Siberian Federal
University

Minimum Program of

Candidate Exam in a Special Subject

Course (module) Title

Final test for graduate students of
02.00.13 Petroleum Chemistry Guide

Course (module)

Krasnoyarsk, 2020

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Course (module) Guide Actual Problems of Petroleum Chemistry

1. Course (module) Description

1.1. Course (module) overview

This minimum program for the candidate exam in the special course Petrochemistry is intended for graduate students (external students) of the Federal State Autonomous Educational Institution of Higher Education Siberian Federal University, studying in framework of 04.06.01 Chemical Sciences, profile is 02.00.13 Petroleum Chemistry. This program is the basic part of the candidate exam in the specialty. The minimum program covers the issues of the chemical composition and properties of crude oils, sources of petrochemicals production and the industrial processing. The minimum program for the candidate exam was developed in accordance with the program for petrochemistry recommended by the expert council of the Higher Attestation Commission of the Ministry of Russia Education with the participation of the Russian University of Chemical Technology named after D. I. Mendeleev and the Institute of Petrochemical Synthesis named after A. V. Topchiev RAS. An additional part of the candidate exam in the specialty is developed individually for each graduate student (external student) after taking into account the area of his/her scientific research and the topic of the dissertation work. The additional program is approved by the Academic Council.

2. Course (module) requirements

2.1 Required text(s)

Main literature

1. Petroleum Chemistry and Refining [Text]: monograph / ed. J. G. Speight. - London: Taylor & Francis, 1998. - xiv p. : ill. - (Applied Energy Technology Series / Editor: J.G. Speight¤). - Glossary: p. 247-262.
2. The chemisty and technology of petroleum [Text] / J. G. Speight. - 4th ed. - Boca Raton ; London ; New York : CRC Press : Taylor & Francis Group, 2006. - 919 p.
3. Applied process design for chemical and petrochemical plants [Electronic resource]. Vol. 1 / E. E. Ludwig. - 3th ed. - Electronic text data (28,8 МБ). - Boston : Butterworth-Heinemann, 1999. - 630 p.
4. Applied process design for chemical and petrochemical plants [Electronic

resource]. Vol. 2 / E. E. Ludwig. - 3th ed. - Electronic text data (38,3 МБ). - Boston : Butterworth-Heinemann, 1999. - 486 p
5. Applied process design for chemical and petrochemical plants [Electronic resource]. Vol. 3 / E. E. Ludwig. - 3th ed. - Electronic text data (24,4 МБ). - Boston : Butterworth-Heinemann, 1999. - 690 p.
6. Handbook of Vinyl Polimers. Radical Polymerization, Process and Technology [Text]: monograph / Y. Vagci; Ed. M.K. Mishra. - 2nd ed. - London: CRC Press, 2009. - 763 p.
7. Handbook of MTBE and Other Gasoline Oxygenates [Text] / ed.: H. Hamid, M. Ashraf Ali. - New York : Marcel Dekker, 2004. - 381 p.
8. Polymer Chemistry [Text]: monograph / W. R. Moore. - London: University of London Press LTD, 1967. - 270 p.
9. Petroleum Processing Handbook [Text]: monograph / ed. J. J. McKetta. - Basel; Hong Kong: Marcel Dekker, 2010. -774 p.
10. Practical Advances in Petroleum Processing [Text] / ed .: C. S. Hsu, P. R. Robinson. - Berlin: Springer, 2006 -. Volume 2. - 2006. - xv, 411 p.
11. Purification of laboratory chemicals [Electronic resource] / Wilfred L. F. Armarego, Christina L. L. Chai. - Electronic text data (20,1 MB). - Amsterdam: Butterworth-Heinemann, 2003. - 634 p. - Ver. with the title. screen. - Electron. version of the printer. publication.
12. Organic chemistry [Electronic resource] / J. Clayden. - Electronic text data (33,9 МБ). - [S. l. : s. n.], 2001. - 1490 p
13. Polymers a Property Database [Text]: monograph / ed .: B. Ellis, R. Smith. - 2nd ed. - London: CRC Press, 2009. - xxii p. : tabul. - Name and Synonym index: p.1089-1106.
14. Petroleum Refining. Tehnology and Economics [Text] / J. H. Gary, G. E. Handwerk, M. J. Kaiser. - 5th ed. - Boca Raton; London: CRC Press; London; New York: Taylor & Francis Group, 2007. - 463 p.
15. Essentials of Petroleum. A Key to Oil Economics [Text]: monograph / P. H. Frankel; foreword by M. A. Adelman. - London: Frank Cass, 2005. - xiii, 188 p.
16. Petroleum Refinery Process Economics [Text]: a monograph / R. E. Maples. - 2nd ed. - Tulsa: Penn Well, 2000. - xxix, 474 p.
17. Peters K.E., Walters C.C., Moldowan J.M. The Biomarker Guide. I. Biomarkers and Isotopes in the Environment and Human History. – New York: Cambridge University Press, 2005.
18. Peters K.E., Walters C.C., Moldowan J.M. The Biomarker Guide. II. Biomarkers and Isotopes in the Petroleum Systems and Earth History. – New York: Cambridge University Press, 2005.

The list of information and telecommunication resources required for mastering the discipline (module) is available via Internet network

1. www.eLIBRARY.RU - Scientific electronic library. Access mode is free.
2. www.sciencedirect.com - Elsevier Database. Access mode is free.
3. www.nature.com - Scientific journal Nature. The access mode is free.
4. www.scopus.com - Scopus peer-reviewed literature database. Access mode is free.
5. www.springerlink.co - Springer Database.
6. www.isiknowledge.com - Web of Science Database. Access mode is free.

2.2 Web page of the course (module)

You can receive the information about the postgraduate program 02.00.13 Petroleum Chemistry and about the course in SibFU website: www.e.sfu-kras.ru. You must be logged in to access to some sections. The section, that shows the main demands and terms of the postgraduate program, is freely available. The applicants can be advised on issues of admission to the program and about other possibilities and questions via electronic services like Skype or Zoom by person responsible for this task. The contact person can be found through SibFU website: www.e.sfu-kras.ru.

3. Prerequisites

Background in general chemistry, organic chemistry, refining.

4. The list of the main questions to the exam.

4.1. Chemical composition and properties of oil.

4.1.1 Origin of oil.

Genesis and chemical evolution of crude oils. Organic theory of the crude oils origin. Source material and its conversion to crude oil. Biodegradation of oil in natural conditions. Oil formation process and chemical composition of oil. Biomarkers. Influence of temperature and natural catalysts. Mineral theory of crude oils origin.

4.1.2 Properties, composition and classification of crude oils.

Physical properties of oils. The chemical composition of oil. Fractional composition of oil. Elemental, individual and structural-group composition of oil. Classification of oils.

4.1.3 Oil research methods.

Physical and physicochemical methods. Rectification. Chromatographic methods. Infrared, electronic spectroscopy in the analysis of hydrocarbon and heteroatomic components. Molecular mass and chromatography-mass spectroscopy. Schemes for the separation of hydrocarbon, heteroatomic and high molecular weight components of oils and their physical basis. Nuclear magnetic and paramagnetic resonance.

4.1.4 Historical overview of research on the chemistry of petroleum hydrocarbons.

The works of D.I. Mendeleev, V.V. Markovnikova, D.P. Konovalova, N. D. Zelinsky, S.S. Nametkina, B.A. Kazansky, A.V. Topchiev and others.

4.1.5 Petroleum hydrocarbons of the methane series (paraffins).

Physical and chemical properties of normal and branched paraffins. Gaseous paraffins. Natural gas. Liquid and hard paraffins. Paraffin and ceresin. Isoprenane oils.

4.1.6 Naphthenes (cyclic petroleum hydrocarbons).

Hydrocarbons of the cyclohexane and cyclopentane series. Their content in oils. Major reactions. Bicyclic petroleum hydrocarbons. Condensed and bridged bi- and polycyclic hydrocarbons. Adamantane and its homologues. Triterpans, sterans and hopans. Thermodynamic stability of cyclanes. Conformational analysis of cyclic hydrocarbons.

4.1.7 Aromatic hydrocarbons of petroleum.

Types of aromatic hydrocarbons in petroleum and their determination in oils.

4.1.8 Sulfur compounds of oil.

Characterization of sulfur compounds and their determination in oils. Prospects for their practical use. Sulfur content in various oils and petroleum products.

4.1.9 Nitrous compounds of oil.

Basic types, their characteristics and definition in oils.

4.1.10 Oxygen compounds of oil.

Petroleum acids. Characteristics and content in oil.

4.1.11 Resinous and asphalt components of petroleum.

Separation and characterization. Metallic compounds of oil. Porphyrins. Microelements.

4.2 Oil refining and gas processing industry as a source of the main petrochemicals, liquid fuels and oils production.

Oil and gas as sources of production of the main group of starting materials for industrial organic and petrochemical synthesis (paraffins, olefins, aromatic hydrocarbons, acetylene, carbon monoxide and synthesis gas), liquid fuels and lubricating oils.

4.2.1 Industrial processes of primary oil and gas processing.

Electrical desalting and primary distillation of oil. Typical schemes of oil

refineries. Processing of natural gas and gas condensates. Processing of associated gas.

4.2.2 Catalytic cracking.

Feedstock and products of a cracking. Cracking catalysts, structure of aluminosilicates and the nature of their catalytic activity. The role of protic and aprotic acidity. Zeolites. The mechanism of the ongoing reactions. Changing the properties and regeneration of catalysts in the cracking process. Industrial catalytic cracking units and main technological parameters.

4.2.3 Catalytic reforming.

Raw materials and products of reforming. Obtaining high-octane components of gasoline and aromatic hydrocarbons. Reforming catalysts, basic reactions and the mechanism of catalytic conversion of naphthenic, paraffinic and aromatic hydrocarbons. Changing the properties and regeneration of catalysts in the reforming process. Industrial catalytic reforming units and main technological parameters.

4.2.4 Hydrogenation processes in oil refining.

The main purpose, catalysts, chemical bases and the mechanism of hydrogenation processes. Hydrotreating of motor fuels, lubricating oils, paraffins, vacuum distillates and 4 secondary gas oils. Hydrodesulfurization of oil residues. Hydrocracking of gasoline fractions to obtain motor fuels, liquefied gases and isoparaffinic hydrocarbons. Hydrogenation processes in the production of lubricating oils. Hydrodealkylation and other hydrogenation processes in the production of aromatic hydrocarbons.

4.2.5 Thermal cracking and pyrolysis.

Thermodynamics and kinetics of decomposition of hydrocarbons of various series and molecular weight. Free-radical mechanism of thermal cracking of hydrocarbons. Obtaining light oil products by thermal decomposition of residual fractions, improving the quality of boiler fuel, obtaining thermogas oil and petroleum coke. Pyrolysis of petroleum fractions and gas feedstock for the production of lower olefins and aromatic hydrocarbons. Processing of gaseous and liquid pyrolysis products. Pyrolysis of methane and other hydrocarbons to produce acetylene. Regenerative, homogeneous and oxidative pyrolysis. Electrocracking. Composition of pyrolysis gases and their separation.

4.2.6 Production of paraffins.

Production of liquid paraffins by dewaxing diesel fractions. Dewaxing of oil fractions to obtain solid paraffins.

4.2.7 Petroleum fuels.

General characteristics of the main types of fuel (automobile, diesel, aviation, jet, boiler, etc.). Behavior and conversion of hydrocarbons during combustion in

engines. Improving the performance of fuels with additives. Antiknock agents and their mechanism of action. Octane number. Cetane number.

4.2.8 Petroleum oils.

Lubricating oils and their main characteristics. Synthetic additives for lubricating oils (antioxidants, depressants, detergents, viscous, antiwear, etc.), their mechanism of action. Complex additives. Technical oils.

4.2.9 The problem of replacing petroleum feedstock in the production of liquid fuels and oils.

Opportunities and prospects of using coal, peat, oil and bituminous shale, plant raw materials for the production of artificial liquid fuel.

4.3. The main processes for industrial processing of petrochemical feedstock.

4.3.1 Halogenation processes.

Scientific basis for the processes of halogenation of paraffins, olefins, acetylene, aromatic and alkylaromatic hydrocarbons. Substitution and addition chlorination. Halogenating agents, catalysts and initiators, halogenation conditions. Thermal, photochemical and oxidative halogenation and the mechanism of these reactions. Hydrochlorination of olefins and acetylene. Obtaining chloromethanes, chloroethanes, allyl chloride, chlorobutenes, chloroparaffins, vinyl chloride, chloro- and polychlorobenzenes.

4.3.2 Hydration of olefins and acetylene.

Thermodynamics, catalysts and mechanisms of hydration reactions. Synthesis of ethanol, isopropanol, sec- and tert-butanols, acetaldehyde.

4.3.3 Alkylation processes.

Alkylation with olefins of aromatic hydrocarbons. Catalysts, reaction mechanism and kinetics. Getting ethyl-, diethyl- and isopropylbenzenes. Alkylation of benzene with higher olefins. Alkylaromatic plasticizers, lubricating oils, additives and surfactant feedstock. Alkylation of phenols, production of polymer and oil stabilizers. Alkylation of paraffins, catalysts and reaction mechanism. Synthesis of high-octane motor fuels. o-Alkylation with olefins and acetylene. Synthesis of methyl tert-butyl ether, vinyl acetate and vinyl alcohol ethers. Vinylated with acetylene. Syntheses of vinyl acetylene, acrylonitrile and vinyl pyrrolidone.

4.3.4 Dimerization and oligomerization of olefins.

Olefin dimerization and oligomerization catalysts. Organoaluminum compounds and syntheses based on them. Production of linear olefins. Synthesis of linear primary alcohols.

4.3.5 Metathesis (disproportionation) of olefins.

Homogeneous and heterogeneous catalysts. Mechanism. The influence of the position of the multiple link. Practical use and prospects.

4.3.6 Oxidation and epoxidation processes.

Oxidizing agents (molecular oxygen, nitric acid, peroxide compounds). Radical chain oxidation of paraffinic and alkylaromatic hydrocarbons. Kinetics and catalysis of the reaction. Obtaining hydroperoxides of tert-butylbenzene, ethylbenzene and isopropylbenzene. Obtaining alcohols and acids by oxidation of paraffins. Oxidation of naphthenes to alcohols and ketones. Oxidation of methylbenzenes to aromatic acids. Heterogeneous catalytic oxidation of hydrocarbons and their derivatives. Oxidation of aromatic and other hydrocarbons with the formation of internal anhydrides of di- and tetracarboxylic acids. Oxidative ammonolysis of olefins and other hydrocarbons to form nitriles. Oxidation of olefins with retention of the double bond. Getting acrolein. Oxidation of ethylene to ethylene oxide. Oxidation catalysts in the listed processes, reaction mechanism and kinetics. Metal complex catalysis of olefin oxidation. Epoxidation of olefins with peroxyacids, hydrogen peroxide and hydroperoxides. Getting propylene oxide and glycidol. Synthesis of acetaldehyde and vinyl acetate from ethylene.

4.3.7 Processes of dehydrogenation and hydrogenation.

Thermodynamics of dehydrogenation and hydrogenation reactions. Catalysts, mechanism and kinetics of dehydrogenation and hydrogenation reactions. Catalytic and thermal dehydrogenation. Dehydrogenation of alkylaromatic compounds. Getting styrene, - methylstyrene, divinylbenzene. Dehydrogenation of paraffins and olefins. Getting butadiene and isoprene. Oxidative dehydrogenation of olefins. Hydrogenation of aromatic hydrocarbons. Getting cyclohexane.

4.3.8 Syntheses based on carbon monoxide.

Synthesis of hydrocarbons from CO and hydrogen. Catalysis, conditions and reaction mechanism. Synthesis of alcohols from CO and hydrogen. Getting methanol. Synthesis of aldehydes and alcohols C3-C9 from olefins, CO and hydrogen (oxosynthesis). Synthesis of carboxylic acids based on the reaction of carbonylation of olefins, acetylene and alcohols. Prospects for syntheses using carbon monoxide and dioxide.

4.3.9 Processes of sulfonation, sulfation, sulfonation and sulfonation.

Sulfurizing agents and conditions for their use. Mechanism of reactions. Obtaining alkyl sulfonates, olefin sulfonates, alkyl benzene sulfonates, alkyl sulfates. Their importance in the synthesis of surfactants. Scopes of surfactants, including oil production.

4.3.10 Nitration processes.

Nitration of paraffins, naphthenes and aromatic hydrocarbons.

5. Grading scale

Grade policy for both home assignments and the exam is:

- A (excellent work) 91–100 points
- B (above average work) 81–90 points
- C (average work) 71–80 points
- D (below average work) 50–70 points
- F (failed work) < 50 points