

TRANSFER PROCESSES IN POLYMER MEMBRANES. PART 3 (p. 4-7)

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The basic thermodynamic parameters and conditions of dissolution of organic liquid in polymers are considered in the paper. Today, the problem of predicting the solubility of organic substances of multicomponent mixtures in polymeric membranes is highly relevant in the selection of polymeric materials to create pervaporation membranes. Clear and unambiguous explanations for the dissolution process, and relationship between the basic thermodynamic parameters of spontaneous dissolution or mixing are given in the paper.

It is shown that at spontaneous dissolution $\Delta G < 0$ and $\Delta \mu < 0$, the more the absolute value of these values is, the further the system is from the equilibrium state, the greater the affinity of the system components is and the higher the solubility degree is. Besides, the solubility will take place at any ratio of components, if the molar enthalpy of mixing ΔH_{mix} is close to zero, i.e. when $\delta p \approx \delta n \Delta H_{\text{mix}} \rightarrow 0$ and $\Delta G < 0$, and then the polymer can be dissolved in the given solvent. It is experimentally proved that some solvents can be adsorbed in the active layer of the polymer, but not penetrate into the zone of dissolution phase, although according to the values of HSP parameters, they should be well dissolved. Such deviations may be connected with the sizes of solvent molecules.

Keywords: polymeric membrane, solubility, pervaporation, organic substances, mass transfer.

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OXIDATION OF ETHYLBENZENE BY OZONE IN ACETIC ACID (p. 8-11)

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Reaction of ozone with ethylbenzene in acetic acid is studied. It is shown that oxidation of ethylbenzene by ozone develops in two directions: on double bonds of an aromatic ring with the formation of aliphatic peroxides and ethyl group with the formation of phenyl methyl carbinol and acetophenone. It is established that the main products of reaction are peroxide compounds - products of destruction of the aromatic ring (60 %) and, to a lesser extent, oxidation products on a side chain - acetophenone (25 %) and phenyl methyl carbinol (10 %). The constants of the rates of ozone reaction with ethylbenzene at various temperatures are defined, and the reaction mechanism, which explains the obtained experimental data is proposed.

During the research, the concentration of ethylbenzene and products of its transformation in solution was determined by a method of gas-liquid chromatography on the chromatograph with flame ionization detector. The content of peroxide compounds was determined by iodometric titration. The constants of the rate of ozone reaction with ethylbenzene were calculated by the method described in the paper [2].

Keywords: oxidation, ethylbenzene, ozone, acetic acid, acetophenone, phenyl methyl carbinol, peroxide compounds.

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QUANTUM-CHEMICAL RESEARCH OF THE MECHANISM OF REACTION OF DEHYDRATION OF 2,3-DIMETHYLBUTAN-2,3-DIOL AND ITS HEXAHYDRATE (p. 11-15)

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It is established that dehydration of 2,3-dimethylbutane-2,3-diol passes two successive stages. During the first stage, the atom of hydrogen H (11) (state DO) approaches the atom of oxygen O (7) of hydroxogroup with the formation of a tense four-member cycle C (1) H (11) O (7) C (2) (transition state TS1), destruction of which leads to the formation of enol EO and a water molecule (state EO + H₂O). At the second stage, in the molecule of enol EO the hydrogen atom H (20) approaches the oxygen atom O (8) of another hydroxogroup with the formation of the tense four-member cycle C (6) H (20) O (8) S (3) (transition state TS2), destruction of which leads to the detachment of the second water molecule and the formation of diene DE (state DE+2H₂O).

The difference between the energies of the formation of molecular structures of enol EO and 2,3-dimethylbuta-1,3-diene DE is positive that indicates the endothermicity of reaction. At the same time, the energy barriers of both stages are proportionate (65.6 and 61.8 kcal/mol, respectively), and the value of the released energy is about 54 kcal/mol, which corresponds to the heat of the water molecule formation. Moreover, the formation of the transition state for these reactions is displaced towards the formation of products and is of late nature. This indicates that the destruction of the bond C-H and formation of the bond O-H (transition of the hydrogen atom of the methyl group to the oxygen atom of hydroxogroup) passes faster than destruction of the bond O-C of enol with simultaneous formation of the bond C=C 2,3-dimethylbuta-1,3-diene.

Reaction of dehydration of hexahydrate 2,3-dimethylbutan-2,3-diol (DO) passes in the presence of the water molecule, the oxygen atom of which acts as an element of the transmission of hydrogen atom of the methyl group DO to the oxygen atom of the hydroxyl DO, resulting in significantly reduced energy barriers of the stages of dehydration reaction of hydrated 2,3-dimethylbutan-2,3-diol in comparison with anhydrous.

Keywords: 2,3-Dimethylbutan-2,3-diol, 2,3-Dimethylbuta-1,3-diene, quantum-chemical calculations, MOPAC2009; Winmostar, RM1

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MODELING OF CONTINUOUS ADIABATIC NITRATION OF BENZENE (p. 15-19)

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The regularities of adiabatic nitration of benzene to nitrobenzene with a simultaneous distillation of the reaction products were investigated on the mathematical model developed by the authors. The influence of molar input ratio benzene - nitric acid, pressure in the system, mass temperature at the input on the composition of liquid and vapor phases at the output was studied. It was shown that carrying out the process under the residual pressure of 450 mm Hg allows to fully transfer the products to the vapor phase due to the heat of reaction and to obtain the spent sulfuric acid with the concentration not less than 80 %, which can be used for nitrate mixture preparation without additional consolidation. The obtained results indicate that in the process of adiabatic nitration, unlike the classical method, two output mixtures can be obtained: sulfuric acid - nitrobenzene (bottom products) and benzene - nitrobenzene - water. In order to extract commercial nitrobenzene, they should be treated separately.

Keywords: adiabatic nitration, benzene, mathematical model, composition of phases, pressure, temperature, concentration.

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SYNTHESIS OF COCARBOXYLASE: PROCESS INTENSIFICATION VIA MICROWAVE RADIATION (p. 20-26)

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Energy saving is the key point in the development of new chemical technologies and industrial scaling of the processes of obtaining chemical reagents, functional materials, pharmaceutical substances, etc. The use of the non-classical process activation methods, including microwave radiation, known as effective heating source, allowing significant process acceleration, is a promising direction in the field of new energy-saving technologies.

The paper gives the results of modeling of the process of synthesis of cocarboxylase - known pharmaceutical substance - in a microwave field. The synthesis includes two stages – preparation of polyphosphoric acid (phosphorylating agent) and phosphorylation of thiamine chloride. The effect of microwave radiation on duration and energy parameters of these processes of various scales (from several grams to several kilograms) was studied. The efficiency of the microwave radiation use at both stages from the point of view of influence on the duration of processes and energy consumption was shown. The effective technique of the preparation of polyphosphoric acid by the method of phosphoric acid dehydration in the microwave field was developed. Optimal parameters of microwave thiamine chloride phosphorylation were found. The comparative assessments of time and energy expenditure in these processes, including taking into account their scaling to the industrial volumes were given for the justification of the economic feasibility of replacing the thermal heating by microwave radiation.

Keywords: microwave radiation, thermal heating, phosphorylation, dehydration, polyphosphoric acid, energy saving, scaling.

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MODELING OF HYDRODYNAMIC CONDITIONS FOR CRUDE HYDROCARBON CRACKING IN MELTS (p. 27-32)

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The paper considers the main problems of hydrodynamics of gas-liquid systems in relation to the developed process of crude hydrocarbon cracking in melts. The experimental study

of hydrodynamic conditions was conducted by physical modeling at objects with similar physicochemical properties. The purpose of the research was to develop a methodology for determining the contact time and the interfacial area for the cracking process. Based on the experimental data, the formulas, the most suitable for the calculation of hydrodynamic parameters of sparging in melts were selected among the available in the literature. The boundaries of hydrodynamic regimes were defined. The experimental results showed the effect of the height of melt layer, diameter of the crude feeding tube, melt properties and space velocity of crude feeding on the time of bubbles ascent and the size of interfacial area. In laboratory experiments on the cracking of hydrocarbons in melts at the bubble mode of sparging (the specified gas velocity no more than 0.2 - 0.3 m/s), the contact time may vary from 0.1 to 0.5 s and a specific interfacial area from 50 to 1800 m²/m³. To achieve the maximum interfacial area, it is recommended to carry out the cracking of hydrocarbons in the melts in the foam mode at the gas phase velocity of 0.3 - 0.5 m/s.

Keywords: hydrodynamics, gas-liquid system, ascent rate, gas content, interfacial area.

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LUMINESCENT NANOSIZED CELL MARKERS ON THE BASIS OF LLANTANUM PHOSFATE (p. 32-35)

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Luminescent properties of Lanthanum phosphate nanoparticles, doped with Europium cations with functional oligoperoxide shell were investigated. Water- and organic dispersion polymerization of a mixture of polar functional monomers, initiated by peroxide groups localized on the surface of LaPO₄ • Eu³⁺ were carried out. Kinetic regularities of polymerization were investigated and the parameters of control were established. Grafting of functional polymer chains by water- and organic dispersion polymerization provides nanoparticles affinity to specific environments and materials, reactivity, biological tolerance and/or the possibility of binding to substrates of different nature for use in creating of luminescent biosensors and cell markers. Nanoparticles LaPO₄ • Eu³⁺ with grafted poly (N-vinylpyrrolidone - glycidyl methacrylate) polymeric shell were studied as analytical reagents for melanoma cancer cells labeling. When performing the study, the optimal concentrations of nanoparticles for cell labeling were determined.

Keywords: luminescent nanoparticles, grafting polymerization, cell markers, functional oligoperoxides.

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DEVELOPMENT OF DISTILLATION SCHEME OF ACETIC ACID WITH LOW CONTENT OF IODIC COMPOUNDS (p. 36-39)

Maxim Shepelev, Sergej Kondratov

The problem of obtaining acetic acid with low content of iodides is considered in the paper. The purpose of the research is to identify ways of the ingress of iodine impurities into commodity acetic acid and to find ways of reduction of the amount of these pollutants to the level no more than 10 p.p.b. The structure of material flows of current production of acetic acid was studied, using the methods of fractional distillation, chromatographic analysis and mathematical modeling. The formation of more than 30 side compounds with a high and low volatility in the system was revealed. Based on the results it was shown that relatively volatile by-products - low-molecular iodine compounds, are formed of the low-volatile iodine compounds, entering the distillation stage from the synthesis unit. The way of reducing the content of iodine-containing impurities in the commodity acetic acid to the level no more than 10 p.p.b was proposed. The synthesis of the advanced technological scheme was carried out. The research results can be used in the design of production of acetic acid by methanol carbonylation.

Keywords: acetic acid, iodides, distillation, mathematical modeling, scheme, carbonylation, methanol, impurities.

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ACRYLIC ACID OBTAINING BY ACETIC ACID CATALYTIC CONDENSATION WITH FORMALDEHYDE (p. 40-42)

Roman Nebesnyi, Volodymyr Ivasiv, Yulia Dmytruk, Nazariy Lapychak

Acrylic acid is a bulk product of organic synthesis. Propylene oxidation is main industrial method of its production. Considering substantial costs for oil-derived raw material (propylene), development of alternative acrylic acid production methods are very important. The method of acrylic acid production by acetic acid gas-phase aldol condensation with formaldehyde has fair implementation prospects. In industry formaldehyde and acetic acid are synthesized from methanol produced from synthesis gas, and a feedstock for synthesis gas obtaining is methane or coal. Thus the method allows using non-oil-derived raw materials.

The present work is dedicated to the development of efficient catalysts of gas phase aldol condensation of carbonyl compounds.

Using of the developed B₂O₃-P₂O₅-WO₃/SiO₂ catalyst allows acrylic acid obtaining with high yield. Temperature and contact time effect on the initial reactants conversion and the target product formation selectivity have been studied in the work. Optimal conditions of the condensation process have been determined.

The research results implementation would enable diversifying the raw materials base of acrylic monomers production and allow.

Keywords: acrylic acid, heterogeneous catalysis, gas phase, aldol condensation, acrylic monomers.

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STUDY OF THE INFLUENCE OF TECHNOLOGICAL FACTORS ON THE EFFICIENCY OF THE PROCESS OF CAVITATION TREATMENT OF OIL PRODUCTS (p. 43-47)

Inna Lavrova, Ammar W. Said

The results of studies of the effect of hydrodynamic cavitation treatment on the fractional composition of oil products with the purpose to improve the content of light fractions and reduction of the content of sulfur compounds are given.

It is noted that the effectiveness of the hydrogenation of crude oil and emulsion « crude oil-water » is influenced by the modes of cavitation treatment and the amount of water, added as the activator of the hydrogenation processes.

It is confirmed that, during the hydrocavitation treatment of water-hydrocarbon emulsions, the microcracking of oil molecules occurs, and dissociation of water with the formation of hydrogen and further hydrogenation of heavy fractions is possible. As a result of the fractional distillation of water-fuel emulsions, which were processed in the cavitation

stand, the yield of light fractions reached 94 % that confirms the proceeding of the hydrogenation processes of hydrocarbon raw materials and the formation of hydrogen during the hydrocavitation treatment.

During the treatment of oil and diesel fuel, significant reduction of the content of total sulfur to acceptable norms was recorded that indicates the appropriateness of using the studied process for the intensification of sorption purification of fuels from sulfur-containing compounds.

The influence of such technological factors as the water content in the reaction mixture and the rotor speed on the efficiency of hydrocracking of oil hydrocarbons was determined.

Keywords: cavitation, hydrocracking, hydrogenation, hydrocarbons, fractions, gasoline, diesel, fuel oil, desulfurization, sorbent.

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INVESTIGATION OF PHYSICAL AND CHEMICAL PROPERTIES OF NONIONIC DEMULSIFIERS BASED ON ETHYLENE AND PROPYLENE OXIDES (p. 47-51)

Alexander Lazorko, Sergey Boychenko, Petro Topylnytsky, Yuri Holych, Viktorija Romanchuk

Water with dissolved inorganic salts is an integral leader of oil in the layer. In the modern conditions of preparation and processing, oil is dehydrated and desalted using the combination of different methods of demulsification: mechanical, thermal, electrical. Along with these methods, adding of reagents-demulsifiers to the emulsion is used. The efficiency of dehydration and desalting is determined by the right choice of demulsifiers. The demulsifier, being adsorbed on the interfacial surface of water drops promotes their dispergation. Nonionic surfactant demulsifiers - block copolymers of ethylene and propylene oxides, show the highest demulsifying activity.

For the most effective use of nonionic demulsifier, the physicochemical properties (density, viscosity, pour point) of active bases of demulsifiers, their solutions with different molecular weight of block copolymer (M=3200, M=3500 and M=6000) and the dependence of the properties on the content of oxyethylene and oxypropylene groups in the molecule (OE/OP) were studied.

Investigation of the physicochemical properties of block copolymers and aqueous and solvent solutions showed that in

all cases with the growth of the ratio of OE/OP and molecular weight density, pour point and viscosity increase.

For further research, namely the determination of demulsifying properties, the samples with molecular weights of 3200, 3500, 6000 were selected. The sample with a molecular weight of 6000 and content of ethylene oxide of 95 % is technologically unsuitable since the solution of this demulsifier, when dissolved in water and solvent freezes to -10 °C that negatively affects the supply of this demulsifier to the installation in winter. Definition of demulsifying ability of the above samples will be described in the next paper.

Keywords: oil, emulsion, dehydration, desalting, demulsifier, demulsifying ability.

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PULP OBTAINING FROM MISCANTHUS STEMS (p. 52-56)

Valerii Barbash, Tatiana Mykytiuk, Roman Menkiv, Irina Trembus

The process of obtaining of neutral sulfite pulp from the stems of Miscanthus giganteus was studied. The dependence of physical-mechanical parameters of the obtained pulp on the concentration of sulfur dioxide, temperature and pulping time is shown. It was established that the temperature increase from 160 to 180 °C and pulping time from 60 to 120 minutes leads to the improvement of physical-mechanical properties of pulp.

The kinetic characteristics of the process of delignification of the Miscanthus stems were defined. It was established that the investigated process of delignification is described by the kinetic equation of the second order. It is shown that the increase in the concentration of sulfur dioxide in the pulping liquor from 20 to 40 g/l leads to the decrease in the activation energy of the specified process from 70.1 to 58,5 kJ/mol.

The selectivity indexes of lignin removal (selectivity, degree of removal of carbohydrates, delignification degree) by the neutral sulfite method of delignification of Miscanthus giganteus were determined.

The pulp, obtained from the stems of Miscanthus giganteus using the neutral sulfite method has the high physical-mechanical

cal properties and can be used for the production of various types of paper and cardboard.

Keywords: *Miscanthus giganteus*, delignification, pulp, rate constant, activation energy, selectivity

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SCALE FORMATION IN CIRCULATING WATER SYSTEMS (p. 57-61)

Sergiy Vysotskiy, Oleksiy Varyvoda

The main form of deposits in the circulating water systems is the crystals of calcium carbonates and iron compounds. The crystals of calcium carbonate are formed as a result of transition of carbon dioxide to the gas phase.

The studies of the crystallization of calcium carbonate from water solutions of calcium hydrogen carbonate with and without the addition of corresponding salts were carried out. To confirm the influence of the surface-active substances (SAS) OP-7 and OP-10 on the crystallization processes, a series of experiments at different dosages of SAS were performed. The increase in the heating temperature and solution concentration leads to the increase in the size of crystals, depositing on the glass plate. Small crystal formations are unstable and can be dissolved under the influence of fluctuations of hydrodynamic flows, as well as under the influence of physicochemical processes due to the shift of the calcium carbonate equilibrium under the influence of fluctuations of the concentration of carbon dioxide.

Anti-scale additives of hexametaphosphate and tripolyphosphate type reduce the intensity of scale formation and change the conditions of calcium carbonate crystallization. In all experi-

ments when using hexametaphosphate with the concentration of 10 mg/dm³ and tripolyphosphate from 1 to 500 mg/dm³ as the additives, very small calcite crystals of 1-2 microns in size are formed. All other things being equal, the reduction in the concentration of tripolyphosphate to 0.5 mg/dm³ leads to the formation of crystals in the form of “needles” and “flowers” with the size of 100-160 microns.

Keywords: circulating systems, crystallization, scale formation, surface-active substances, calcium carbonate, anti-scale additives

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USE OF ALCOHOLIC WASTE OF CYCLOHEXANE OXIDATION (p. 61-64)

Nicholas Kozhushko, Anatoly Ludyn, Viktor Reutsky

In the process of cyclohexane oxidation, we obtain a number of side compounds, including alcoholic fraction, which has no target purpose. Accordingly, the topical issue is the further use of alcohol fraction since the division of this mixture into components is a difficult and expensive process, therefore, other methods of recycling and use of this mixture are considered.

Also, in this case it is possible to use such additional alcoholic waste as fusel oil, which has the structure similar to the above given alcoholic fraction, which also has no practical use. One of the possible ways to use the alcoholic fraction (fusel oil) is to add it as an additive to motor fuels as it has long been known that alcohols (in particular, ethanol) are used as additives in the production of fuels.

Accordingly, the use of alcoholic waste as a new source of cetane additives for diesel fuel was proposed, and this method was considered as the possible direction of recycling of alcohol-containing waste of chemical production - fusel oil, alcoholic fraction, which implies the improvement of technological and environmental performance of production. The positive effect of alcoholic additives on the operational performance of diesel fuel was also established. It was determined that the optimal content of alcoholic additives in diesel fuel is 12 %.

The obtained results indicate the possibility of the use of alcoholic waste as additives to diesel fuel.

Keywords: waste, cyclohexane, diesel fuel, alcoholic fraction, fusel oil, methane index.

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