A. Cancela, J. L. Salgueiro, V. Alfonsin, and A. Sanchez. Simulating a Versatile Plant for Obtaining Biodiesel	9
D. A. Sharipova, D. S. Kopitsyn, M. Yu. Ziangirova, A. A. Novikov, and V. A. Vinokurov. Fatty Acid Composition of Basidiomycetes Lipids — a Promising Feedstock for Obtaining Biodiesel	12
CHEMICAL ENGINEERING AND EQUIPMENT	
Zhao Chunli, Zhang Nan, Guo Jianchun, Yang Tianji, and Yang Zhi. A Study of the Mechanism of Separation in a Multi-Cup Downhole Gas-Oil Separator	16
RESEARCH	
<i>M. A. Lurie and F. K. Schmidt.</i> Possible Paths of Origin of Gas-Oil Systems and Causes of Differences in Their Properties	22
S. E. Mamedov, Kh. V. Akhmedova, N. F. Akhmedova, S. S. Dadasheva, and E. I. Akhmedov. Transformation of Straight-Run Gasoline Fraction on High-Silica Zeolite Modified by Gallium and Zirconium	28
N. N. Sviridenko, E. B. Krivtsov, and A. K. Golovko. Effect of Ferrospheres as Additives on Composition of Cracking Liquid Products of Mordovo-Karmal Native Asphalt	31
<i>E. Yu. Kovalenko, T. A. Sagachenko, V. P. Sergun,</i> <i>T. V. Cheshkova, S. S. Yanovskaya, and R. S. Min.</i> Composition of Sulfur-Containing Structures in Resinous-Asphaltenous Substances and Lube Components of Usa Heavy Oil	35
Liu Zhen, Qi Na, Luan Yaning, Yang Xiang, and Zou Anlong. Analysis of Green Waste Composting and the Effects of Humic Acid Content Using Near-Infrared Spectroscopy	40
Yang Xinliang and Ai Chi. Demulsification Performance and Mechanism of Demulsification of Dendritic Polyamidoamine	44
Zhang Hui, Sun Tengfei, Huang He, and Gao Deli. Experimental Investigation of Formation Rock Drillability under Bottomhole Differential Pressure Conditions	46
METHODS OF ANALYSIS	
<i>B. I. Koval'skii, A. N. Sokol'nikov, O. N. Petrov, and V. G. Shram.</i> Photometric Monitoring of Thermal Stability of Motor Oils and Effect of Thermal Degradation Products on Antiwear Properties	50
R. S. Manapov, D. O. Shulyakovskaya, and M. Yu. Dolomatov. Evaluation of Physicochemical Properties of Diesel Fractions from Color Characteristics of RGB Colorimetric System	54
METHODS OF ANALYSIS	
Wang Peng, Yu An-feng, Dang Wen-yi, and Han Zhong-shu. Modeling Thermal Radiation of Enclosed Ground Flare	57
Liu Yong, Li Qian, Yao Aiguo, and Zhang Xianyong. Experiments for Selecting Optimal Foam Drilling Fluid Formula	62
Wang Chunsheng and Xu Yujian. Solving Problems of Freezing and Blocking of Tail Gas Pipelines while Developing Oil Fields by Fire Flooding	66

# Development of E30 bioethanol fuel composition based on low-octane fractions of exhaustive hydrocarbon feedstock processing

M. A. Ershov, E. V. Grigor'eva, I. F. Khabibullin, and V. E. Emel'yanov

### E-mail: ErshovMA@vniinp.ru

The results of studies aimed at developing E30 bioethanol fuel composition using heavy low-octane hydrocracking gasoline as the basic component are reported. The dependencies of knock resistance, saturated vapor pressure, and fractional composition on bioethanol concentration in a mixture with heavy hydrocracking gasoline are shown. The maximally permissible concentrations of additional components (light hydrocracking gasoline, toluene, and reforming gasoline) in the fuel are indicated. The results of tests of experimental specimens in compliance with OAO VNII NP (OJSC All Russian Scientific Research Institute of Petroleum Refining) technical specifications and calculation of economic feasibility of production and use of E30 bioethanol fuel are presented.

Key words: bioethanol, medium ethanol fuel, automotive gasoline.

### Simulating a versatile plant for obtaining biodiesel

R. Meceiras, A. Cancela, J. L. Salgueiro, V. Alfonsin, and A. Sánchez

### E-mail: rmaceiras@uvigo.es

A versatile biodiesel production process, which allows simulation of a plant that can produce biodiesel by converting vegetable oils of any composition to methyl esters by transesterification reactions, is proposed. The validity of the simulation was verified by producing biodiesel and glycerin from different amounts of algal oil feedstocks. The versatile model can be used for different types of oils by changing only the input parameters. It provides a series of advantages not only in terms of resource and time saving when building a real plant, but also when selecting the most suitable feedstocks for biodiesel production.

Keywords: biodiesel, simulation, vegetable oil, algal oil, transesterification, waste, renewable.

### Fatty acid composition of basidiomycetes lipids — a promising feedstock for obtaining biodiesel

D. A. Sharipova, D. S. Kopitsyn, M. Yu. Ziangirova, A. A. Novikov, and V. A. Vinokurov *E-mail: gubkin.biotech@gmail.com* 

Xylotrophic basidial fungi capable of accumulating lipids while growing on inedible plant materials are a promising source of feedstock for obtaining biodiesel. Screening of 30 strains of xylotrophic basidial fungi are screened for accumulation of lipids and the content of fatty acids in 9 strains chosen by screening is determined. It is shown that the strains Piptoporus betulines MT-30.04 and Rus-

sula puellaris MT-32.06 are characterized by maximum content of oleic acid in the lipids and are therefore most promising as lipid formers for biodiesel production. **Keywords:** biodiesel, basidial fungi, lipids, fatty acid composition.

### A study of the mechanism of separation in a multi-cup downhole gas-oil separator Chunli Zhao, Nan Zhang, Jianchun Guo, Tianji Yang, and Zhi Yang *E-mail: zclstorage@126.com*

A mathematical model (numerical simulation) of gas-oil flow in a multi-cup downhole gas-oil separator is proposed. The model takes into account the Gibbs wave equation to obtain the pump plunger velocity and the population balance model (PBM) for describing bubble aggregation and breakage. The gas-oil flow field distribution and the bubble behavior in the multi-cup gas-oil separator were simulated using computational fluid dynamics (CFD). The numerical simulation results showed that the main role of gas-oil flow distribution in the process of oil separation from the separator cup wall is the viscous effect. Small bubbles in the center tube aggregate into large bubbles, and interaction of the bubbles along the flow and the fluid running down the cup wall forms a clockwise spiral, which accelerates separation of the gas and oil phases in the separator cup. During the upstroke, the oil volume being sucked out by the center tube through the small hole is larger than the oil volume in the separator cup, which causes entry of air into the center tube and failure of the separator cup.

Keywords: gas-oil separation, multi-cup gas-oil separator, CFD, bubble, simulated analysis.

### Possible paths of origin of gas-oil systems and causes of differences in their properties

### M. A. Lurie and F. K. Schmidt

### E-mail: miklur@rambler.ru

A sequence of possible reactions occurring during evolution of deep-lying fluids, components of which could be sources of biogenous oil substances, is studied within the confines of biogenetic concept of formation of oil. Oxidative condensation transformation of methane and its immediate homologs under the action of sulfur present in some fluids might have facilitated formation of various types of hydrocarbons and organosulfur compounds. A proof of the possibility of such transformations are stable direct correlations between sulfur concentration in oils, their density, viscosity, content of asphaltic-resinous components and heavy fractions, and the scale of oil deposits. The proportion of gas in oil-gas systems decreases with increase of sulfur content. Metals, like V and Ni, in deep-lying fluids affect the geochemical type of oil. Vanadium oils are heavier (V > Ni),

high-sulfur, and occur closer to the surface, while Ni oils are lighter (Ni < V), low-sulfur, and occur in deeper strata. These characteristics apparently stem from the different nature of catalytic properties of the metals and the structures containing them. Transformations of oil fluid with the involvement of heterocomponents thus affect the characteristics of fractional and chemical composition of oil-gas systems.

Keywords: abiogenous oil, origin of oil, sulfur content in oil, asphaltite, vanadium, nickel

# Transformation of straight-run gasoline fraction on high-silica zeolite modified by gallium and zirconium

S. É. Mamedov, Kh. V. Akhmedova, N. F. Akhmedova, S. S. Dadasheva, and É I. Akhmedov *E-mail: n\_akhmed@mail.ru* 

The effect of gallium and its combination with zirconium on the acid and catalytic properties of pentasil in the process of straight-run gasoline fraction upgrading in the absence of hydrogen is studied. It is demonstrated that hydrogenating-dehydrogenating centers and acid centers of medium strength are formed upon simultaneous modification of phosphorus-containing N-ultrasil by gallium and zirconium. At 1:1 Zr:Ga mass ratio an optimal ratio of these centers is attained, which accelerates isomerization of n-paraffins and aromatization of aliphatic and naphtheninc hydrocarbons. Insertion of phosphorus into zeolite facilitates increased yield of liquid products because of weakening and redistribution of acid centers.

Keywords: pentasil, N-ultrasil, gallium, zirconium, straight-run gasoline fraction.

### Effect of ferrospheres as additives on composition of cracking liquid products of mordovokarmal native asphalt

N. N. Sviridenko, E. B. Krivtsov, and A. K. Golovko

### E-mail: dark\_Elf26@mail.ru

Thermocracking products of high-sulfur Mordovo-Karmal asphalt containing 3.7 wt. % sulfur and 6.7 wt. % ibp-200°C fraction are analyzed. Additional 8.1% ibp-360°C fraction can be obtained by cracking the asphalt at 450°C for 120 min with maximum gas and coke yield totaling more than 20 wt. %. The effect of fly ash microspheres on the direction of transformations of asphalt components is studied. Asphalt cracking in the presence of 10% microspheres raises the yield of the ibp-360°C fraction by 10% with a total by-products (gas and coke) yield of only 4 wt. %. Structural-group composition analysis of resins and asphaltenes of asphalt cracking products indicates significant degradation of resin and asphaltene molecules in the presence of microspheres. The average molec-

ular mass of asphaltenes decreases by 703 amu, the number of blocks in a molecule decreases from 4 to 3, and the number of naphthene rings decreases threefold, which leads to increase in aromaticity factor, and the quantity of aliphatic fragments and the length of substituents diminish. The average asphaltene molecule becomes more compact and aromatic structural fragments dominate. **Keywords:** native asphalt, cracking, ferrospheres, microspheres, fly ash, resins, asphaltenes.

### Composition of sulfur-containing structures in resinous-asphaltenous substances and lube components of Usa heavy oil

E. Yu. Kovalenko, T. A. Sagachenko, V. P. Sergun, T. V. Cheshkova, S. S. Yanovskaya, and R. S. Min

### *E-mail: azot@ipc.tsc.ru*

The composition of structural fragments of resin and asphaltene molecules of Usa heavy oil containing C-S bonds of sulfides and containing organosulfur compounds of lube components of this oil is studied. The composition of sulfur-containing fragments of asphaltenes is studied separately for their low- and high-molecular fractions and occluded maltenes. It is shown that alkanes, naphthenes, mono- and polycyclic aromatic hydrocarbons, dibenzothiophenes, and monobasic aliphatic acids occur in the fragments of resinous-asphaltenous substances linked via sulfide bridges. The sulfur-containing structures of lube components are represented by alkyl-substituted thiophenes, benzo-, dibenzo- and benzonaphthothiophenes, and bicyclic sulfides. On thermal treatment of the oil the resin and asphaltene molecules breakdown along sulfide bridges with transition of individual fragments to the composition of the distillates, which must be taken into account while upgrading them.

**Keywords:** heavy oil, resins, asphaltenes, sulfur-containing structures, organosulfur compounds, sulfides.

### Analysis of green waste composting and the effects of humic acid content using near-infrared spectroscopy

Zhen Liu, Yaning Luan, Xiang Yang, and Anlong Zou

### E-mail: luanyaning@bjfu.edu.cn

In order to investigate the mechanism of transformation of green (plant) waste materials into compost, changes in the components of samples of composts produced over different composting periods and with addition of 0, 5, 10, and 15% of humic acid (HA) were analyzed by near-infrared spectroscopy (NIRS). The results indicated that addition of HA can not only accelerate the composting process, but also improve the quality of the compost by increasing its maturity. Addition of HA does not change the functional groups, but changes their number and the structure of the materials. Addition of 10% HA was found to have the most beneficial effects on the composting process and on the resulting compost.

Keywords: green waste, compost, near-infrared spectroscopy (NIRS), humic acid (HA).

### Demulsification performance and mechanism of demulsification of dendritic polyamidoamine

Yang Xinliang and Ai Chi

#### E-mail: yangdagang2012@163.com

The process of synthesis of 1st-, 2nd- and 3rd-generation dendritic polyamidoamines (PAMAM), using ammonia and ethylenediamine, is described. It is shown that the oil drops disintegration rate constant and the degree of breakdown of stable oil-water emulsion increase with each subsequent generation of the dendrimer and with its increase. The maximally attained degree of separation of water containing 68 mg/liter of oil was 84.6% with addition of 20 mg/liter of 3rd-generation PA-MAM. The demulsification mechanism is shown to be associated with the spherical shape of the dendritic PAMAM macromolecules and the presence of a large number of polar amino functional groups on the surface of these spheres.

**Keywords:** dendrimer, polyamidoamine, oil-water emulsion, demulsification performance, demulsification mechanism.

# Experimental investigation of formation rock drillability under bottomhole differential pressure conditions

### Zhang Hui, Sun Tengfei, Huang He, and Gao Deli

#### E-mail: zhanghui3702@163.com

Quantitative evaluation of rock drillability is of vital importance for selecting drilling bits and optimizing drilling parameters. The existing drillability evaluation methods are mostly designed for balanced and near-balanced drilling situation (roughly 0 bottomhole differential pressure), while investigations of under-balanced drilling are rare. In this work, rock drillability and acoustic velocity testing devices are used to investigate rock drillability in under-balanced drilling situation. The experimental results showed that bottomhole differential pressure produces a great impact on both rock drillability and acoustic characteristics. Mathematical statistics methods have been applied to analyze the correlations between rock drillability and acoustic characteristics as well as between differential pressure and acoustic characteristics, and to build a model for forecasting rock drillability under various bottomhole differential pressures. The model provides a sound approach to quantitative assessment of rock drillability based on log data.

**Keywords:** rock drillability, acoustic wave travel time, bottomhole differential pressure, rock mechanics.

# Photometric monitoring of thermal stability of motor oils and effect of thermal degradation products on antiwear properties

B. I. Koval'skii, A. N. Sokol'nikov, O. N. Petrov, and V. G. Shram

### E-mail: shram18rus@mail.ru

The results of determination of thermal stability of mineral and partly synthetic motor oils are presented. The criterion of thermal stability is substantiated and the correlation between it and antiwear properties of the oils is determined. Direct photometric measurement method, which helps obtain an integral parameter of accumulation of all degradation products in the studied oil that can be determined from the luminous flux absorption coefficient, is chosen as the basic method of evaluation of thermal degradation processes. The essential feature of the method consists in comprehensive evaluation of thermal stability and antiwear properties of lube oils from the parameters, namely, the coefficient of luminous flux absorption, relative viscosity, vaporizability, and wear. Correlations of optical properties, viscosity, vaporizability, and antiwear properties of the lube oils with thermostating temperature are obtained, and based on them the limiting temperature of lube oil performing ability was established.

**Keywords:** coefficient of luminous flux absorption, coefficient of vaporizability, criterion of antiwear properties, criterion of thermal stability, resistance to thermal effects

# Evaluation of physicochemical properties of diesel fractions from color characteristics of rgb colorimetric system

R. S. Manapov, D. O. Shulyakovskaya, and M. Yu. Dolomatov

### E-mail: manapoff@yandex.ru

Correlations between some physicochemical properties of diesel fractions of crude oil and color coordinates in sRGB color system are established. Based on these correlations, an express method is proposed for determining relative density, flash point, and initial boiling point of diesel fractions from photoimages, the adequacy of which is confirmed by statistical processing results. This method can find application for prompt monitoring of quality of diesel fractions of technological processes of refineries. Keywords: density of oil fractions, flash point, initial boiling point, color characteristics.

### Modeling thermal radiation of enclosed ground flare

Peng Wang, An-feng Yu, Wen-yi Dang, and Zhong-shu Han

### *E-mail: wangpeng.qday@sinopec.com*

The amount of heat radiated by flares is important for designing and locating flare systems. No methods are reported in the literature for predicting radiation of enclosed ground flares. To investigate radiation of enclosed ground flares, a series of gas flares were simulated in this work by computational fluid dynamics (CFD). The radiation values derived by CFD simulation match the experimental data. For methane, propane, and butane flaring, the radiation flux attained 15.77 kW/m<sup>2</sup> only above the flare system, so radiation will not affect the integrity of the structures. The radiation flux at the ground level was below 1.58 kW/m<sup>2</sup>, so this area is safe for personnel. For hydrogen, the radius of isopleth of radiation flux of 15.77 kW/m<sup>2</sup> can reach 33 m, so towers and elevated structures should not be located in these areas. The radius of isopleth of radiation flux of 6.31 kW/m<sup>2</sup> can reach 70 m, and on the ground the radius of isopleth of 1.58 kW/m<sup>2</sup> radiation flux can reach 120 m. Radiation decreases with increase in enclosed ground flare height, so the safe distance of enclosed ground flare can be reduced by increasing the ground flare height. **Keywords:** enclosed ground flare, thermal radiation, flare height, CFD.

### Experiments for selecting optimal foam drilling fluid formula

Yong Liu, Qian Li, Aiguo Yao, and Xianyong Zhang

### E-mail: a.yao@cug.edu.cn

Drilling gas drainage holes in soft coal seams is essential for preventing coal and gas explosion. After analyzing and summarizing the advantages and disadvantages of existing spiral drilling and wind pressure drilling processes, a new technology of drilling in soft coal seam using foam drilling fluid is proposed in this paper. Experiments were conducted to determine the optimal drilling fluid formula for drilling to depths greater than 200 m. The most effective foam stabilizers are selected and the correlations of half-life period and volume of foam with stabilizer concentration were determined. Based on analysis and comparison of all drilling fluid formulas, the following additives are recommended: 5% K12 + 0.6% Sesbania powder + 1.0% Konjac powder or 5 % K12 + 0.8% Sesbania powder + 1.0% HEC. In field tests, 5 holes deeper than 200 m were drilled successfully by using this formula.

Keywords: soft coal, foam drilling fluid, foam producer, foam stabilizer, foam half-life, field test.

# Solving problems of freezing and blocking of tail gas pipelines while developing oil fields by fire flooding

Chunsheng Wang and Yujian Xu

### E-mail: 1376434643@qq.com

In the process of oil field development by fire flooding, some sections of the tail gas gathering pipelines may get frozen and blocked due to high content in the gas of moisture, methane, ethane, carbon dioxide, and hydrogen sulfide. To solve this problem, investigations were conducted to determine the effect of tail gas components, flow rate, pipeline length, and surrounding temperature on the process of reduction of transmission capacity of the gas pipelines due to freezing and blocking. It was found that the methane content in the gas is mainly responsible for gas hydrate formation and wall freezing, which occur predominantly in the back parts of straight pipes and pipe elbows and junctions. According to calculations, 70% methanol concentration is the best hydrate inhibitor.

**Keywords:** fire flooding, tail gas, pipeline blocking, wall freezing, hydrate formation, SECT (heating by electric current skin effect).