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КАТАЛИЗ В ПРОМЫШЛЕННОСТИ

CATALYSIS IN INDUSTRY

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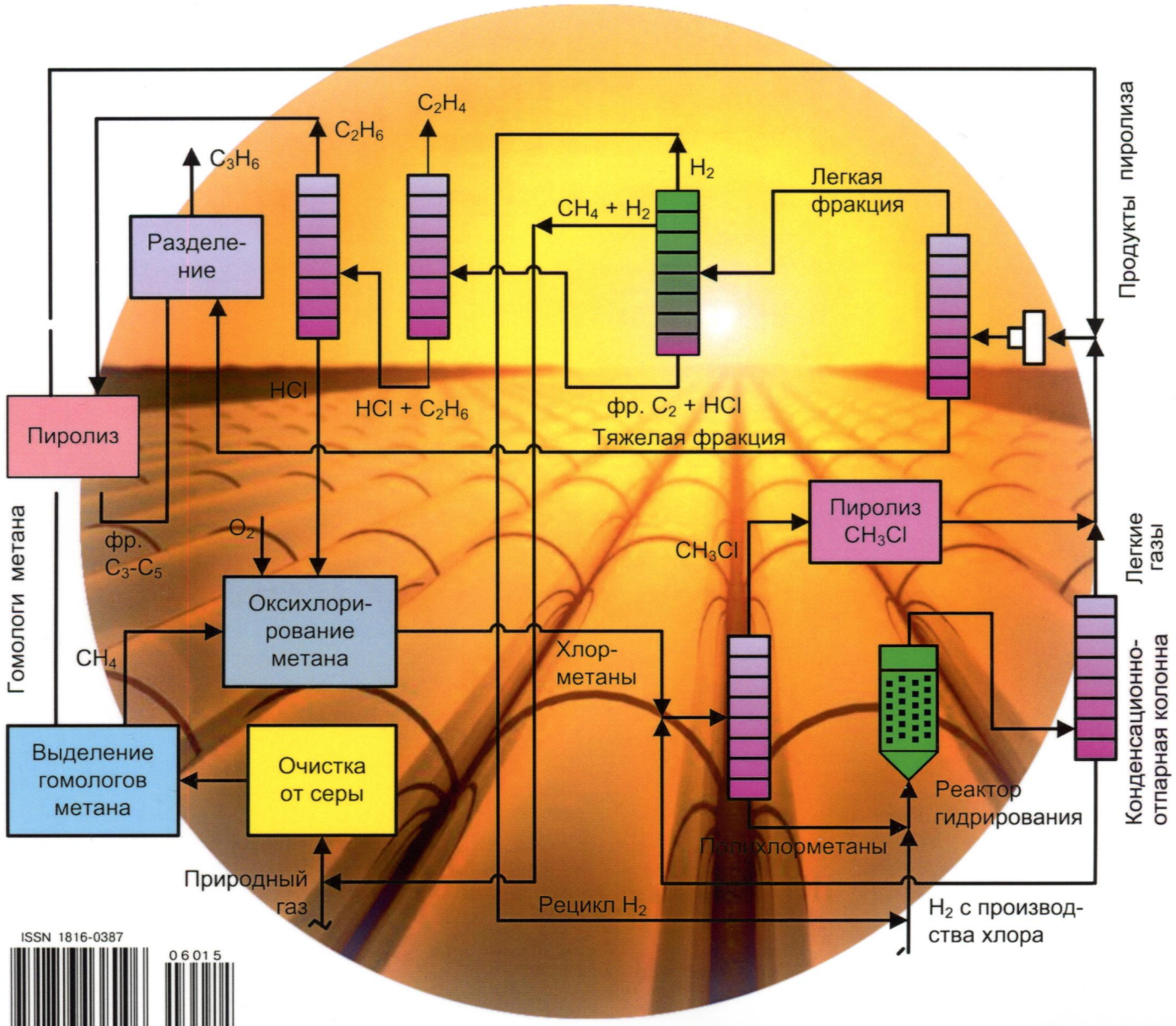

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КАТАЛИЗ В НЕФТЕПЕРЕРАБАТЫВАЮЩЕЙ ПРОМЫШЛЕННОСТИ

КАТАЛИЗ И ОХРАНА ОКРУЖАЮЩЕЙ СРЕДЫ

ИНЖЕНЕРНЫЕ ПРОБЛЕМЫ. ЭКСПЛУАТАЦИЯ И ПРОИЗВОДСТВО

БИОКАТАЛИЗ

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GENERAL PROBLEMS OF CATALYSIS

An experimental setup was designed for studying the solubility of a catalyst-deactivating compound – polyisoprene – in pure supercritical carbon dioxide ($SC\text{-}CO_2$) and in $SC\text{-}CO_2$ with a co-solvent (3,5 wt % chloroform). In pure $SC\text{-}CO_2$, the crossover-type variations in the solubility was observed in isotherms t = = 70, 100 and 120 °C at the pressure region between 15 and 34 MPa, and the pressure of ca. 19 MPA determined in the top crossover point. Addition of chloroform to $SC\text{-}CO_2$ was shown to result in an average 2 to 2,5 times increase in the solubility. The process of supercritical fluid CO_2-extraction regeneration of the aluminopalladium catalyst LD-265 for hydrogenation was studied. Dimethylsulfoxide and ethanol were used as co-solvents for $SC\text{-}CO_2$. The maximal efficiency of the regeneration was observed at the co-solvent concentration of 5,5–6,5 wt %, dimethylsulfoxide being more effective co-solvent than ethanol. With the catalysts subjected to the $SC\text{-}CO_2$ regeneration, the resulting diene and bromine numbers, as well as conversions of styrene and methylcyclopentadiene, meet the standards on catalytic systems for selective hydrogenation of diene hydrocarbons to benzene-toluene-xylene fractions.

Keywords: catalyst, regeneration, supercritical carbon dioxide.

Dynamics of ammonia activation of the industrial cement-containing nickel catalyst KDA-10A (NIAP-13-02) at temperatures up to 750 °C was studied using methods of temperature-programmed reduction and high-temperature XRD. The activation dynamics was studied at 600, 650, 700 and 750 °C. The outlet ammonia concentration was observed to become constant at 700–750 °C after thermostatting for 6 h that indicated practically complete activation of the catalyst. The high nickel dispersion and high catalytic activity at 700–750 °C was accounted for by the thermal stability of the catalyst under study. The shortened activation process was recommended for the industrial implementation.

Keywords: protective atmosphere, catalytic dissociation of ammonia, nickel-containing catalyst, activation dynamic, activation process.

CATALYSIS IN CHEMICAL AND PETROCHEMICAL INDUSTRY

Quantitative information was obtained on the effect of process parameters on main relationships of the liquidphase epoxidation of propylene with aqueous solution of hydrogen peroxide in the presence of extruded titanium silicalite in methanol. The influence of the solvent concentration (13,7–19,1 mol/l), reactant ratio of propylene: hydrogen peroxide ((2–5) : 1), and temperature (30–60 °C) on the yield – propylene oxide and byproducts – 1,2-propylene glycol, 1-methoxy-2-propanol and 2-methoxy-1-propanol was examined. Conditions of synthesis of propylene oxide in a lab-scale continuous setup were recommended based on the results obtained.

Keywords: propylene oxide, epoxidation, methanol, titan containing zeolite, optimal conditions.

An effective catalyst for synthesis of ethylene at the stage of hydrodechlorination of methylene chloride and chloroform was chosen through comparative studies of alumina-supported palladium, nickel-molybdenum and nickel-lanthanum-magnesium catalysts. A flow reactor with the fixed catalyst bed was used for the studies at 300 °C, 3,8 s contact time, molar ratio of hydrogen to methylene chloride equal to 3 : 1. The nickel-molybdenum catalyst was shown the best. The process flow sheet was improved in order to favor preferable synthesis of ethylene to be used for production of vinyl chloride: Ethylene was proposed to synthesize during an additional stage of pyrolysis of methane homologues which were extracted from natural gas and from reaction gas of methyl chloride pyrolysis, as well as at the stage of hydrodechlorinaiton of methane polychlorides.

Keywords: hydrodechlorination of methylene chloride and chloroform, synthesis of ethylene by phyrolysis of methyl chloride.

Commercial alumina – the support of hydrotreatment catalyst IC-GO-1 ($AO_{IC\text{-}GO\text{-}1}$), sorbents AN-2H and AOC-63-22, catalyst AOC-78-59 were tested for dehydration of ethanol to ethylene. The activities were measured using a flow reactor at the temperature range 375–400 °C, contact time 0,3 s. The influence of process temperature on the ethanol conversion and selectivities to the target and side products was determined. The specific activity was established

CATALYSIS IN PETROLEUM REFINING INDUSTRY

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heating characteristics of unit 2. The constructed patterns of main circulative flows of the catalyst accounted for the considerable differences in the catalyst concentration and gas temperature fields. The numerical solutions were used for comparative analysis of the operation efficiencies of the units to show good agreement with the analytic results on industrial reactors. The proposed approach can be used for the design of new and optimization of operating units.

Keywords: fluidized bed, dehydrogenation of isoparaffins, industrial reactor, mathematical model, numerical solution.

BIOCATALYSIS

Enzymatic hydrolysis in aqueous media was studied using a lignocellulosic material (LCM) prepared from miscanthus and LCM prepared from oat covering (OC) as substrates to obtain bioethanol. LCM synthesis was a one-step processing of the feedstock with nitric acid (Pilot Plant of IPCET SB RAS). Commercially available enzymatic agents CelloLux-A and BrewZyme BGX were used for enzymatic hydrolysis in aqueous media at high initial concentrations (90 g/l) of the substrates. The yields of reducing substances (monosaccharides, mainly glucose) were established to equal 65,4 % and 73,3 % of the substrate weight for miscanthus LCM and OC, respectively. The composition of monosaccharides as products of biocatalytic decomposition of LCM was studied for the first time to show the predominant content of glucose. It was first time to synthesize bioethanol from LCM. The yield of bioethanol per unit of feedstock was 19,4 dal/t for miscanthus biomass and 16,2 dal/t for OC. A low methanol content (0,002–0,005 vol %) was characteristic of the experimental bioethanol samples.

Keywords: enzymatic hydrolysis, nitric acid process, miscanthus, oat covering, bioethanol.

Application of modern technologies of enzymatic hydrolysis of cellulose-containing raw materials makes it possible to obtain sugars that undergo microbiological conversion to synthesize alcohols (biofuels), organic and amino acids, biopolymers, food additives and other value-added products. Cellulolyticus enzymes of three types – endoglucanase, cellobiohydrolase, beta-glucosidase – are required for the bioconversion of cellulose-containing raw material. The present work is aimed at studying a possibility of application of genetic engineering for improvement of the hydrolytic ability of secretory enzyme complex *Penicillium verruculosum* by adding homologous and the heterologous cellulases in different combinations and ratios – endoglucanase IV (EGIV) from *Trichoderma reesei*, endoglucanase II (EGII) and cellobiohydrolase I (CBHI) from *P. verruculosum*, and also beta-glucosidase (b-GLU) from *Aspergillus niger*. The optimal ratio of components is determined to double the catalytic activity of the new enzyme complexes.

Keywords: *Penicillium verruculosum*, enzymatic hydrolysis, optimal ratio, endoglucanase II, cellobiohydrolase I, beta-glucosidase.

The studies dealt with the efficiency of a biocatalyst for modifying commercial bleached hardwood sulfate pulp. The biocatalyst was based on recombinant enzymatic agents prepared using *Penicillium verruculosum* fungus. The influence of the treatment with cellulase complex on the structure, morphology and surface state of cellulose fibers was estimated. It was shown that the biocatalytic treatment of cellulose led to improved beatability and bond-formation in paper sheets, to higher strength. Application of enzymatic modification of cellulose will help to solve some energy- and resource-saving problems in the paper industry.

Keywords: biocatalysts, cellulose, modification, cellulases, beating, properties of paper.

A heterogeneous biocatalyst BCL based on recombinant extracellular lipase of thermophilic bacterium *Geobacillus stearothermophilus* G3 with the activity of 23,6 act.un./g was prepared by covalent immobilization on aminated silica gel. The influence of the solvent nature, temperature (30–60 °C), proportion of water (1–10 %) and catalyst (0,25–25 %) on the yield of methyl esters of fatty acids (MEFA) was studied in the reaction of methanolysis of sunflower oil over the BCL catalyst. The observed maximal MEFA yield was 43 %. A high operation stability of the catalyst under study was demonstrated: The catalyst kept more than 50 % of its initial activity after 480 h operation (20 cycles) that makes it promising for synthesis of fatty acid esters used for production of biodiesel fuel.

Keywords: immobilized lipase, *Geobacillus*, re-esterificaiton, biodiesel fuel.

CHRONICLE