

КАТАЛИЗ



В ПРОМЫШЛЕННОСТИ

CATALYSIS IN INDUSTRY

Том 15 № 5 2015



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Calcite is used in the combustion of high-sulfur fuels to reduce emissions of SO₂. However, at temperatures above 700 °C, calcite and resulting calcium sulfate begin to sinter, which negatively affects the binding of SO₂ and complicates the mathematical modeling of the process. Catalytic combustion reduces the maximal temperature of fuel combustion from 1200 °C to 700 °C, thereby reducing the sintering of materials and allowing the use of simpler model calculations. The aim of this work was to develop a simplified model of the observed kinetics of the process on the basis of experimental data obtained at 500–600 °C in a reactor with fixed-bed calcite. According to the model, the absorption of SO₂ is the reaction of the second order (the first order with respect to the concentration of SO₂ and the first order with respect to a number of free centers capable of binding SO₂), and vacancy centers decreases linearly with an increase in the amount of absorbed SO₂. Kinetic parameters of the model — the reaction rate constant and the ultimate capacity of calcite toward SO₂ — were determined.

Keywords: sulfur dioxide, calcite, cleaning gas kinetics.

Kinetic Laws of Impregnation of Inorganic Supports with Metals Nanodispersed in Liquid (Sols) during the Preparation of Supported Metal Catalysts 11

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Kinetic analysis of the interaction of inorganic supports (e.g. CeO₂) with sols of highly dispersed metals (iron, nickel, and silver) produced by electrocondensation was performed. The formulas for the kinetics of the process are obtained, and the duration of the process that provides supported metal catalysts with specified parameters is determined. The calculation results have been used to develop a technology for production of supported metal catalysts.

Keywords: sols of highly dispersed metals, electrocondensation, kinetics, impregnation.

CATALYSIS IN CHEMICAL AND PETROCHEMICAL INDUSTRY

The Problems in Increase of Selectivity in the Ethylene Oxychlorination Process.
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The main regularities of the chloroorganic by-products formation in the ethylene oxychlorination process in the fluidized bed catalyst are examined in the round-up article. On the basis of published literature data conclusions about by-products formation by the reactions of dichloroethane dehydrochlorination and partial oxidation are drawing. The increase of the process temperature promotes to the rise of the by-products yield. There is indicated that the use of the catalysts containing cupric chloride and chlorides of alkali or alkali-earth metals helps to reduce of the side reactions part. In the industrial conditions the best results are reached at the use of the catalysts with the not high copper content at the external surface of the granule. The iron penetration to the catalyst due to the erosion of the industrial reactor walls leads side by side with the decrease of the oxychlorination process rate to the increase of the chloroorganic by-products yield.

Keywords: ethylene oxychlorination, dichloroethane dehydrochlorination, selectivity, cupric chloride, alkali and alkali-earth metals chlorides.

CATALYSIS IN PETROLEUM REFINING INDUSTRY

Four Generations of Technology for Production of Synthetic Liquid Fuel Based on Fischer – Tropsch Synthesis.
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The paper provides an overview of the development of technology for production of synthetic liquid fuels based on the Fischer – Tropsch process. Special attention is paid to recent trends in the technological development. We give general information about the technology of producing synthetic fuels, including process chemistry, typical instrumental solutions, the problem of raw materials, information about catalysts. It is shown that modern industrial technologies based on the Fischer – Tropsch synthesis (XTL) differ significantly from those used in the 1st generation of

the process in the 30–40 years of the last century. The most acute problems of the current, third, generation of technology are high specific capital investments and a too wide range of by-products. Technologies of a new, 4th, generation are in transition from pilot to commercial realization. The purpose of development of the 4th generation of XTL is to develop a technology that would open new industrial applications due to simplicity, compactness, and a radical reduction of specific investment and operating costs.

Keywords: Fischer – Tropsch synthesis; synthetic fuels; historical overview.

ENGINEERING PROBLEMS

Modernization of Industrial Technology for Dehydrogenation of Methylbutenes to Isoprene. Part I. Mathematical Analysis of Options to Upgrade the Technology..... 46

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To determine a most energy-efficient method for technology modernization, a mathematical modeling of a number of technologies for dehydrogenation of methylbutenes was performed. The traditional technology (the process in an adiabatic reactor) was compared with the following three embodiments of the process in the «pseudo-isothermal» mode: 1) a single-reactor scheme with a fractional supply of steam to the upper and middle parts of the catalyst layer; 2) a consecutive two-reactor scheme with intermediate heating of a contact gas in an interstage superheater; 3) a consecutive two-reactor scheme with the addition of superheated steam into an interreactor volume. It is shown that each of the new schemes can significantly increase the process efficiency compared with the conventional technology. A comparative analysis of the dependence of the yield and selectivity toward isoprene on the thermal energy Q fed in the modified schemes has shown that the highest increase in the yield of isoprene (5,5 %) and selectivity (5,6 %) at large contact times is provided via Scheme 2, especially when $Q > 8,5 \cdot 10^6$ J/kg.

Keywords: dehydrogenation of methylbutenes to isoprene, mathematical modeling of a technological design.

BIOCATALYSIS

Properties and Efficiency of a Biocatalyst Based on Immobilized Fungal Amylase 54

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Preparations based on native enzymes have found limited industrial application because of their instability and sensitivity to changes in pH, temperature, and other external factors. Therefore, the acute task is to develop biocatalysts based on immobilized enzymes, which are more stable and therefore more effective in the practice. To stabilize the fungal amylase (KF 3.2.1.1.), we applied the covalent immobilization of the enzyme on chitosan-containing cellulose. It is shown that in comparison with native amylase, the thermal stability of the immobilized amylase increased 3,5-fold, and the resistance against pH inactivation increased as well. The decrease in the rate constants of inactivation of the immobilized enzyme indicates the increase in its stability due to steric factors associated with the formation of azomethine bonds with cellulose and chitosan. It is shown that when using an immobilized enzyme preparation in place of the native amylase, the product yield of the hydrolysis of barley malt increases by 1,5 times, which makes it of practical use in the food industry.

Keywords: amylase, immobilization, stabilization, chitosan-containing cellulose.

Kinetics of Enzymatic Hydrolysis of Lignocellulosic Materials at Different Concentrations of Substrate..... 60

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The kinetics of enzymatic hydrolysis in an acetate buffer of two substrates — lignocellulosic material from miscanthus and from oat husk (OH) — was studied at different concentrations of the substrates. The substrates were produced by a single-step treatment with a dilute solution of nitric acid. The content of a nonhydrolyzable component — acid-insoluble lignin — was 11 and 14 % for miscanthus and OH, respectively. As a catalyst, a multi-enzymatic composition of commercially available enzyme preparations Tsellolyuks-A and Bryuzaym BGX was used. It is shown that the treatment with nitric acid produces reactive substrates for enzymatic hydrolysis. Scientific novelty of the results is confirmed by Russian patent RF 2533921. The kinetics of enzymatic hydrolysis of substrates in the acetate buffer can be described by a mathematical model based on the modified Michaelis-Menten equation. On the basis of experimental data, basic kinetic constants were determined for both substrates. The equilibrium concentrations of reducing substances (RS) were calculated for substrates depending on their initial concentration. It is found that the initial rate of the enzymatic hydrolysis for the OH-derived lignocellulosic material is 1 g/(L·h) above that for the miscanthus-derived lignocellulose material in the entire range of studied substrate concentrations (33,3–120,0 g/L). It is shown that with an increase in the initial substrate concentration from 33,3 to 120,0 g/L, the RS yield decreases 1,5–2,0-fold because of substrate inhibition. At low initial concentrations, the yields of RS for both substrates are similar. In contrast, at the high initial concentration of substrate (120,0 g/L), the yield of RS from the miscanthus-derived lignocellulosic material is about 20 % higher than that from the OH-derived material. The obtained experimental dependence and the suggested mathematical model allow one to optimize initial concentrations of the substrate for efficient enzymatic hydrolysis.

Keywords: oat husk, miscanthus, substrate concentration, kinetics of enzymatic hydrolysis, mathematical model.

Comparative Analysis of Reactivity of Aspen Wood in Enzymatic Hydrolysis in Dependence on its Pre-treatment in Aqueous and Aqueous-organic Solutions of Sulfuric and Nitric Acid	67
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Various methods for pretreatment of aspen wood were studied. The methods included the pretreatment of the wood with aqueous solutions of sulfuric and nitric acids and with water-organic (ethanol, butanol) solution of sulfuric acid (organosolvent). The effect of the methods on the conversion of raw material into simple sugars during the enzymatic hydrolysis was comparatively studied. The effects of temperature, acid concentration, composition of the organic phase (for sulfuric acid), and pressure (for nitric acid) on the pretreatment efficiency are analyzed. It is shown that the use of organosolvent of 0,5 % sulfuric acid allows one to increase the reactivity of ground aspen wood by 3–4 times as compared with that of the feedstock. The most effective pretreatment was found to be the pretreatment in a 4,8 % aqueous solution of nitric acid (125 °C, 1,8 MPa, 60 min), which increases the reactivity of ground aspen wood more than by 5 times.

Keywords: aspen wood pretreatment, organosolvent, reactivity of lignocellulosic feedstock, enzymatic saccharification, *Penicillium verruculosum*.

Parchment as a Potential Feedstock for Production of Sugars by Enzymatic Hydrolysis	74
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The possibility of conversion of parchment to glucose by enzymatic hydrolysis using enzyme preparations (EP) based on fungi of the genera *Penicillium* and *Trichoderma* was studied. Parchment was hydrolyzed at 50 °C and pH = 5 under constant stirring. The dosage of cellulase EP (*P. verruculosum* B1-221-131 and *T. reesei* BioACE) was respectively 10 and 15 enzyme units with respect to filter paper per 1 g of dry substrate. The process was carried out both in the absence and in the presence of excess cellobiase (β-glucosidase) of *P. verruculosum* F10. It was found that the conversion of parchment to glucose can achieve 70 % without any pretreatment. It is shown that the cellulase EP from *P. verruculosum* provides a higher yield of glucose than the EP from *T. reesei* does. Cellobiase (β-glucosidase) plays an important role in the hydrolysis of parchment wastes: in the presence of excess cellobiase, hydrolytic ability of cellulase EP increases. Thus, the possibility of using the parchment as a raw material for production of sugars and, further, of other valuable products is demonstrated.

Keywords: *Penicillium verruculosum*, parchment, enzymatic hydrolysis, cellulases, cellobiase.

Biocatalytic Conversion of Kraft Pulp Using Cellulase Complex <i>Penicillium verruculosum</i>	78
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The efficiency of biocatalysts based on a cellulase complex obtained using the fungus *Penicillium verruculosum* in the hydrolysis of kraft pulp of softwood and hardwood timber was studied. The activity of biocatalysts toward unbleached and bleached pulp and the dependence of conversion of cellulose on the content of non-cellulosic components were determined. It is shown that wet kraft pulp is highly reactive in the enzymatic hydrolysis by a cellulase complex from *P. verruculosum* and is of great interest as a substrate when scaling biotechnological processes of bioconversion of renewable raw materials.

Keywords: biocatalysis, kraft pulp, enzymatic saccharification, cellulases, *Penicillium verruculosum*.

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