Production of Motor Fuel from Lignocellulose in a Three-Stage Process (Review and Experimental Article)

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Abstract—A three-stage process for the production of motor fuel (MT) components from lignocellulosic raw materials is described. In the first, pretreatment stage, lignocellulose is subjected to hydrolysis with cellulases followed by fermentation of the resulting sugars into ethanol; then, dilute ethanol solutions are concentrated by membrane vapor separation to obtain 70–80% solutions. At the third stage, aqueous ethanol solutions (water content 0–50%) in the presence of a $Pd–Zn/Al_2O_3/MFI$ catalyst at 350°C and a space velocity of 0.6 h^{-1} are converted into alkanes, and $C_3–C_8$ olefins and $C_6–C_{12}$ aromatic compounds (MT components). It has been found that water in an amount of up to 30% in ethanol solutions effectively inhibits the detrimental hydrocarbon cracking and catalyst coking processes, thereby leading to a decrease in the formation of undesirable C_1 and C_2 products and an increase in the catalyst on-stream time to 100 h wherein the yield of the desired fraction is reduced only by 10–15%. The subsequent treatment of the catalyst surface with steam and hydrogen completely restores its catalytic activity.

INTRODUCTION

List of abbreviations:

FPIU	international filter paper unit for cellulase activity
MVP	membrane vapor permeation
PV	pervaporation
VP	vapor permeability
VLE	vapor–liquid equilibrium
PDMS	polydimethylsiloxane
PTMSP	polytrimethylsilylpropyne
PMP	poly-4-methyl-2-pentyne
MDK-1	Russian-made commercial siloxane membrane
MFI, ZSM-5	aluminosilicate zeolites of the pentasil family

Biofuel, as a fuel from renewable plant or animal feedstock, is intended to replace fossil non-renewable sources of energy, such as oil, coal, and natural gas. The use of fossil fuels has led to an increase in the concentration of CO_2 in the atmosphere and, consequently, the emergence of global warming. Biofuels are considered as the most carbon-neutral energy sources and their widespread use should lead to a decrease in the CO_2 content in the atmosphere and thereby reduce the negative greenhouse effect on the Earth [1].

The development of biofuels as a renewable energy source is most advanced in the field of ethanol production. Lignocellulosic biomass is most suitable as a substrate for mass production of bioethanol, since it is cheap, affordable, and produced annually on the Earth in large quantities. However, to reduce the concentration of CO_2 in the atmosphere, lignocellulosic bioethanol should be produced in amounts equivalent to 50 EJ per year [2], whereas it is manufactured from grain, beets, and sugarcane at a level as low as about 3.1 EJ [3]. It should also be noted that the production of lignocellulosic ethanol will lead to job creation and improvement in the economic situation in remote areas of developing and even industrialized countries [4–6].

The production of first-generation bioethanol was organized in the United States and Brazil, using corn starch and sugarcane as substrates, and in Europe using sugar beets [7]. Research on the use of lignocellulosic feedstock for the production of bioethanol began in the 1970s, and this product should be considered as second-generation biofuel [8, 9]. Its produc-

tion did not compete with food substrates and did not occupy the area of agricultural land.

The third generation of biofuels (mainly ethanol and butanol) is also produced from nonfood substrates such as synthesis gas $(CO-H_2)$ and, to a lesser extent, uses algae biomass to produce biodiesel [8−10].

With political and financial support, several companies in the West have already begun industrial production of lignocellulosic bioethanol at a rate reaching 45 million liters per year [11].

However, due to the presence of a significant amount of lignin in the lignocellulosic feedstock, the microbial conversion of plant cellulose into ethanol is not as straightforward and simple as in the case of using simple sugars [12].

The layer of plant lignin is developed by nature to protect the external membranes of plants from damage by microorganisms and impart wind stability to them. Accordingly, the first step in the lignocellulose conversion to bioethanol is the removal of lignin by substrate pretreatment, which simultaneously makes cellulose more accessible for enzymatic hydrolysis.

Alkaline thermal pretreatment of lignocellulose usually leads to the dissolution of lignin and its removal; in addition, it does not promote the dissolution of cellulose and hemicellulose, unlike the case of acid hydrolysis [13, 14]. Therefore, sodium hydroxide is considered as the most suitable reagent for the primary chemical pretreatment of biomass, in which the bonds of lignin with the rest of the plant material break down to partially dissolve the lignin and increase the swelling of cellulose fibrils with their partial hydrolysis, thereby reducing the degree of crystallization of cellulose and, ultimately, leading to an increase in the degree of its hydrolysis by cellulases [15].

Before alkaline treatment of lignocellulose, it is necessary to mechanically mill it, the smaller the particles obtained, the more complete being the lignin recoverability (ideal size 0.5−1.0 mm) [16]. In addition, such treatment with moderate heating (100−120°C) or without it is the most environmentally friendly, as it leads to the transition of cellulose fibrils from the crystalline to the amorphous state, which also promotes better digestion by cellulases [17, 18].

Cellulosic bioethanol is obtained by fermenting glucose solution with yeast after cleaving cellulose molecules by enzymes, with final concentrations of alcohol rarely reaching 10% (usually 4−5%). After fermentation, ethanol is distilled off, and then anhydrous ethanol is obtained by membrane pervaporation to have a residual water content below 0.4 vol %; in this form, it can be directly used as motor fuel or be blended with gasoline in various proportions. The annual ethanol production reaches 86 million tons at present, with 82% of this volume being used as fuel in the United States, Brazil, China, and Canada [19] and European countries [20].

Bioethanol is produced in the industry by *Saccharomyces cerevisiae* yeast or *Zymomonas mobilis* bacteria. However, yeasts dominate in industrial processes due to their productivity, high degree of resistance to ethanol formed, and resistance to toxic process inhibitors formed as a result of biomass pretreatment. Their physiology has been well studied, and genetic systems have been developed to produce more productive strains [21, 22].

In the case of fermenting lignocellulosic feedstock with yeast, the final ethanol concentration rarely exceeds 5%. For the distillation of such dilute solutions by conventional methods, a considerable amount of heat energy is required; therefore, membrane methods for concentrating dilute solutions become preferable.

Based on the foregoing, we devoted this work to exploring the possibility of obtaining motor fuel from first- and second-generation bioethanol with the use of concentration by membrane vapor separation and the subsequent catalytic conversion of aqueous ethanol solutions into alkanes according to the following scheme:
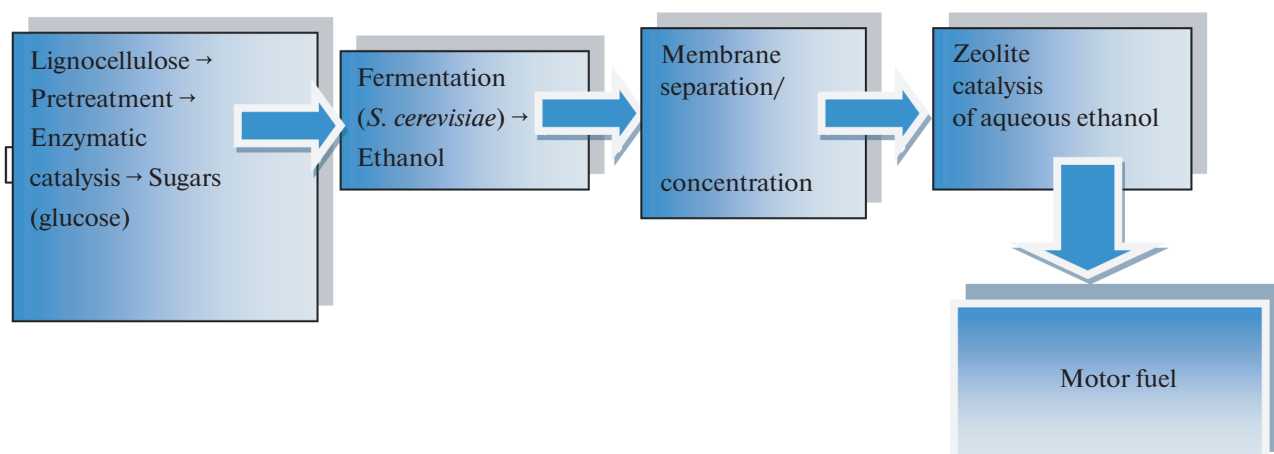
Schematic diagram of the process for producing renewable motor fuel from lignocellulose.

In this work, we studied the process for producing motor fuels from lignocellulosic bioethanol as the most developed of cellulosic fuels with the aim to develop the scientific basis for the creation of new technologies that will have promise to make breakthrough in this area of obtaining renewable energy.

Production of First- and Second-Generation Bioethanol

The first-generation bioethanol for use as a fuel additive is obtained using yeast or bacteria, and final concentrations of the alcohol in this process can reach 10−12 vol %. Therefore, to concentrate the alcohol by distillation, considerable energy is required. The second-generation ethanol, obtained from lignocellulosic feedstock after its pretreatment, is even more diluted, up to 5 vol % due to both the density of plant pulp, subjected to enzymatic hydrolysis, and inhibition of cellulase activity by the product formed (glucose). To compare the effectiveness of the subsequent membrane separation and concentration of the alcohol, fermentation samples of fermented glucose of the first- and second-generation bioethanol were tested.

Microorganisms and Their Cultivation

The strain of *Saccharomyces cerevisiae* yeast was obtained from the Moscow State University Collection of Microbial Cultures. The culture medium contained, g/L: glucose, 20; peptone, 5; and yeast extract, 3 at the natural pH (6.0). Cultures were grown on an orbital shaker at 180 rpm at 30°C for 24 h, followed by introducing cells into a fermentation medium. The fermentation medium for ethanol fermentation contained, g/L: glucose, 100; peptone, 0.5; a yeast extract, 0.3 at pH 6.8. Fermentation was carried out at 30°C for 48 h under anaerobic conditions without stirring. The medium for fermentation of cellulosic ethanol contained, g/L: fermented cellulose (glucose equivalent), 50; peptone, 0.5; and yeast extract, 0.3 at pH 6.8. Fermentation was carried out under the same conditions.

Pretreatment of Lignocellulose

A 100-g portion of milled dry lignocellulose (average size 0.5−1.0 mm) was suspended in 1 L of 5% (w/v) NaOH (final concentration, 10% (w/v)), and the mixture was autoclaved at 121 C (gauge pressure of 1 atm) for 30 min. The precipitate was filtered off under vacuum and washed with 1% HCl to pH 5.0. The precipitate of lignin-free biomass was dried under vacuum and stored at room temperature until treatment with cellulases. The filtrate containing all the extracted lignin was neutralized with HCl (10%, v/v), held at 4°C to form a precipitate, centrifuged, dried under vacuum, and weighed.

Enzymatic Hydrolysis of Cellulose

After extraction of lignin, the residual biomass was subjected to enzymatic hydrolysis with cellulases in 2-L Erlenmeyer flasks in a working volume of 1 L containing 50 mM citrate buffer (pH 4.8), 100 g/L of substrate (biomass), 2500 FPIU of enzyme cocktail (25 FPIU/g of biomass; SibPharm, Novosibirsk, Russia). The flasks were incubated at 50°C on an orbital shaker at 50 rpm for 48 h. After hydrolysis, the pH of the mixture was adjusted to 6.8 and a suspension of yeast (5 wt %) was added to the mixture, after which sugars were subjected to fermentation for 36 h at 30°C. All the experiments were performed in triplicate and their data were presented in the mean ± standard deviation form.

Analytical Measurements

The amount of glucose formed by enzymatic hydrolysis of cellulose was measured spectrophotometrically with the Photo-Glucose test reagents (Impact, Moscow, Russia) at 595 nm in the glucose oxidase/peroxidase reaction using special-purity grade glucose as a standard. The concentration of ethanol was measured by GLC using water−ethanol mixtures as a standard.

Fermentation Processes for Producing First- and Second-Generation Ethanol

Anaerobic fermentation of glucose by yeast for 48 h at 30°C (first generation) results in a bioethanol concentration of 10% (v/v), whereas the fermentation of lignocellulose (36 and 48 h) results in a second-generation bioethanol concentration as low as 2.5% (Table 1).

The fermentation broth after two days of fermentation to produce first-generation bioethanol contained less than 0.05% residual glucose, which indicates that the yeast consumes 20% of the substrate within two days and can convert an additional 10% of glucose for the next day of fermentation (data not shown) to give an additional 5% ethanol. Thus, the studied yeast strain demonstrated an exceptional potential for glucose uptake and ethanol accumulation up to 15% during 72 h of fermentation.

The fermentation medium for producing bioethanol of the 2nd generation showed after 36-h fermentation the presence of a very small amount of residual glucose formed after the hydrolysis of cellulose; however, hemicellulose molecules remained intact, since the yeast strain used does not have hemicellulase enzymes. For the hydrolysis and the subsequent use of C5 hemicellulase sugars, other types of yeast are needed that would be able to ferment pentoses to produce 2nd-generation bioethanol [23]. The resulting low concentrations of 2nd-generation bioethanol (Table 1) are the result of a generally low degree of

Table 1. Production of first- and second-generation bioethanol using yeast (*Saccharomyces cerevisiae* strain) fermentation

Time	First-generation bioethanol		Second-generation bioethanol	
	substrate, g/L (glucose)	bioethanol concentration, % (v/v)	substrate, g/L (glucose hydrolyzate)	bioethanol concentration, % (v/v)
0	100 ± 0	0 ± 0	50 ± 3	0 ± 0
24	2 ± 1 (+100*)	5 ± 0.2	10 ± 2	2 ± 0.2
36	50 ± 1	7.5 ± 0.2	1 ± 1	2.5 ± 0.1
48	0.5 ± 0.1	10 ± 0.2	0.1 ± 0.1	2.5 ± 0.2

* 100 g/L of glucose was added after 24 h of fermentation. The results in the table are the average of three independent experimental runs ± standard deviation.

conversion of cellulose to bioethanol. First of all, the concentration of sugars in the broth medium depends on the amount of hydrolyzable biomass, which does not exceed 10% (w/v) in the cellulose hydrolysis medium after the extraction of lignin. Accordingly, the concentration of the resulting sugars will rarely exceed 50 g/L, providing that all the cellulose will be effectively hydrolyzed by cellulase cocktails, since hemicellulases occur in lignocellulose in significant quantities and the cocktails are not hydrolyzed by cellulases. As a result, even with very deep utilization of glucose by the yeast strains applied, the final concentration of bioethanol rarely exceeds 2.5%. Therefore, for isolating and concentrating such dilute bioethanol solutions, the use of conventional distillation techniques will be extremely inefficient from an economic point of view. To create cost-effective technologies for producing bioethanol of the 2nd generation, it seems necessary to apply membrane separation methods which do not require high energy expenditures compared to conventional distillation. To compare the efficiency of recovery and concentration of bioethanol using membrane vapor separation, samples of bioethanol of the 1st and 2nd generations, obtained after fermentation of glucose in the former case and hydrolyzed sugars after cellulose conversion by enzymes, were tested.

Membrane Recovery of Ethanol from Fermentation Broth

Conventional methods and membrane processes for recovery of alcohols. The traditional methods for separation of liquid mixtures are distillation, extraction, and adsorption [24, 25]. Membrane methods for separating liquid mixtures have appeared relatively recently, but they are already considered as reagentless or non-adsorbent technologies with a higher energy efficiency compared to distillation [26]. Membrane pervaporation is one of the most appropriate membrane methods for recovering and concentrating ethanol from a fermentation broth. However, it has such a significant drawback as direct contact of the membrane with the biological environment, which leads to membrane fouling by microorganisms and nonvolatile organic substances [26]. In addition, pervaporation

modules limit the membrane contact area with the biological medium inside the bioreactor, precluding the effective recovery of ethanol as an inhibitor. A new membrane vapor separation method proposed by the authors [27] for recovering ethanol from fermentation broth holds promise for these purposes. The method is based on a combination of gas sweeping (gas stripping) and membrane separation of water and ethanol vapors. Stripping is used to transfer ethanol from the liquid phase of a fermentation broth to the vapor phase in accordance with a positive deviation from Raoult's law for aqueous ethanol solutions at low alcohol concentrations in the aqueous phase [28, 29]. The membrane vapor separation method per se is used to recover ethanol from the fermentation broth immediately after gas sweeping (stripping) [24, 27]. This approach allows the continuous recovery of ethanol from the bioreactor as is the case of pervaporation, while avoiding the disadvantages of pervaporation. In addition, this method can be used to isolate other volatile products if an appropriate membrane is selected. It should be noted that the maximum ethanol concentration, above which the bioprocess is inhibited, usually does not exceed 10 wt % [30]. In our case, the concentration of cellulosic ethanol is no more than 2.5%. The recovery of ethanol as an insignificant admixture in water requires the use of organophilic membranes, which are more permeable to organic molecules than to water, a property typical of rubbery membrane materials, for example, polydimethylsiloxane (PDMS).

Membranes on the basis of PDMS have been studied in detail in the processes of pervaporative recovery of bioalcohols. However, the permeability of PDMS membranes and their resistance to biological media are insufficient for its industrial use [31]. Modern views on the membrane vapor permeation (MVP) phenomena from fundamental positions [32], as well as from the standpoint of their application potential [33], demonstrate the importance and prospects of developing inorganic and polymeric membranes for separation of gaseous mixtures containing condensable components. Research activity in the field of inorganic membranes is reflected in a variety of publi-

cations and focuses on the synthesis conditions for ensuring a defect-free thin layer based on zeolites or metal−organic frameworks (MOFs). In the future, varying the hydrophilic−hydrophobic balance of molecular-sieve membrane can provide the separation of various organic (aqueous organic) mixtures (see, for example, [34, 35]).

The most important properties of inorganic membranes include high temperature application and resistance to organic substances. The combination of inorganic and polymeric components in a composite membrane is also of particular interest [36]. However, historically, polymeric membranes were the first to be used for pervaporation and vapor separation [33, 37]. Both processes proceed under the vapor partial pressure gradient, which is close to the saturation pressure in the case of pervaporation [32].

Characteristic of membrane vapor permeation processes. In fact, the need to create integrated MVP systems arises in relation to the fundamental feature of stripping phenomena: a positive or negative deviation from Raoult's law for vapor−liquid equilibrium. In general, a positive deviation from Raoult's law for water−organic systems (enrichment of the vapor phase in an organic compound) provides favorable conditions for the recovery of the organic components. In the case when water is a minor component (for example, the ethanol−water azeotrope), the use of conventional pervaporation and hydrophilic membranes will be preferable. Hydrophilic membranes with a water/organic selectivity of $\geqslant 1$ are more elaborated and used in the processes of dehydration of water−organic mixtures [33−35, 37]. For example, SULZER PERVAP membranes are used for the continuous drying of solvents, which makes it possible to economically and effectively dehydrate organic components to the ppm level [38].

Another class of vapor-permeable membranes is based on rubbery polymers and highly permeable hydrophobic glassy polymers with an organic/water selectivity of >1 [32, 33]. To some extent, membrane vapor separation with such membranes may find application in the production of energy carriers based on biosources. In practice, this technology requires the use of a less energy-intensive separation system for the recovery and concentration of bioalcohols [30, 37−39].

This paper describes new research-and-development works on the membrane separation of vapor−gas mixtures, which can find wide application, e.g., in the recovery of energy carriers from biomass processing products [40]. A number of membranes suitable for this purpose have been considered recently in [41].

The main tendencies of membrane vapor separation are considered using the example of recovery of bioalcohols from dilute aqueous alcohol solutions. Bioalcohols can be concentrated with the use of organophilic membranes, which are usually more permeable for organic than for water molecules. This property is typical of rubbers, for example, PDMS (see above).

Since highly permeable membranes can be fabricated from glassy organophilic polyacetylenes, they are also considered now as promising materials for membrane separation of aqueous organic solutions. For example, the most permeable of the currently known polymers is poly-1-trimethylsilyl-1-propyne (PTMSP) [42, 43]. It has been intensively investigated as a pervaporation membrane material for the separation of water−alcohol mixtures in a large number of studies [43].

Poly(4-methyl-2-pentyne) (PMP) is the carbon-chain analogue of PTMSP and a fairly new membrane material. It shows high mass transfer coefficients for gases and vapors and has a higher resistance to various organic solvents compared to PTMSP [41]. To understand the practical potential of MVP, special attention is paid to the fundamental aspects of separation: the contribution of the liquid/vapor phase transition and the vapor-selective properties of organophilic membranes. In fact, these two stages are merged as one in pervaporation. The data obtained so far have been considered in detail for organophilic and hydrophobic membranes [41] and patented [44].

In general, laboratory and commercial vapor separation membranes can be classified as follows: (1) highly permeable elastomeric membranes (for example, based on PDMS) and hydrophobic glassy polymeric membranes with an organic/water selectivity of >1 (for example, based on PTMSP and PMP), (2) hydrophobic glassy polymer membranes of medium permeability with organic/water selectivity < 1 (for example, based on polyvinyltrimethylsilane (PVTMS), and (3) hydrophilic membranes with a water/organic selectivity of 1 (for example, membranes based on polyvinyl alcohol (PVA), cellulose membranes). Membranes of practical interest are commercial and laboratory membranes based on hydrophobic and hydrophilic polymers:

— dense hydrophobic membrane based on poly-1-trimethylsilyl-1-propyne (PTMSP);

— dense hydrophobic membrane based on poly-4-methyl-2-pentyne (PMP);

— hydrophobic composite membrane MDK-1 based on a PDMS copolymer manufactured by Vladipor (Russia);

— hydrophobic asymmetric membranes based on polyvinyltrimethylsilane (PVTMS), manufactured by the Kuskovo chemical plant (Russia) [45];

— dense hydrophilic membrane based on industrial cellophane film;

— hydrophilic composite membrane NaRM manufactured by RM Nanotech (Russia).

It should be noted that water-selective membranes concentrate ethanol in the retentate (see below). All

the investigated membranes demonstrate high vapor permeability, which is of practical interest. The experimental setup and procedure are detailed in [40]. All of the main engineering aspects, including the role of the membrane unit, are considered in [46].

Results of the vapor permeation study. The driving force of vapor transport through a membrane is the differential vapor partial pressure across the membrane. The main mechanism of vapor transport in both cases is solution–diffusion [32].

The membrane permeability (Q) and the permeability coefficient (P) are defined as follows:

$$Q_i = \frac{J_i}{A(p_{i0} - p_{il})}, \tag{1}$$

$$P_i = \frac{J_i h}{A(p_{io} - p_{il})}, \tag{2}$$

where J_i is the vapor flux, A is the membrane area, p_{i0} is the partial pressure of component i upstream of the membrane, p_{il} is the partial pressure of component i downstream of the membrane, and h is the membrane thickness.

The ideal membrane selectivity (α_{ID}) is calculated as the ratio of the permeability coefficients obtained for the pure components:

$$\alpha_{ID} = \frac{P_i}{P_j}. \tag{3}$$

The overall separation factor (α_O) consists of the phase transition separation coefficient (α_{PhT}) according to the vapor/liquid phase diagram and the membrane separation factor (α_M), which are calculated as follows:

$$\alpha_O = \alpha_{Ph.T} \alpha_M, \tag{4}$$

$$\alpha_O = \frac{C_{EtOH}^C / C_{H_2O}^C}{C_{EtOH}^S / C_{H_2O}^S}, \tag{5}$$

$$\alpha_{Ph.T} = \frac{C_{EtOH}^V / C_{H_2O}^V}{C_{EtOH}^S / C_{H_2O}^S}, \tag{6}$$

$$\alpha_M = \frac{C_{EtOH}^C / C_{H_2O}^C}{C_{EtOH}^V / C_{H_2O}^V}, \tag{7}$$

where C^C, C^S, and C^V are the concentrations of the components in the condensate, the feed solution, and the vapor phase, respectively.

Note that the separation factor α_M additionally depends on operational parameters, such as stage cut and vapor phase composition.

Some of the published data and the results obtained in this study on vapor transport of pure components through hydrophobic polymers are given in Table 2. As can be seen, most of the investigated membranes exhibit high vapor fluxes and low ideal

water/ethanol selectivity (with the exception of PVTMS).

PVTMS membranes exhibit water-selective properties (ideal water/ethanol selectivity (α_{ID}) > 1) and can be used to recover ethanol by the MVP method from the fermentation broth.

In accordance with the solution–diffusion mechanism of vapor transport in a polymer, the vapor flux through the membrane is proportional to the gradient of vapor concentration in the membrane and the level of diffusion in the polymer medium (thermodynamic and kinetic terms) [32, 33]. In the case of water–ethanol mixtures for PTMSP, PMP, and MDK-1, this balance leads to a water/ethanol selectivity close to unity. For PVTMS, the balance is in favor of water vapor.

The membranes under investigation are among the most permeable ones, as evidenced by the results of search in the functional database of the Topchiev Institute of Petrochemical Synthesis (TIPS RAS) [27]. Thus, bioalcohols (bioethanol) can be efficiently concentrated using combined membrane systems with hydrophobic membranes (some technical solutions have already been patented [44]).

However, the study of vapor separation by means of hydrophilic water-selective membranes shows that the use of these membranes is more promising. As a rule, membranes of this type having high selectivity for water are used in the dehydration of organic solvents (especially in the case of azeotrope formation) by pervaporation. Examples can be found in [32, 33], but such a process is not appropriate for dilute aqueous solutions because of high energy consumption, since almost all of the water present in the solution must be evaporated.

Table 3 shows the results of studying vapor transport in cellophane and NaRM membranes for water–ethanol mixtures. As can be seen from the presented data, hydrophilic membranes have significant selectivity for water vapor, which makes it possible to concentrate ethanol vapor with high efficiency in the retentate, wherein the permeate contains mostly water vapor, which can be recycled to the bioreactor.

We used the obtained experimental data on vapor permeability for mathematical modeling of the membrane vapor separation process as applied to dilute (10 wt %) ethanol aqueous solutions. The corresponding process diagram is shown in Fig. 1. Calculated relationships of the characteristics of the process at a temperature of 90°C for water–ethanol mixtures are shown in Figs. 2 and 3.

As can be seen from the histograms in Figs. 2 and 3, a high ethanol recovery is achieved with the use of the cellophane membrane, which, however, has a low productivity. Optimal results are demonstrated by the NaRM membrane, which simultaneously provides a high ethanol recovery and a high flux (about 3.5 kg/(m^2 h) of ethanol concentrated from the initial level of 10 to 95 wt % (Fig. 3 shows the range of 60–

Table 2. Permeability of PTMSP, PMP, MDK-1*, and PVTMS membranes to vapors of pure components at 50°C ([40], this work)

Polymer	Component	Vapor permeability, L (STP)/(m^2 h atm)	Ideal alcohol/water selectivity
PTMSP	H_2O	2700	—
	C_2H_5OH	2900	1.1
ПМП	H_2O	1000	—
	C_2H_5OH	1000	1.0
MDK-1	H_2O	11500	—
	C_2H_5OH	8000	0.7
PVTMS	H_2O	10400	—
	C_2H_5OH	930	0.09

* MDK-1 is the brand of commercial siloxane membranes manufactured in Russia.

Table 3. Separation of a water–ethanol mixture by membrane vapor permeation using hydrophilic membranes

| Membrane	Temperature, °C	Ethanol content in liquid phase, wt %	Ethanol content in permeate, wt %	Permeate flux kg/(m^2 h)	Water/ethanol separation factor of membrane (α_M)
Cellophane	50–60	10–15	0.21–0.76	0.048–0.270	180–480
NaRM	50–60	15	1.70–6.20	0.460–1.600	20–90

95% ethanol). It should be noted that MVP makes it possible to evaluate the same parameters in the case of a lower ethanol concentration (for example, 2.5 wt %, as we expected). In the latter case, we will see a decrease in productivity accordingly by a smaller driving force.

The process can be additionally intensified, for example, by vapor compression before membrane vapor separation, as described in [28, 29]. Thus, the information presented above shows that using the membrane vapor separation method for the recovery of alcohols and their concentration from dilute aqueous solutions makes it possible to achieve the required high level of alcohol concentration in one stage, which is often sufficient for the further utilization of the alcohol in catalytic processes for producing motor fuels.

Catalytic Synthesis of Fuel Components from Aqueous Bioethanol Solutions

Biomass-derived products as feedstock for catalytic production of motor fuels. Much attention has been paid recently to the development of efficient approaches to the use of renewable raw materials as a feedstock for the production of energy carriers, MT
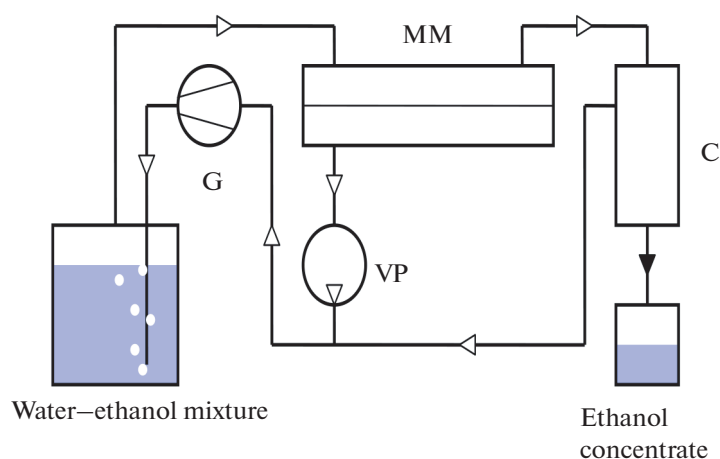
Fig. 1. Flow diagram of a single-stage membrane vapor permeation recovery of ethyl alcohol from a dilute aqueous solution (VP—vacuum pump; G—gas blower; C— condenser; MM—membrane module).
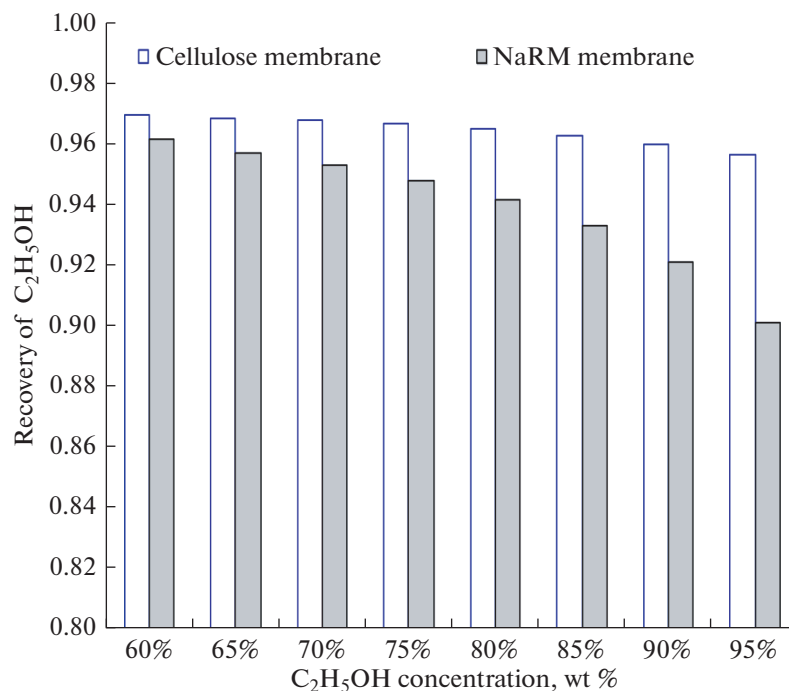
Fig. 2. Dependence of the ethanol recovery on the concentration of ethanol in the product (retentate) of the membrane vapor separation process.
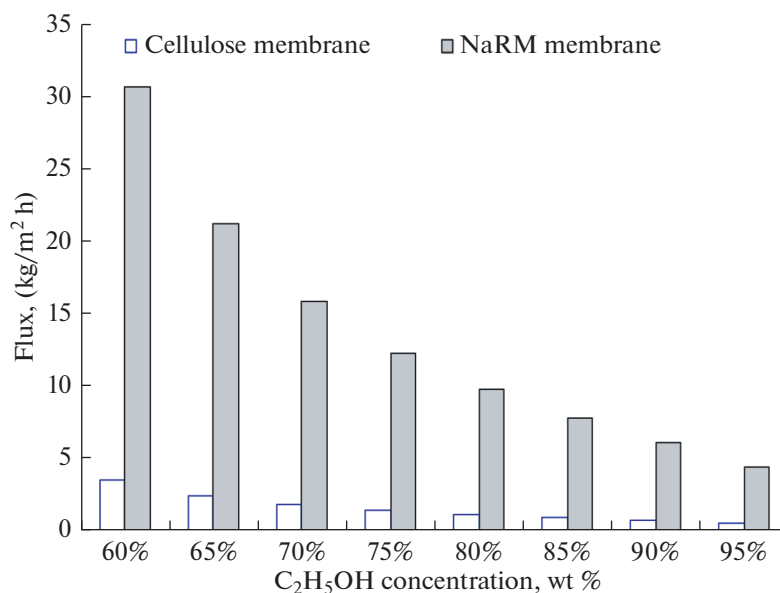

Fig. 3. Dependence of the membrane flux on the ethanol concentration in the product (retentate) of the phase membrane vapor separation process.

components, and important monomers [46–50]. These tasks are solved by the so-called "green chemistry" based on the use of renewable biomass and its products as a source of initial materials [47, 51, 52]. The most promising sources for producing hydrocarbons as fuel components and some important monomers primarily include ethanol, butanol, acetone, glycerin, and vegetable oils. Promising schemes for involving biomass products in industrial processes for the production of monomers and fuels are presented in [46].

Depending on the type of catalyst used, ethanol is converted to the C_3–C_{12} alkane–olefin or aromatic

fraction [47, 51, 52]. In [47, 51, 52], it was shown that in the presence of alumina-supported metal catalysts, ethanol enters the cross-condensation reaction of the carbon skeleton with coreactants, such as propanol, glycerol, and acetone, leading to the formation of alkane and olefin hydrocarbons.

In the presence of Pd–Zn- and Au-containing zeolite catalysts of the ZSM-5 type, ethanol is almost completely converted into alkane and aromatic hydrocarbons of the gasoline and kerosene fractions [52, 55]. The formation of aromatic hydrocarbons is accompanied by the release into the reaction medium of hydrogen, which is consumed for the hydrogenation of the olefins, initially produced from ethanol, to alkanes. The occurrence of conjugate reactions made it possible to demonstrate the feasibility of ethanol and rapeseed oil co-conversion into C_4–C_{18} alkane–aromatic hydrocarbons in the presence of a Pd–Zn/MFI catalyst prototype without using molecular hydrogen in the process [55]. A disadvantage of zeolite-containing catalysts is their rapid deactivation (for 3 h on stream) as a result of condensation of aromatic hydrocarbons on the catalyst surface and subsequent coking [46, 56, 57]. The products of microbiological synthesis contain dilute aqueous solutions of organic substrates in which the ethanol content does not exceed 10–15% [58, 59]. As a result, the energy-consuming stage of rectification is used in their separation technology. In this case, the energy cost of fractional distillation processes is mainly determined by the need to obtain highly concentrated substrates. In this connection, studies on the conversion of aqueous ethanol over H-ZSM catalysts were carried out [46, 60–62]. In those studies, it was shown that the presence of water at temperatures not exceeding 400°C provides a higher stability of the zeolite catalyst to coking and a higher selectivity for aromatic hydrocarbons of the gasoline fraction [46, 62]. At higher temperatures, the presence of water leads to irreversible loss of activity as a result of dealumination of the zeolite catalyst.

The deposition of Pd–Zn-containing components on the MFI surface made it possible to enhance the catalyst on-stream stability in the ethanol conversion reaction to 20–25 h [46, 52, 62]. The modified Pd–Zn-containing catalyst exhibits a higher selectivity in the conversion of ethanol to the C_5–C_{12} alkane–aromatic fraction compared to the unmodified catalyst. At the same time [47, 50–52], it was shown that depending on the ratio of active components, it is possible to change the selectivity of alkane formation to C_8 or aromatic hydrocarbons.

To develop the most efficient production of hydrocarbon components of the gasoline and kerosene fractions according to the process flowchart comprising microbiological fermentation–membrane recovery of ethanol–ethanol conversion to hydrocarbon fuel components, it is important to study catalytic transformations of aqueous ethanol into hydrocarbon fuel

components and monomers in the presence of a pilot sample of the Pd–Zn/[ZSM-5 + Al_2O_3] catalyst [63–65].

PROCEDURE FOR CATALYTIC EXPERIMENTS

The catalytic experiments were carried out on a PID Eng & Tech microcatalytic unit at a temperature of 350°C, an Ar pressure of 5 atm, and a feed space velocity of ethanol and its aqueous mixtures of 0.6 h^{-1}. These conditions are optimal for the conversion of ethanol on a zeolite-containing catalyst [52].

Analysis of Conversion Products of Ethanol and Its Aqueous Solutions

Gaseous products of the reaction were analyzed by on-line gas chromatography. Analysis for C_1–C_5 hydrocarbon gases was used to determine the **conversion of ethanol or its aqueous solutions to the hydrocarbon fraction**. Pilot samples of the Pd–Zn/TsVM catalyst, manufactured by the Angarsk plant, having active-component loadings of 0.6 wt % Pd and 1 wt % Zn and an Al/Si ratio of 30 were used in the study. The reactant was analytical-grade ethanol (GOST 5964-93) used without further purification, as well as its aqueous solutions.

Catalytic experiments were carried out on a PID Eng & Tech microcatalytic unit at a temperature of 350°C under Ar pressure using a Kristall-4000 chromatograph (FID, He 70 cm^3/min; 120°C; P 1.65 MPa; HP-PLOT/Al_2O_3, 50 m × 0.32 mm). The analysis for CO, CO_2, and H_2 was carried out on a Kristall-4000 chromatograph (TCD; Ar (special purity), 30 mL/min; SKT column, 150 × 0.4 cm; 130°C). Low concentrations of CO (<0.4 vol %) were determined using a Riken Keiki gas analyzer with an IR cell (model RI-550A).

Liquid organic products in the aqueous and organic phases were identified by gas chromatography–mass spectrometry (GC–MS) using Agilent MSD 6973 and Delsi Nermag Automass-150 instruments at EI = 70 eV, sample volume 1 μL, columns: HP-5MS, 0.32 × 50, D_f = 0.52, 50°C (5 min), 10°C/min, 270°C, T_{inj} = 250°C, constant flow rate 1 mL/min, split ratio 1/(100–200); CPSil-5, 0.15 × 25, D_f = 1.2, 50°C (8 min), 10°C/min, 270°C, T_{inj} = 250°C, P_{inj} = 2.2 bar, split ratio 1/300.

Quantification of the composition of liquid products was carried out by GLC on a Varian 3600 instrument using a Chromtech SE-30 column: 0.25 × 25, D_f = 0.3, 50°C (5 min), 10°C/min, 280°C, T_{inj} = 250°C, P_{inj} = 1 bar, split ratio 1/200, FID, trifluoromethylbenzene as internal standard for the organic layer. The ethanol content in the aqueous phase was determined by GC–MS from the ratio of the integral

signals of alcohol and water using the absolute calibration method, with the internal standard for the aqueous layer being internal normalization.

RESULTS AND DISCUSSION

Table 4 presents data on the yield and composition of the conversion products of lignocellulosic ethanol with different amounts of admixed water.

As can be seen from the data in Table 4, ethanol in aqueous solutions in the presence of the zeolite-containing catalyst is converted into a wide range of hydrocarbons consisting of the fraction of $C_3–C_8$ alkanes and olefins and the fraction of $C_6–C_{12}$ aromatic hydrocarbons. It is noteworthy that an increase in water content to 50 vol % leads to a decrease in the formation of gaseous products, mainly, methane. This result indicates that the presence of water vapor reduces the contribution of the thermolysis of organic substrates. Another important result is a decrease in the yield of the ethane–ethylene fraction of the gas formed by the dehydration of ethanol, which are undesired products. The conversion of concentrated ethanol leads to the formation of mainly aromatic hydrocarbons [52, 55]. In this regard, an important result obtained using high-water-content ethanol is that the amount of aliphatic hydrocarbons in the composition of organic products exceeds that of the aromatics, which are known to form on metal-containing zeolite catalysts of the ZSM type [56, 66].

It was previously shown that the conversion of ethanol proceeds via two routes to give alkylaromatic and unsaturated aliphatic hydrocarbons [48, 50, 52, 53, 66–68]. The formation of aromatics proceeds through the so-called hydrocarbon pool mechanism [66]. The aliphatic hydrocarbons are most likely produced via the route of oligomerization of ethylene formed by ethanol dehydration [54, 65, 67].

It is important to note that aliphatic hydrocarbons formed from aqueous ethanol contain up to 80% branched alkanes, which are valuable motor fuel components. Aromatic hydrocarbons consist mainly of alkylsubstituted benzenes. A small amount of methylnaphthalene is also present (Table 4).

An unexpected result was obtained in experiments on studying the on-stream stability in the presence of a 70% aqueous ethanol solution. It was established that during the conversion of 95% ethanol, the catalyst operates stably for 20 h, after which its activity sharply declines, resulting in a decrease in the yield of $C_3–C_{10}$ aliphatic and aromatic hydrocarbons from 90 to 8 wt % and a sharp increase in the yield of ethylene from 15 to 71 wt % (Fig. 4). During the conversion of high-water-content ethanol, the activity of the catalyst system decreases by no more than 10–15% after running the experiment for at least 100 h (Fig. 4).

Steaming the catalyst at 450°C for 1 to 2 h followed by reduction in a hydrogen atmosphere at a pressure of 50 atm makes it possible to completely restore the activity of the Pd–Zn/MFI/Al$_2$O$_3$ catalyst (Fig. 4).

Main Limits and Potentialities of the New Process

Limitations in the production of cellulosic ethanol are the high cost of cellulase enzymes for the enzymatic hydrolysis of cellulose and a relatively low concentration of resulting sugars, which consequently leads to low concentrations of bioethanol produced by microorganisms and thus makes the subsequent simple distillation processes uneconomical. Therefore, for recovery and concentration of lignocellulosic ethanol, a new process that is more cost-effective from the viewpoint of energy demand should be used for separating and concentrating water–ethanol mixtures, implying the application of membrane vapor permeation technologies.

The presence of water reduces the catalyst activity in the thermolysis reaction of hydrocarbons formed from ethanol and significantly improves the stability of the zeolite-containing catalyst in the process of ethanol conversion to $C_3–C_{12}$ aliphatic and aromatic hydrocarbons.

Previously, using the temperature programmed desorption of ammonia, it was shown that after preliminary reduction of zeolite- or alumina-based metal-containing catalysts, surface treatment by steaming leads to a significant increase in the acid strength of active sites [67, 69, 70]. The results obtained suggest that there are at least two factors that determine the influence of water vapor on the catalyst activity. The action of water vapor during the ethanol conversion process probably leads to the formation of strong acid sites in the cavity of zeolite pores on aluminum-containing centers, which increase the selectivity in the oligomerization of ethylene, formed from ethanol, into aliphatic hydrocarbons and isomerization of their structure. It is most likely for this reason that the amount of aliphatic hydrocarbons exceeds that of aromatics in the presence of water. Another factor that enhances the catalyst stability is the so-called surface stripping, which prevents the development of both the condensation reaction of aromatic hydrocarbons in zeolite pores and the formation of coke deposits.

The possibility of efficient catalytic processing of dilute aqueous solutions of ethanol significantly simplifies the technology for producing fuel components and monomers based on renewable raw materials according to the next-generation process flow scheme: microbiological fermentation–membrane concentration of ethanol–catalytic conversion to energy carriers and valuable products.

CONCLUSIONS

Due to the intrinsic features of the fermentation technology, the final concentration of bioethanol pro-

Table 4. Yield and composition of hydrocarbon products in the conversion of aqueous ethanol, wt %

| Water content, vol %	5	20	30	40	50
Ethanol conversion, %	100	100	100	100	100
Product yield					
Hydrocarbons	57.83	48.70	42.61	36.52	30.43
Water	42.17	51.30	57.39	63.48	69.57
Yield of hydrocarbon products, wt %					
C_1	0.83	0.51	0.27	0.32	0.10
C_2	12.02	7.68	5.79	6.89	3.20
$C_{2=}$	4.82	8.73	12.33	6.71	11.87
aliphatic C_3–C_8 hydrocarbons	48.53	48.44	47.53	46.54	47.05
aromatic C_6–C_{12} hydrocarbons	33.80	34.64	34.08	39.45	37.69
Composition of aliphatic C_3–C_8 fraction, wt %					
C_3	15.71	13.35	12.44	13.34	9.81
$C_{3=}$	3.06	4.29	5.37	4.40	6.07
C_4	30.30	28.53	27.40	10.98	24.71
$C_{4=}$	4.34	6.19	5.60	5.34	7.65
C_5	20.56	17.67	17.29	21.49	14.92
$C_{5=}$	2.17	2.70	2.74	3.39	2.16
C_6	12.33	12.05	11.51	18.00	10.31
$C_{6=}$	1.48	1.51	1.47	1.93	1.36
C_7	7.91	8.57	9.81	13.75	10.72
$C_{7=}$	0.56	0.61	1.19	0.77	4.14
C_8	1.60	4.53	5.18	6.61	8.16
Composition of aromatic C_6–C_{12} fraction, wt%					
Benzene	0.58	0.81	0.88	0.78	0.82
Toluene	10.27	9.12	8.10	8.08	6.99
Xylenes	26.28	25.32	25.24	24.45	23.39
Trimethylbenzene	39.90	40.85	41.23	41.96	42.47
Dimethylethylbenzene	20.11	21.08	21.70	22.33	23.19
Alkylnaphthalene	2.85	2.82	2.85	2.41	3.14
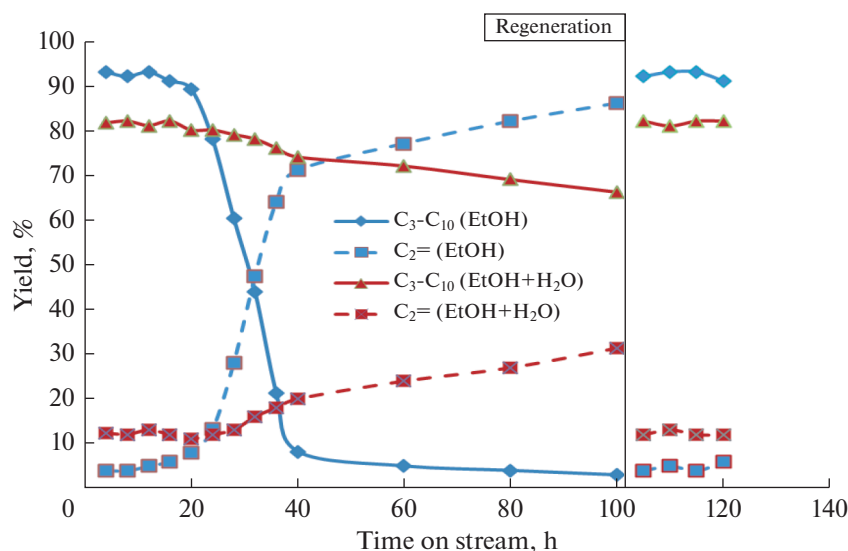
Fig. 4. On-stream stability of the Pd−Zn/MFI/Al$_2$O$_3$ catalyst (350°C, 0.6 h^{-1}) in the conversion of 95% (blue) and 70% ethanol (red).

duced from lignocellulose does not exceed 3%, which makes it necessary to look for new ways to concentrate it, and these ways are associated with the use of membrane methods, in particular, vapor permeation technology, which has no analogues in the world. The results obtained convincingly demonstrate the advantages of the new method of water stripping for extending catalyst on-stream time and for regeneration of a catalyst for production of motor fuel components based on lignocellulosic bioethanol.

The studies have shown significant scientific novelty, paving the way for further development in the field of renewable energy based on the use of plant biomass and organic agricultural waste (straw), which will lead to the creation of highly efficient and cost-effective processes for producing motor fuels of the future, with a significant reduction in the global warming.

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