

**NATIONAL ACADEMY OF SCIENCES OF UKRAINE  
V.P. KUKHAR INSTITUTE OF BIOORGANIC CHEMISTRY AND PETROCHEMISTRY**

APPROVED

by the decision of the Scientific Council  
of the V. P. Kukhar Institute of Bioorganic Chemistry  
and Petrochemistry of the NAS of Ukraine

Protocol No. 5

June 07, 2017.

**SYLLABUS FOR  
“PETROCHEMISTRY AND COAL CHEMISTRY”**

Third (PhD) educational level

Field: 102 “Chemistry”

Specialty “Petrochemistry and Coal chemistry”

**I. PETROCHEMISTRY**

**1. Fundamentals of Theoretical Organic Chemistry**

Chemical reaction at the molecular level. Stable substances and intermediates. Material balance of chemical reactions. Stoichiometric analysis. Basic concepts of chemical kinetics. Kinetic model of chemical reaction. Construction of kinetic models of reactions that take place with the participation of stable substances. Experimental installations for studying the laws of chemical reactions: an ideal batch reactor; continuous reactors. The course of simple reactions in continuous reactors. First order reaction. Irreversible reaction of the second order with the participation of two reagents. Equilibrium reaction. Kinetics, composition of products and selectivity of complex reactions. Integral method of analysis of kinetic curves. Choice of conditions for simple reactions.

**2. Introduction. Raw materials and starting materials of Organic Synthesis**

Industry of basic organic and petrochemical synthesis, its main features and prospects of development. Main types of products: intermediates, monomers, plasticizers and excipients, synthetic fuels and oils, surfactants, solvents, pesticides.

### **3. Starting materials. Paraffins, their technical properties and applications.**

Isolation of low paraffins from natural and associated gases. Isolation of hard and soft paraffin. Isomerization of paraffins. Characteristics of paraffin hydrocarbon fractions and their purification.

### **4. Olefins, their technical properties and applications.**

Theory of cracking and pyrolysis reactions. Technology of pyrolysis of hydrocarbons, equipment and schemes of pyrolysis and separation of gases, directions of development of process. Thermal cracking of paraffin, catalytic cracking. Characteristics of olefin fractions, their purification, processing of butylene and amylene fractions. Acid polymerization of olefins and products. Organoaluminum synthesis of olefins and its products. Disproportionation of olefins.

### **5. Aromatic Hydrocarbons, their technical properties and applications.**

Aromatic hydrocarbons of pyrolysis. Coking of coal and catching of products. Theoretical bases and technology of reforming processes, received products. Separation of flavoring products and their purification. Characteristics of aromatic hydrocarbon fractions. Isomerization of polymethylbenzenes and their separation. Obtaining benzene and naphthalene by dealkylation and disproportionation processes.

### **6. Acetylene, its technical properties and applications.**

Production of acetylene from calcium carbide and its purification. Theoretical basics and methods of obtaining acetylene from hydrocarbons. Production technology and release of acetylene.

### **7. Carbon monoxide and synthesis gas, their technical properties and applications.**

Theoretical bases and methods of hydrocarbon conversion. Production technology synthesis gas and its purification. Obtaining concentrated carbon monoxide.

### **8. Halogenation processes.**

Classification of reactions, their energy characteristics. Halogenating agents. Occupational safety during the halogenation process. Chlorination of methane hydrocarbons and their chlorine derivatives. Process theory and chlorination methods. Chlorination of olefins. Products and olefin substitution chlorination technology. Chlorination of acetylene. Products and additive chlorination of acetylene technology. Chlorination of aromatic compounds. Theoretical bases and technology of chlorination in aromatic kernel. Chlorination in the side chain and additive chlorination, theory and technology of these processes. Products received chlorination of aromatic compounds.

Chlorine cleavage reaction, combined and combined processes. Technology of synthesis of vinyl chloride from ethylene, other applications of combined and combined processes.

Chlorination of other organic compounds. Theoretical foundations, products and technology chlorination of alcohols, carbonyl compounds, carboxylic acids, acid amides. Synthesis phosgene.

Fluorination processes. Fluorination with elemental fluorine and fluorides of metals, process theory and technology. Hydrogen fluoride fluorination, theoretical foundations process. Freon production technology. Organofluorine monomers and methods thereof obtaining.

### **9. Processes of hydrolysis, hydration, dehydration, esterification and amidation.**

Classification of reactions. Hydrolyzing agents and catalysts. Hydrolysis and alkaline dehydrochlorination of chlorine derivatives, the theory of these reactions, the obtained products and types reactors. Technology of epichlorohydrin production.

Esterification, process theory and main products. Types of reactors and technology esterification with carboxylic acids, anhydrides and acid chlorides. Reaction amidation, dehydration, hydrolysis and esterification of amides. Hydrolysis of nitriles. Technology obtaining methyl methacrylate. Isocyanates, carbamates and dithiocarbamates. Production melamine.

Sulfuric acid esters and sulfuric acid hydration of olefins. Synthesis theory sulfates from alcohols and olefins, influence and choice of parameters. Surfactants such as alkyl sulfates, properties and applications, technology of their production. Hydrolysis of alkyl sulfates and sulfuric acid hydration products. Types of reactors and production technology.

Direct hydration and dehydration processes. The theory of direct dehydration of olefins, choice of conditions. Ethanol production technology. Hydration of acetylene, theoretical basics, methods and reaction equipment. Dehydration reaction with the formation of ethers and saturated substances, process methods and products. Dehydration carboxylic acids, acetic anhydride and ketene.

### **10. Alkylation processes.**

Classification of reactions and their energy. Alkylating agents.

Alkylation on the carbon atom. Theory of aromatic alkylation reactions hydrocarbons, choice of conditions. Products and methods of alkylation, reaction apparatus. Alkylbenzene production technology. Alkylation of phenols, choice of conditions. Alkylphenols and the technology of their production. Chemistry and technology of alkylation of isoparaffins. Isooctane.

Alkylation on oxygen, sulfur and nitrogen atoms. The theory of these reactions is obtained products. Choice of conditions and types of reactors. Technology of amine synthesis.

Processes of  $\beta$ -oxyalkylation and other reactions of  $\alpha$ -oxides. Chemistry and theoretical basics of oxyethylation reaction, choice of conditions. Products of processing of ethylene oxide and propylene,

nonionic surfactants. Types of reactors and technology of oxyalkylation processes. Other syntheses based on  $\alpha$ -oxides.

Vinyl processes. Chemistry and theoretical foundations of the process. Production technology vinyl acetate. Acetylene oligomers and their synthesis. Vinyl esters. Vinyl amides and carbazole.

Alkylation by atoms of other elements. Direct synthesis of organochlorosilanes, reactors and process technology. Organosilicon monomers and other products. Theoretical bases and technology of synthesis of aluminum trialkyls, their application. Production of tetraethyl lead.

### **11. Sulfation and nitration processes.**

Sulfation of aromatic compounds, process theory, sulfonating agents. Choice of conditions and types of reactors. Sulfonation products, surfactants such as alkylarylsulfonates, technology their production. Sulfonation of paraffins, chemistry and theoretical bases of reaction sulfochlorination and sulfoxidation. Surfactants such as alkylsulfonates and their technology production.

Nitration. Chemistry and theoretical bases of nitration of aromatic compounds, technology synthesis of nitro compounds. Nitration of olefins and acetylene. Chemistry and technology of nitration paraffins. Nitroparaffins.

### **12. Oxidation processes.**

Classification of reactions, oxidizing agents. Energy characteristics of reactions. Occupational safety in oxidation processes.

Homogeneous oxidation processes. Oxidation of lower paraffins in the gas phase. Liquid-phase oxidation of n-butane and gasoline. Synthetic production technology fatty acids. Oxidation of naphthenes, the basic laws of the process obtained products. Technology of cyclohexane oxidation and adipic acid production. Cyclic ketones and aliphatic dicarboxylic acids. Oxidation of aldehydes, basic patterns of the process and products. Obtaining acetic acid. Technology joint production of acetic acid and acetic anhydride. Oxidation of hydrocarbons to hydroperoxides, the basic laws of the process. Production technology hydroperoxides. Technology of cumene method of phenol and acetone synthesis. Others methods of phenol production and their comparison. Oxidation of side chains aromatic compounds and carboxylic acids, the basic laws of the reaction and products. Technology of dimethyl terephthalate production. Other ways to obtain aromatic polycarboxylic acids.

Heterogeneous catalytic oxidation processes, their mechanism, kinetics and catalysis, selectivity, choice of conditions and type of reaction apparatus. Oxidation of olefins by saturated carbon atom, the basic laws of the process and the resulting products. Oxidative ammonolysis reaction, its theoretical bases, regularities and obtained products. Acrylonitrile production technology. Prussic acid. Vapor

phase oxidation of aromatic compounds into acid anhydrides, the basic laws of the process and received products. Ethylene oxide production technology, comparison of methods its receipt.

Oxidation of olefins with metal complex catalysts. Reaction epoxidation, its scientific bases and laws. Combined syntheses based on epoxidation by olefins, their technology. Oxidation of olefins with palladium catalyst, theoretical foundations and patterns of the process. The received products and technology of their production.

### **13. Dehydrogenation and hydrogenation processes.**

Classification of reactions, mechanisms, catalysis and kinetics of reactions. Basics of choice hydrogenation and dehydrogenation parameters. Dehydrogenation processes. Dehydrogenation and oxidative dehydrogenation of alcohols. The basic laws of the process and obtained products. Formaldehyde production technology. Dehydrogenation of alkylbenzenes, chemistry and methods of obtaining styrene and its homologues. Styrene production technology. Dehydrogenation of paraffins, basic laws of the process. Comparison of methods obtaining divinyl and isoprene. Technology of two-stage production of butadiene and isoprene. One-stage process and its patterns. Technology of separation of mixtures and the release of dienes. Oxidative dehydrogenation processes.

Hydrogenation processes. Chemistry and basic laws of hydrogenation reactions. Hydrogenation of hydrocarbons by double, triple and aromatic bonds. Reactions aromatic redistribution of hydrogen. Hydrogenation and selective hydrogenation of alcohols, carbonyl compounds, nitriles, nitro compounds. Hydroammonolysis reaction. Destructive hydrogenation. Technology of hydrogenation processes. Liquid-phase hydrogenation, its parameters and types of reactors. Technology of obtaining higher alcohols from acids. Gas phases hydrogenation, its parameters and types of reactors. Benzene hydrogenation technology in cyclohexane. General features of hydrogenation technology.

### **14. Syntheses based on carbon monoxide.**

Classification of reactions. Syntheses from carbon monoxide and hydrogen, their conditions and received products. Theoretical foundations and technology of methanol production.

Oxosynthesis, its chemistry and theoretical foundations, products. Choice of conditions and schemes of reaction units of aldehyde oxosynthesis. Process technology.

Carboxylation processes, chemistry and theoretical bases of reaction. Carboxylation alcohols and ethers. Obtaining formic acid and its esters.

Condensation by carbonyl group. Classification of reactions, their theoretical bases.

### **15. Acid-catalytic and basic catalytic processes.**

Condensation of carbonyl compounds with aromatics, chemistry and reaction products. Technology of synthesis of DDT and diphenylpropane. Chloromethylation reaction. Synthesis acetals and the Prince reaction. Chemistry and technology of isoprene production from butylene. Condensation of carbonyl compounds with nitrogenous bases, chemistry and reaction products. Synthesis of oximes and their rearrangement in elbows. Production technology caprolactam, other methods of its production.

Chemistry of aldol condensation, products. Choice of reaction conditions and types reactors. Production technology of 2-ethylhexanol and pentaerythritol. Synthesis cyanhydrides and vinylpyridines. Alkynol synthesis, chemistry and process technology, received products.

### **16. Metathesis reaction.**

Metathesis of olefins: catalysts, mechanisms. The main types of metathesis reactions. Industrial processes.

### **17. Cluster catalysis**

Cluster catalysis: ideas about metal clusters, examples of catalytic mechanisms.

### **18. Alternative raw materials for petrochemical synthesis**

Methods of processing coal into hydrocarbons (thermal dissolution, hydrogenation, destructive hydrogenation). Coal gasification. Semi-coking and coking. Coke resin is a source of aromatic raw materials. Coal is an alternative oil and natural gas as raw materials for the petrochemical industry. The use of oxide carbon in the production of fuels and petrochemical raw materials. Fischer-Tropsch process. Modern ideas about the mechanism of the Fischer-Tropsch process. Methanol - fuel and raw materials for petrochemical synthesis. Conversion of methanol to hydrocarbons. Simple methyl esters - an additive to gasoline.

Bioresources are potential raw materials for organic and petrochemical synthesis.

### **19. Biofuels**

Biodiesel. Raw materials. Chemistry of technological processes. Biogasolines. Raw materials. Gasoline recipes. Pros and cons of using biogasoline.

## II. COAL CHEMISTRY

### 1. Introduction. Solid fuel is a source of heat and electricity and chemical raw materials.

A brief history of the development of chemical fuel technology. The most important deposits of fossil fuels. Resources of combustible minerals in Ukraine and around the world. Mining and consumption of various types of combustible minerals in Ukraine and other countries.

Prospects for the development of production and thermal processing of various types of fuel minerals in Ukraine. The main directions and methods of processing combustible minerals for obtaining high-quality fuels and chemical raw materials.

### 2. Chemistry of Solid Combustible Minerals (SCM)

General systematics of various SCM's and their defining features (peat, brown coal, coal, anthracite, sapropel, bogheads, oil shale). Stages of SCM development (peat, lignite, coal). The origin of SCM. Carbohydrates. Origin of petrographic components. The origin of humic coal and sapropels. Mixed coal. Striped coal.

Known methods of classification of fossil coal (Potone, Pearl, Ginzburg, Stadnikov, Gruner, Stops, Karavaev, etc.). Characteristic of SCM for data of their technical analysis. Moisture, mineral components and ash content of coal. The yield of volatile substances from SCM. Characteristics of solid non-volatile residue. General sulfur and types of sulfur compounds in coal. Conditional and true organic (combustible) mass coal. Relationship between technical analysis data and chemical nature, maturity and composition of combustible minerals.

Characteristics of SCM according to elemental analysis. The relationship between data elemental analysis and the chemical nature of SCM. Classification of coal according to data elemental composition. Elemental composition and heat of combustion of SCM.

Interaction of SCM with various solvents and chemical reagents. Action on SCM various organic solvents (benzene, anthracene oils, pyridine, etc.) and chemical reagents (mineral acids, alkalis, halides, etc.). Group chemical composition different types of SCM. Humic acids. Mountain wax. Bitumens. Thermobitumen of coal.

Molecular structure of SCM. Physical and physicochemical research methods (X-ray diffraction analysis, electron and optical microscopy, ICS, EPR, NMR, dielcometry). Study of physico-mechanical, thermophysical and electrophysical properties. Possibilities of using Navy chemistry methods. Study of chemistry and mechanism of thermochemical transformations of coal. Modern ideas about molecular structure of substances of different types of SCM. Molecular structure (MS) and Supramolecular organization (SMO) of natural coal. Chemical bonds in coal.

Known models of the coal macromolecule (Stadnikov, Kasatochkina, Givena, Van-Crevelen, Weiser, Solomon, Lazarov, Shinn, etc.). Two-phase structure model coal. The nature of the interactions between the phases (Marzhets). The model of self-associated multimer with a three-dimensional structure (Gagarin, Skripchenko, Krychko). Model vitrenized organic mass of coal (OMC) as “labile polyconjugate supersaturated structure of mainly non-aromatic character” (Rusyanova).

Scientific and industrial classifications of SCM. International classification of stone and brown coal. Preparation of solid fuel for processing and quality control. Theoretical bases of SCM enrichment, their desulfurization.

### **3. Theoretical foundations of the process of thermal destruction of THC**

Regularities of pyrolysis of solid fuels in isothermal and non-isothermal conditions. Influence of temperature and heating time on the degree of THC decomposition. Impact on the process of thermal destruction of fuels of their nature, heating rate, particle size, pressure, composition of the gaseous medium. Two main stages of heat treatment of fuels: heating of the fuel mass and a process involving physicochemical changes in the organic mass fuel.

Methods of research of transient (10<sup>-1</sup>, 10<sup>-4</sup> p.) Reactions and processes destructive pyrolysis of organic matter fuels with heating rates on several orders of magnitude larger than those used for these purposes in industry. High-speed process of fuel decomposition.

Homogeneous and heterogeneous pyrolysis reactions of solid fuels. Qualitative and quantitative yield of products of thermal destruction of fuels as a result of chemical and physical reactions changes in the reaction medium. Determination of macrokinetic characteristics of pyrolysis fuels in isothermal and non-isothermal conditions. Chain and radical chain mechanisms of the process of destruction and compaction of carbon mass. Autocatalysis in the process of pyrolysis of pitch materials.

Modern methods of studying the mechanism and kinetics of the destruction process organic substances of solid fuels. Determination of kinetic characteristics of decomposition solid fuels by derivatographic method in low thermal mode.

### **4. Theoretical bases of the process of gasification of fuels and conversion of hydrocarbons gases**

Chemical equilibrium of the main reactions of carbon with gases. Kinetic method interpretation of chemical equilibria. Calculation of the equilibrium composition of the gas in the process interaction of carbon with gases. Chemical equilibrium in imperfect gas mixtures.

Mechanism of reaction of carbon with gases and reactions of conversion of hydrocarbon gases. Inverse, sequential and parallel-sequential reactions of the process of interaction of carbon with gases and conversion of hydrocarbon gases. Scheme of the reaction mechanism of carbon with CO<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>.

Chemical adsorption. Formation and disintegration of a solid surface complex. Inhibitory action of reaction products. Chain mechanism of carbon reactions with gases. Kinetic equations based on the concepts of the mechanism of carbon reactions with gases.

Basic diffusion-kinetic theories of combustion and gasification of solids fuel. Equity participation of individual reactions in the total process. The dependence of the total process speed from chemical and physical factors. Determination of basic kinetic characteristics of carbon reactions with gases. Derivation of kinetic equations taking into account changes in the volume of the gas phase in the response for inverse, sequential and parallel-sequential reactions of carbon with gases. Kinetic method of determination equilibrium constants of carbon reactions with gases.

Calculation of the reaction zone under isothermal conditions. Reaction calculation zones in non-isothermal conditions. Types of non-isothermal. Thermal regime of endothermic and exothermic reactions. System of equations for determining concentrations, temperature gas and solid phase in the reaction zone. Calculation of the carbon response process with gases in non-stationary and non-isothermal conditions.

## **5. Technology of thermochemical destruction of THC without access of air**

Influence of heating method on yield and quality of products of thermal processing of fuels and their use. Coke residue (semi-coke), primary resin, gas, tar water.

Features of shale processing technology. Chemical products of processing shales. Thermal processing of shales with solid coolant. Features of technology thermal destruction of peat and methods of its direct use.

Energy-technological methods of fuel use. Necessary connection conditions power plants with industrial furnaces for thermal fuel processing. High process intensity. Process management. Getting high-calorie gas and high-quality small-component liquid products. Energy technology methods heat treatment of shale. Integrated energy use of fuels in conditions of the new fuel balance structure. Chemical products of thermal processing brown coal and peat and their characteristics as raw materials for synthesis.

Use of coal, peat, oil shale and products of their processing in agriculture. Humic fertilizers, herbicides, etc.

Semi-coking and coking. Basic technologies. Influence of heating rate, temperature and type of coal. Known methods of semi-coking and coking coal. Processes that occur during the coking of hot coal and coal charge. Assembly of coal charges. Plastic state as a result of thermal destruction of coal. Swelling and expansion pressure. Sintering, transformation of semi-cokes in coke. Shrinkage and cracking. Isolation of gaseous products on different stages of the coke formation process. Sintering, spiken and coking ability of stone coal and methods of their determination. The influence of various factors on the

coking process. Coke quality assessment. Modern coke production technology. Ways to expand raw material base for coking.

Chemical products of semi-coking and coking of coal. Condensation and capture. Extraction of crude benzene. Processes of rectification, crystallization, adsorption. Obtaining concentrated ammonia and ammonium sulfate. Coal resin. Methods of its processing.

## **6. Residual gasification of fuels**

Gasification of fuels as a method of residual use of organic matter fuel. Raw materials for gases (solid and liquid fuels, natural gases, related gases and gases of oil production, oil refining). The main ways of gasification development solid fuels. The intensity of the process. Energy efficiency. Analysis of shortcomings and opportunities to intensify and increase the economic efficiency of production gases from solid fuels. Physico-chemical bases of the process. Autothermal and allothermic processes.

Characteristics of the gas formation process in a dust flare, in a fluidized bed and in a dense layer of fuel. Disadvantages of modern industrial production methods gas. The need to include in the energy scheme of the gas generating process.

Gasification of steam and gas products formed during thermal decomposition brown coal. Methods of production of air, steam, water and steam oxygen gases from pulverized, fine-grained and piece fuel.

Characteristics of liquid fuels used for gasification. Production of gases from liquid fuels for the synthesis of alcohols and ammonia. Obtaining olefins and acetylene hydrocarbons. Gasification of liquid fuels under high pressure. Basic indicators of fuel gasification.

## **7. Destructive hydrogenation of fuels and synthesis of hydrocarbons from hydrogen and carbon monoxide**

Features and purpose of destructive hydrogenation processes. Chemical basics of the process. Evaluation of the suitability of coal for hydrogenation. Catalysts and technological parameters of destructive hydrogenation. Step destructive hydrogenation of resins and oil residues. Liquid-phase and vapor-phase hydrogenation. Yield and characteristics of hydrogenation products. Obtaining chemical products by the method of hydrogenation of fuels. Compatible hydrogenation of coal and oil. Industries hydrogenation equipment.

Hydrogenation of individual substances. New promising areas destructive hydrogenation of THC and their economic feasibility.

Physico-chemical bases of the process of synthesis of hydrocarbons with CO and H<sub>2</sub>. Gas requirements, coming to the synthesis. Catalysts for the synthesis process. Mechanism of action of catalysts. Schematic diagram of the synthesis at atmospheric and medium pressure. Characteristic synthesis products. Methods of processing synthesis products.

## **8. Other methods of processing combustible minerals**

Extraction of THC with organic solvents. Yield, composition and properties bitumen depending on the type of raw material and extraction conditions. Catalytic extraction. The mechanism of the process. Catalysts.

Oxidation of THC. Types of oxidants, the influence of oxidation conditions on the composition and yield products. The use of oxidation products of THC.

## **9. Technology of carbon graphite materials**

Properties of carbon-based materials (physical, electrical, magnetic, mechanical and chemical), their use. Electrodes of metallurgical, electrochemical and chemical production. Fire-resistant products. Electrocarbon products (shields, lighting coal). Antifriction materials. Carbon fibers and fabrics. Fiberglass. Use of graphite for the synthesis of artificial diamonds.

Raw materials (fillers and binders). Carbon graphite technology materials. Hardening of carbon graphite materials. Grinding and scattering carbon materials. Technology of cooking masses. Mix. Pressing. Roasting carbon graphite materials. Obtaining carbon fabrics and fibers. Obtaining carbon fiber. Prospects for the development of technology and industry. Materials based carbon.

## **10. Environmental protection in the process of processing solid fuels**

Legislative measures in Ukraine in relation to nature protection. The main sources pollution of the atmosphere, water sources, soil at chemical processing plants fuel and carbon. Prospects for the transition to drainless technological management processes. Tubeless, waste-free technology.

### **SUGGESTED READING REFERENCES**

1. Martin Bajus. *Petrochemistry: Petrochemical Processing, Hydrocarbon Technology and Green Engineering*. Wiley; 1<sup>st</sup> ed., 2020.
1. James G. Speight. *Handbook of Petrochemical Processes (Chemical Industries)*. CRC Press; 1<sup>st</sup> ed., 2019.
2. James G. Speight. *The Chemistry and Technology of Petroleum*. CRC Press; 5<sup>th</sup> ed., 2014.
3. James G. Speight. *Petroleum Chemistry and Refining*. CRC Press; 1<sup>st</sup> ed., 1997.
4. Nour S. El-Gendy, Hussein N. Nassar, James G. Speight. *Petroleum Nanobiotechnology*. Apple Academic Press; 1<sup>st</sup> ed., 2021.
5. James G. Speight. *The Chemistry and Technology of Coal*. CRC Press; 3<sup>rd</sup> ed., 2016.