Conversion of Isopropanol and Mixed Alcohols to Hydrocarbons Using HZSM-5 Catalyst in the MixAlco™ Process

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HZSM-5 (SiO_2/Al_2O_3=280 mol/mol) is used to produce hydrocarbons from reagent-grade isopropanol and mixed alcohols made from lignocellulosic biomass (waste office paper and chicken manure) using the MixAlco™ process. All studies were performed at 101 kPa (abs). The experiments were conducted in two sets: (1) vary temperature (300–T_{max}°C) at weight hourly space velocity (WHSV)=1.31 h^{-1}, and (2) vary WHSV (0.5–11.5 h^{-1}) at T=370°C. For isopropanol, T_{max}=450°C and for mixed alcohols T_{max}=520°C. For isopropanol, higher temperatures produced more gaseous products and more aromatics. High WHSV gives high concentration of C6+ olefins, whereas low WHSV gives high concentrations of C9 aromatics. For mixed alcohols, changes in temperature affected the product distribution similar to isopropanol. In contrast, WHSV did not affect the concentration of reaction products; only dehydration products were observed. *AIChE J*, 59: 2549–2557, 2013
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Introduction

High global demand for fuels and the depletion of fossil fuels have motivated research into renewable fuels. Lignocellulosic biomass is one of the most abundant and sustainable sources of liquid fuels. One option for converting lignocellulosic biomass to liquid fuels is the MixAlco™ Process (Figure 1), which uses the following steps: pretreatment, fermentation, descumming, dewatering, ketonization, alcoholization, and oligomerization.[1–3] The MixAlco™ process is a version of the carboxylate platform[4] that does not require sterilization to obtain fuels. Depending how many steps are employed, the final product is ketones, alcohols, or hydrocarbons. Potential biomass feedstocks include municipal solid waste, animal manure, and energy crops.[5–9]

This article explores oligomerization, the last step of the MixAlco™ process. The objective is to produce hydrocarbons similar to commercial fuel (gasoline, jet fuel) using a solid catalyst in a packed-bed reactor.

Gasoline hydrocarbons include paraffins (46 wt %), isoparaffins (36 wt %), naphthenes (14 wt %), and aromatics (4 wt %).[10] The carbon number ranges from C5 to C11 with C8 the most abundant.[11] Jet fuel hydrocarbons include aromatics (25 wt %), paraffins (38 wt %), isoparaffins (29 wt %), and naphthenes (7 wt %). The carbon number ranges from C8 to C14 with C11 the most abundant.[12]

Beginning with the discovery of the methanol-to-olefin (MTO) process in 1976, methanol conversion to hydrocarbons studies employed HZSM-5 catalyst, a medium-pore zeolite with channel size ~0.54 nm.[13–17]

Chang and Silvestri published the first experimental results showing the effectiveness of HZSM-5 catalyst for converting methanol to gasoline. The reaction products were hydrocarbons (C1–C11) and dimethyl ether. About 75% of the hydrocarbons produced are in the gasoline fraction (C5–C11).[18] Small-pore zeolites (e.g., erionite, chabazite, zeolite T, ZK-5, sapo-17, and sapo-34) also received attention as catalysts for methanol conversion. The channel size was ~0.34–0.41 nm. The products were mainly light olefins ranging from C1–C4 because the small-pore zeolite was selective to low-molecular-weight hydrocarbon. Large-pore zeolites such as Faujasite-type (e.g., X, Y, modernite ZSM-4) have been applied in the MTO process. Faujasite-type zeolites contain large channel size (~1.3 nm). The reaction products were mainly high-molecular-weight aromatics.[16] For small- and large-pore zeolites, coke formation was rapid; in contrast, for medium-pore zeolites, coke formation was slow.[16]

Methanol was not the only oxygenated feedstock oligomerized by zeolite catalyst, but also a number of alcohols, ethers, ketones, aldehydes, carboxylic acids, esters, and cyclic compounds. Chang and Silvestri studied the conversion of 1-butanol, 1-heptanol, acetone, acetic acid, propanal, and *n*-propyl acetate over HZSM-5. Alcohols were easily converted to hydrocarbons and the product distribution was similar to the methanol reaction. Propanal (aldehyde) is efficiently converted to hydrocarbon with high selectivity to aromatics. Acetone undergoes an acid-catalyzed condensation to form mesitylene, a derivative of benzene with three methyl substituents symmetrically placed on the ring. The cracking reaction of mesitylene produces xylene, toluene, and

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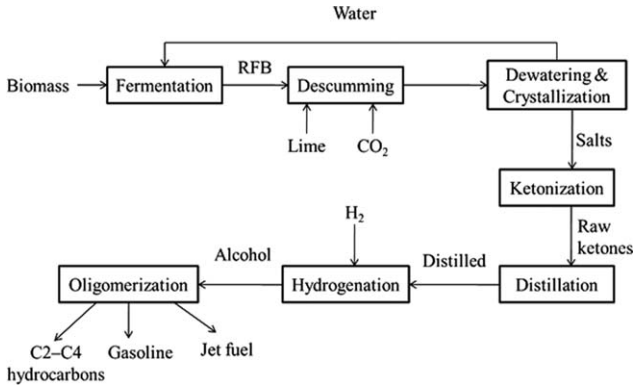

Figure 1. Simplified process block diagram of the MixAlco™ process. (RFB=raw fermentation broth).

benzene. For acids and esters, dehydration occurs producing ketones and propylene. Then, the ketones react to form mesitylene in an acid-catalyzed condensation.[13] Fuhse and Bandermann published experimental results of 39 different oxygenated compounds over HZSM-5. The compounds were easily converted to hydrocarbons when the carbon to hydrogen (C/H) ratio of the molecule fragment, remaining after eliminating oxygen as water, is less than 0.62.[19]

Oxygenated compounds derived from biomass were also studied over zeolites. The catalytic transformation of bioethanol to ethene (BETE) and bioethanol to gasoline (BETG) has been studied because sugarcane and bioethanol production has increased since 1950, especially in Brazil and India. Ethanol reaction over zeolites produces mainly ethene with small quantities of other olefins. Gayubo and coworkers studied the conversion of ethanol over HZSM-5 at different conditions. They studied the effects of temperature, space time, and catalyst activity.[20] At very low space time, ethene was the only product (85%); however, at high space times, ethene dropped drastically (15%); and, C5+ olefins increase (50%). Also, they found that temperatures lower than 450°C resulted in less coking.

Although there is a vast amount of literature about hydrocarbon production from methanol and other alcohols, very few articles show a detailed compositional analysis of the product. In contrast, this article provides detailed information about the types of liquid-phase hydrocarbons from reagent-grade isopropanol and mixed alcohols produced from biomass. The liquid is characterized by carbon number (C5–C13) and types of products (i.e., paraffins, alcohol, linear and branched olefins, isoparaffins, naphthenes, and aromatics). Also, this article is the first to describe hydrocarbon products resulting from the oligomerization of mixed alcohols made by the MixAlco™ process. All studies were performed at 101 kPa (abs). HZSM-5 (280) catalyst is selected because it is stable and forms less coke. The experiments were conducted in two sets: (1) vary temperature (300–T_{max}°C) at weight hourly space velocity (WHSV)=1.31 h^{-1}, and (2) vary WHSV (0.5–11.5 h^{-1}) at T=370°C. For isopropanol, T_{max}=450°C and for mixed alcohols T_{max}=520°C.

Experimental

Reactor

The packed-bed reactor was a stainless steel tube with dimensions 10 mm (i.d.) × 357 mm (long). Commercial HZSM-5 (280) was purchased from Zeolyst International in Malvern, PA (CBV 28014, SiO_2/Al_2O_3=280 mol/mol, surface area=400 m^2/g 20% alumina binder). The manufacturer supplied cylindrical extruded pellets (diameter=1.6 mm, length=3.5 mm), which were packed near the middle section of the reactor. The top and bottom sections of the reactor were filled with α-Al_2O_3 as an inert packing before and after the catalytic bed. As received, the catalyst had a total acidity (determined by NH_3-TPD) of 0.79 mmol/g in which weak and strong acids were 0.42 and 0.37 mmol/g, respectively.[21] To obtain an acid structure, the catalyst was activated with a N_2 stream at 550°C for 1 h, which drove off the ammonia.[22]

The reactor unit (Figure 2) consists of a packed-bed reactor, a preheater, an HPLC pump, mass flow meters, and gas lines for nitrogen and air. The reactor and the pipes are constructed of type-316 stainless steel.

To vaporize the alcohol feed, the pump injects liquid into the preheater, which operates around 420°C. Then, the alcohol vapor enters the reactor where it contacts the HZSM-5 catalyst and reacts. Later, the reaction products are heated by heating tape (T=~200°C), which ensures that all the products are in the gas phase for the gas chromatograph. Finally, an ice-cooled condenser separates liquid from gas. The gas goes to a vent whereas the liquid is collected for analysis by a gas chromatograph–mass spectrograph.

Product Analysis

The reaction products were analyzed by two gas chromatographs: a gas chromatograph (GC) Agilent Technology Model 6890N and gas chromatograph–mass spectrograph (GC–MS) HP Model G1800C. The GC was connected online with the reactor. This GC had two detectors: (1) flame ionization detector (FID) and (2) thermal conductivity detector (TCD). The TCD analyzed light hydrocarbon products (C1–C4), CO, CO_2, and water. The FID analyzed heavier hydrocarbons (C5–C13). The GC has six 30-m mega-bore capillary columns: one methyl silicone HP-1, two HP Plot Q, one HP Mole Sieve, one HP Plot Alumna, and one 5%

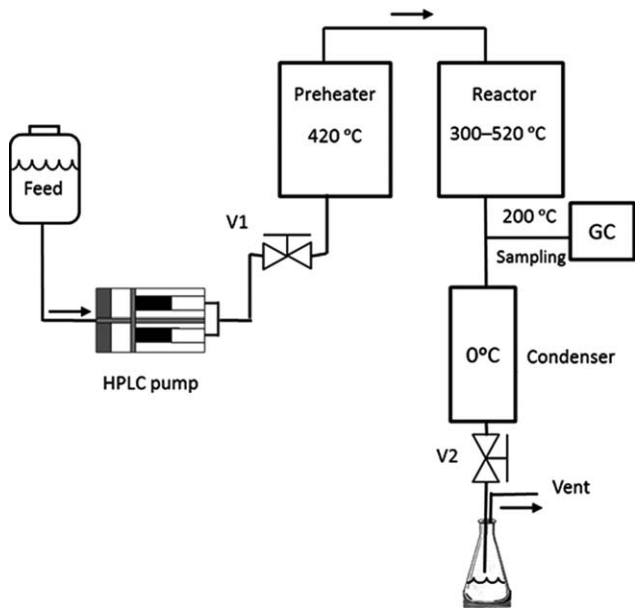

Figure 2. Schematic diagram of the oligomerization apparatus.

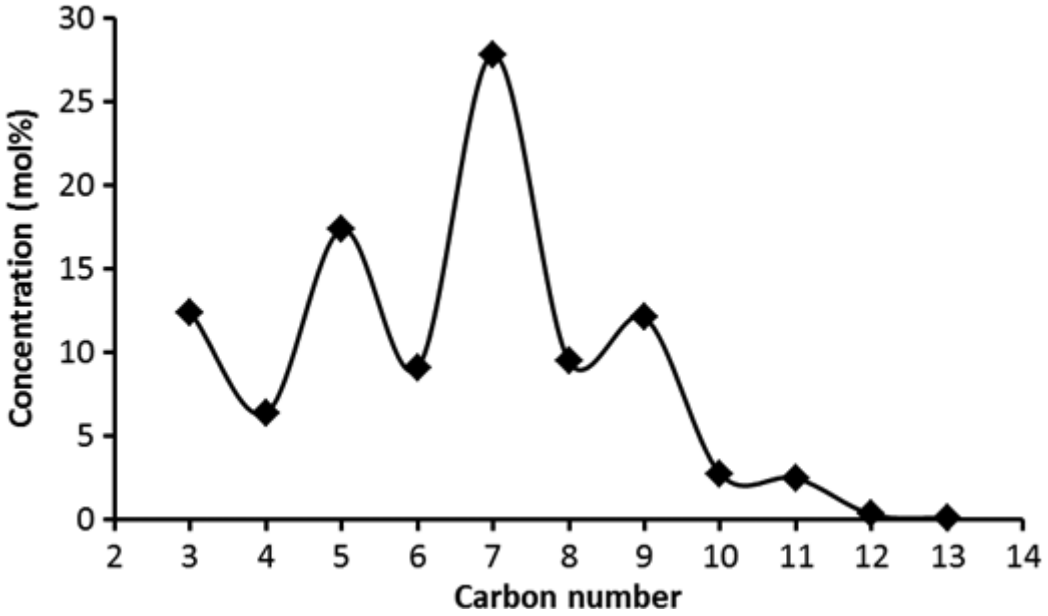

Figure 3. Distribution of alcohols obtained from paper and chicken manure.

phenyl methyl silicone HP-5 (Agilent Technologies, Santa Barbara, CA). All columns have about 40- to 50-μm-thick adsorption phases. The GC has three valves that split the carrier gas into six columns, which better separates the samples and consequently gives more accurate results. All the reaction products were analyzed with this chromatograph; however, heavier hydrocarbons (C5–C13) were lumped by carbon number. To identify all the isomers in the liquid phase, the GC–MS analyzed the liquid product samples. Before the analysis, all reaction products were cooled to 0°C to ensure that all C5+ hydrocarbons were in the liquid phase. A GC–MS analysis of the liquid phase typically determined that the liquid samples had over 100 compounds.

Isopropanol

Reagent-grade isopropanol (99% pure) was obtained from Mallinckrodt Chemicals (Phillipsburg, NJ).

Mixed alcohol

Mixed alcohols were made in the pilot-scale MixAlco™ process located at Texas A&M University (Figure 1).

Fermentation

Using a mixed culture of microorganisms derived from Galveston, TX marine sediment, office paper (97%), chicken manure (2%), and urea (1%) were fermented at 45°C using $CaCO_3$ buffer. The resulting raw fermentation broth (RFB) contained mixed calcium carboxylates.

Descumming

The fermentation broth was descummed by adding slaked lime ($Ca(OH)_2$) to increase the broth pH from 5.5–7 to 10.5–11.5. Descumming was a batch process. A positive-displacement pump loaded the fermentation broth into a stainless steel steam-jacketed mixing tank. The tank was heated to about 80–90°C. During lime addition, the tank was continuously mixed by circulating the broth using a high-temperature centrifugal pump. Thereafter, CO_2 gas was bubbled from a compressed CO_2 cylinder to remove excess $Ca(OH)_2$ as $CaCO_3$. To remove the precipitated scum, the broth was centrifuged (1700 rpm, 7 gpm, Model MAPX-204 centrifuge, Alfa Laval). By precipitating $CaCO_3$ from the mother liquor, it was possible to recover more than 95% of the carboxylate salts from the broth.

Dewatering

Using a single-effect evaporator, the broth was concentrated to obtain solid carboxylate salts. When half the liquid broth evaporated, the carboxylate salts started precipitating. First, the high-molecular-weight calcium salts precipitated and floated to the top. A fine-mesh stainless steel screen was used to skim the floating salts for collection. Then, the hot high-molecular-weight salts were filtered using a laboratory-scale vacuum filter unit equipped with a 25-μm cloth filter. Meanwhile, the low-molecular-weight salts were collected from the bottom of the tank and were filtered while hot. Continuous removal of salts from the top and bottom of the tank and immediate filtration after collection improved salt quality. The salts from the bottom and top were mixed. The filtered carboxylate salts were 45 to 50% moisture; they were dried in a bench-scale oven (120°C, 1.4-kW, Model 17-Y-11, Precision Scientific Co.).

Ketonization

The low- and the high-molecular-weight salts can be ketonized separately, but there is no benefit because the resulting ketones would be low and high molecular weight, respectively. Instead, the dry salts were mixed and thermally converted into ketones and calcium carbonate in the ketonization unit. The ketone unit has a reaction section and a condensing section. For the reaction section, 4 kg of mixed carboxylate salts were charged inside the reactor vessel. The reactor head was bolted in place. Excess air inside the reactor was removed with a vacuum pump until the pressure reached 3.12 kPa (abs). The vacuum pump was turned off and sweep gas (CO_2) was run through the system at 1 L/min. The condensation system was turned on and the reactor stirring speed was set to 25 rpm. The reactor temperature

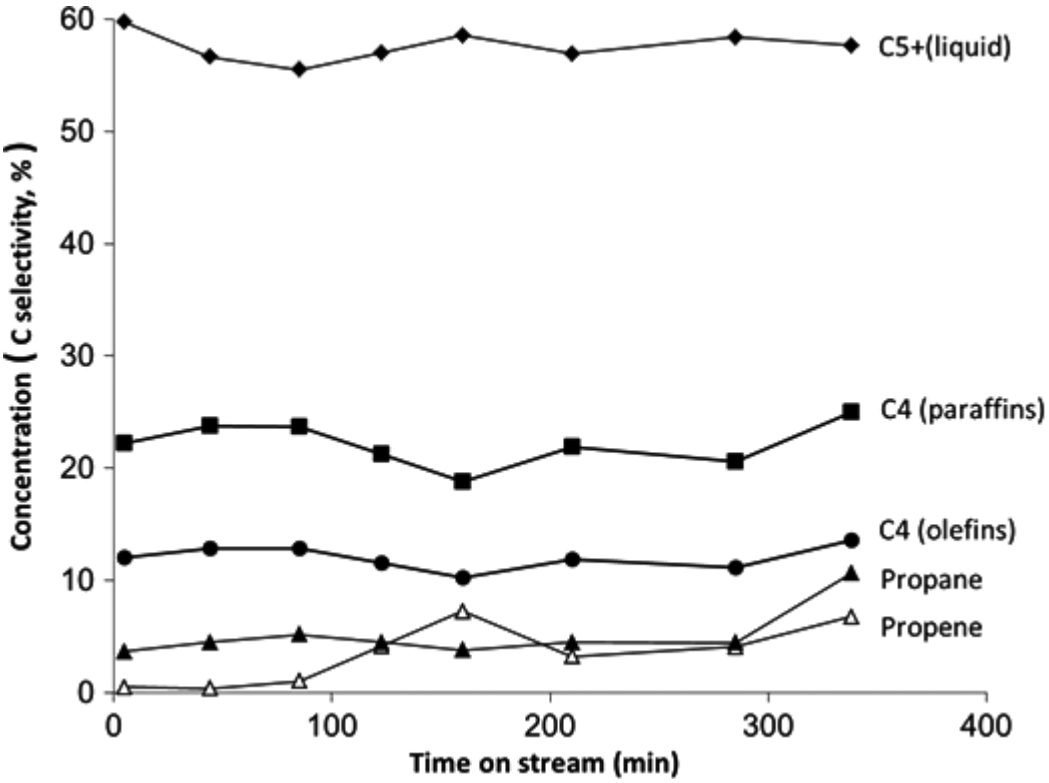

Figure 4. Product distribution for isopropanol reaction over HZSM-5 (280), WHSV=1.31 h^{-1}, P=101 kPa (abs), T=370°C.

was set to 400°C. As salts heated to 180–290°C, they went through a plastic state and the stirrer became very hard to turn causing the magnetic drive to slip. Above 290°C, the stirrer again became functional. Routinely, the stirrer was turned off between 180 and 290°C. The reaction was completed after 3 h. For each 4-kg salt batch, 1.5 L of raw ketones was collected. The condensing section was a series of three condensers connected to the reactor exit. These condensers progressively cooled the reactor product effluent to 0°C (first condenser), −50°C (second condenser), and −78°C (last condenser). To collect the raw ketone product during each run, a glass flask was mounted below each condenser.

Raw ketones had a dark brown color with many impurities (e.g., pyrolysis products) and water, so distillation was necessary to purify the mixture. If these impurities were not removed, they would adversely affect the hydrogenation process. The ketone mixture ranged from acetone (BP=56°C) to 7-tridecanone (BP=259°C). To avoid high-temperature distillation, the batch distillation was divided into two phases: atmospheric and vacuum. For the atmospheric distillation, 15 L of raw ketones were poured into the distillation flask. The first fraction was obtained at 85°C, and recovered light ketones (C3–C5). The second fraction was water obtained between 85–90°C. The vapor from this fraction was white and foggy. The condensed water was disposed as a waste material. The third fraction was collected between 90 and 160°C; most of this fraction was C6–C9. The C6–C13 ketones have a low solubility in water (for example, 2-hexanone solubility 14 g/L). If some water remained in the third fraction, the collection flask would have two layers. Water carries too many impurities, and it affects the following catalytic processes, so the water phase was discarded.

For the vacuum distillation fraction, the remaining raw liquid ketones were left in the flask. The vacuum pump was connected to the system, and the system generated a pressure of 3.12 kPa (abs). Distillate was collected from 60 to 120°C. To reduce bumping, a capillary tube was placed in the 20-L flask (Figure 4), which stirred the liquid with gas bubbles. (Note: For convenience, air was used as the gas but an inert gas is a better alternative.) The distillate obtained above 120°C had a black color, which resulted from oxidation. These oxidized ketones were not collected because they were difficult to hydrogenate. Finally, all the distillate from both the atmospheric and vacuum distillations were mixed and stored with a nitrogen blanket to prevent oxidation. Then, the ketones were hydrogenated into mixed alcohols.

Hydrogenation

Hydrogenation was performed in a 7.5-L stainless steel batch reactor (230-V, 2.3-kW Parr Model 4522M Press React APP26 Cart-MA). The catalyst was Raney nickel (Sigma Aldrich, Cat 221678). The catalyst was in a slurry form with water (50% Raney nickel). The hydrogen was industrial quality from Praxair. First, 5 L of distilled ketones and 100 mL of Raney nickel catalyst were charged to the reactor. The reactor head was bolted in place. Excess air inside the reactor was purged with hydrogen. Hydrogen was added until the reactor pressure reached 6900 kPa (abs). The stirrer rotated at 750 rpm. The heating jackets increased the reaction temperature to 155°C. During heating, fresh hydrogen was added to maintain the reactor pressure at 6900 kPa (abs). After 1 h, the temperature stabilized to 155°C and fresh hydrogen was added until the reactor pressure was 8600 kPa (abs). The reaction was completed after 24 h. The

alcohol product was collected and centrifuged to separate the catalyst from the liquid. Figure 3 shows the carbon distribution concentration of the mixed alcohol ranged from C3 (isopropanol) to C13 (6-tridecanol). For the 5 L of distilled ketone, the amount of hydrogen consumed was 0.076 kg.

Results

The reaction of isopropanol and mixed alcohols over HZSM-5 is exothermic. Compared to the inlet temperature, the reactor temperature increased about 40°C. The alcohols react to form hydrocarbons and water.

$$\text{R-OH} \rightarrow [\text{CH}_2]_n + \text{H}_2\text{O}$$

where $[CH_2]$ represents hydrocarbons, such as olefins, paraffins, naphthenes, and aromatics. The product distribution ranged from C3 hydrocarbons (e.g., propene) to C13 hydrocarbons (e.g., 6-tridecene).

The alcohol feed rate is characterized by the WHSV, which is defined as the weight of feed per hour per unit weight of catalyst loaded in the reactor.

$$\text{WHSV} \equiv \frac{\dot{m}_{\text{feed}}}{m_{\text{catalyst}}}$$

where $\dot{m}_{\text{feed}}$ = mass flow rate to the reactor (g/h), m_{catalyst} = mass of catalyst (g)

For example, if the feed rate is 10 g per hour to the reactor and 10 g of catalyst is loaded in the reactor, the WHSV is 1.0 h^{-1}.

Isopropanol

Catalyst stability

For the isopropanol reaction, Figure 4 shows gas and liquid product distribution over HZSM-5 during time on stream. During the first 360 min, the product concentration was always constant; therefore, the catalyst did not deactivate during this time. The C4 olefins include 1-butene and isobutylene, whereas C4 paraffins include butane and isobutane. C5+ products were lumped together as liquids. For all experiments of varying temperature and WHSV, the reported concentrations were the average of all values recorded during the first 360 min. Approximately eight samples were measured for each temperature and WHSV.

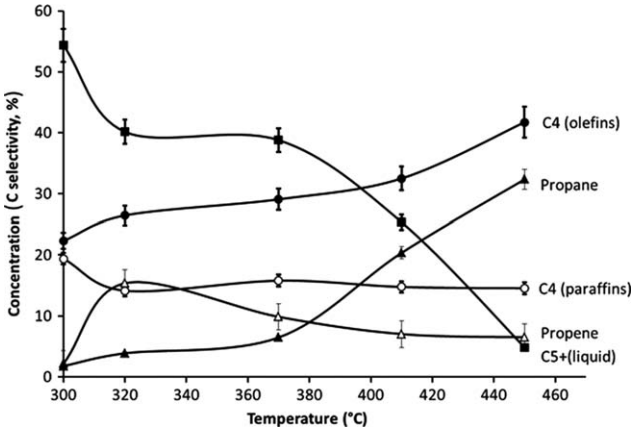

Figure 5. Product distribution of gases and liquids for isopropanol reaction over HZSM-5 (280), WHSV=1.31 h^{-1}, P=101 kPa (abs). (Error bars are ±1σ).

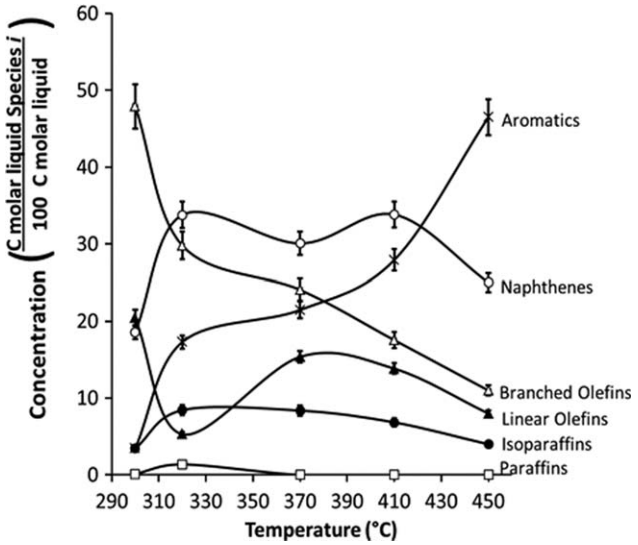

Figure 6. Liquid product distribution for isopropanol reaction over HZSM-5 (280), WHSV=1.31 h^{-1}, P=101 kPa (abs). (Error bars are ±1σ).

Effect of varying temperature

Approximately 300°C was the lower temperature bound. Below this, the temperatures were not stable because of the heat of reaction. For example, when the reaction temperature was set between 250 and 300°C, the temperature always increased until it reached 300°C. On the other hand, if the temperature was lower than 250°C, the isopropanol did not react.

Figure 5 shows the gas and liquid product distribution, which is affected by temperature. As the temperature increases, the amount of liquid (C5+) decreased from 70% (300°C) to 10% (450°C) and the gaseous products increased from 30% (300°C) to 90% (450°C). At high temperatures, gaseous products increase from cracking C5+ olefins.[23] For instance, the amount of propane increases from 2% (300°C) to 22% (450°C). Because of the dehydration reaction, the amount of olefinic gaseous products is larger than the paraffinic products.

Temperature affects the type of liquid reaction products obtained (Figure 6). At higher temperatures, the concentration of aromatics increases from 5% (300°C) to more than 48% (450°C).[23] Because aromatics and gaseous products form, the amount of branched olefins decreases from 48% (300°C) to 10% (450°C). At all temperatures, the concentration of isoparaffins, linear olefins, and naphthenes are constant. The concentration of isoparaffinic compounds is always below 10% and the paraffin concentration is negligible.

Effect of varying WHSV

At T=370°C and WHSV=0.52–11.23 h^{-1}, Figure 7 shows the distribution of gas and liquid is not affected by the change of WHSV. At all WHSV, the amount of liquid is constant (~60%). The amount of propene increases from 1% (0.52 h^{-1}) to 15.5% (11.2 h^{-1}); at high WHSV (low residence time), propene forms first and does not have time to continue reacting.

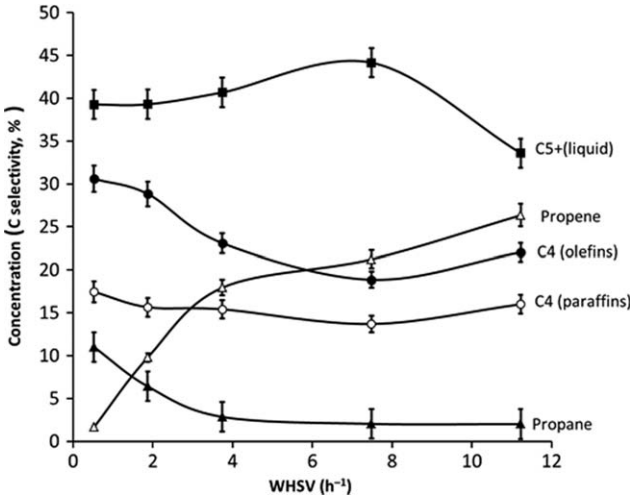

Figure 7. Product distribution of gases and liquids for isopropanol reaction over HZSM-5 (280), T=370°C, P=101 kPa (abs). (Error bars are ±1σ).

Figure 8 illustrates the types of liquid-phase products at different WHSV. At very low WHSV, aromatics are high (60% at 0.52 h^{-1}); however, at high WHSV, aromatics are much less (8% at 11.2 h^{-1}). On the other hand, when the WHSV increases, branched olefins also increase, from 5% (0.52 h^{-1}) to 40% (11.2 h^{-1}). At all WHSV, naphthenes are constant, and the amount of paraffins always stayed below 5%.

Figure 9 illustrates the carbon distribution of the liquid products at different WHSV. At lower WHSV, the most abundant component is C9 whereas at higher WHSV, the most abundant component is C6. At low WHSV, the olefins undergo more oligomerization reactions to produce larger molecules, whereas at high WHSV, the molecules do not have time to form larger molecules. It is noteworthy that the carbon number in the liquid can be changed by WHSV and not temperature.

Liquid product distribution

Table 1 shows the most abundant compounds in the liquid-phase product at 370°C for the different WHSV studied.

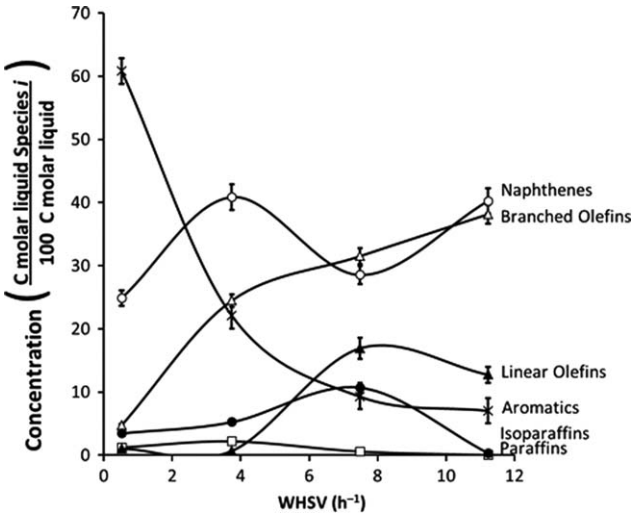

Figure 8. Liquid product distribution for isopropanol reaction over HZSM-5 (280), T=370°C, P=101 kPa (abs). (Error bars are ±1σ).

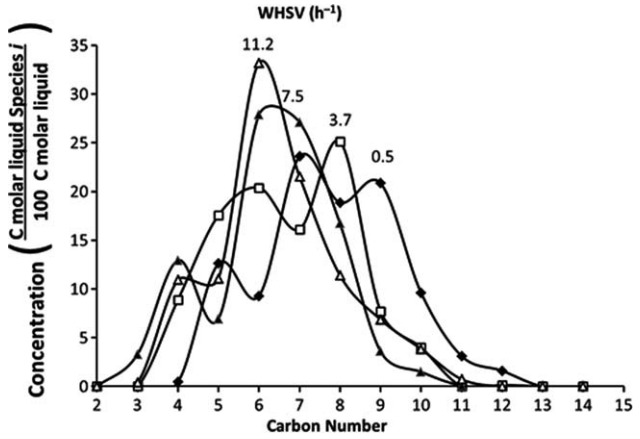

Figure 9. Liquid product distribution of isopropanol reaction over HZSM-5 (280), T=370°C, P = 101 kPa (abs).

Branched olefins are more abundant than linear olefins; during oligomerization, the reactive double bond is on a secondary carbon, which forms branched molecules. C6 olefins are the most abundant because of the dimerization of propene. Also present are branched naphthenes that are unsaturated (e.g., cyclohexene, 1,3-dimethyl) or saturated (e.g., cyclopentane, 1,3-dimethyl). For aromatics, branched meta and ortho substitutions are very common. For all the liquids analyzed, approximately 80 to 150 compounds were found by the GC–MS. Usually, ~20 compounds comprised 80% of the molar distribution. The remaining compounds had a concentration less than 1%.

Mixed Alcohols

Catalyst stability

For the mixed alcohols, Figure 10 shows the distribution of gas and liquid products during time on stream. During the first 360 min, the product distribution is stable (Figure 4). The most abundant fraction (C5+) has a constant concentration over time. Figure 4 shows that mixed alcohols produce more hydrocarbon liquids (~90%) than isopropanol (~60%).

Effect of varying temperature

Figure 11 shows that temperature affects the selectivity of gas and liquid products. As temperature increases, the amount of liquid (C5+) decreases from 80% (300°C) to 40% (520°C). The gaseous products increase from <10% (370°C) to 30% (520°C); the increase results from cracking C5+ olefins at high temperatures. This also occurs with isopropanol; however, isopropanol cracks at lower temperatures (300°C) compared to mixed alcohols (370°C). For instance, the amount of C4 olefins increases from 2% (300°C) to 30% (520°C). It is notable that there are more olefinic gaseous products than paraffinic products, which is similar to the isopropanol reaction.

Figure 12 shows the effect of temperature on product distribution at WHSV=1.31 h^{-1}. The unreacted alcohol decreases from 12% at 300°C to 0% at 320°C. Between 300 and 410°C, branched and linear olefins are the only reaction products. Above 410°C, aromatics and naphthenes appear as reaction products. At higher temperatures, aromatics increase from 3% (410°C) to 55% (520°C), which is similar to the isopropanol reaction.

Table 1. Most Abundant Liquid Compounds for the Isopropanol Reaction over HZSM-5, T=370°C, WHSV=0.5–11 h^{-1}, P=101 kPa (abs)

Olefins and Naphthene Olefinics	Concentration (mol %)	Naphthenes	Concentration (mol %)
2,3-dimethyl-1-butene	2.4–6.8	1,2-dimethyl cyclopropane	2.7–7.5
3 methyl-2-pentene	3.7–9.5	1-methylethenyl cyclopropane	1.4–2.7
1,3-dimethyl cyclohexene	2.0–2.9	1,3-dimethyl cyclopentane	1.8–2.7
2-methyl-2-hexene	1.2–7.8	1,2-dimethyl-3-methylene cyclopentane	1.3–2.7
1,3-dimethyl cyclohexene	1.4–2.9		
1-methyl cyclohexene	1.8–2.3		
Aromatics	**Concentration (mol %)**	**Isoparaffins**	**Concentration (mol %)**
Methyl benzene	1.8–10	2-methyl pentane	4.2–4.4
1,3-dimethyl benzene	2.9–5.5	2-methyl hexane	2.4–2.8
1-ethyl-2-methyl benzene	2.2–4.4		

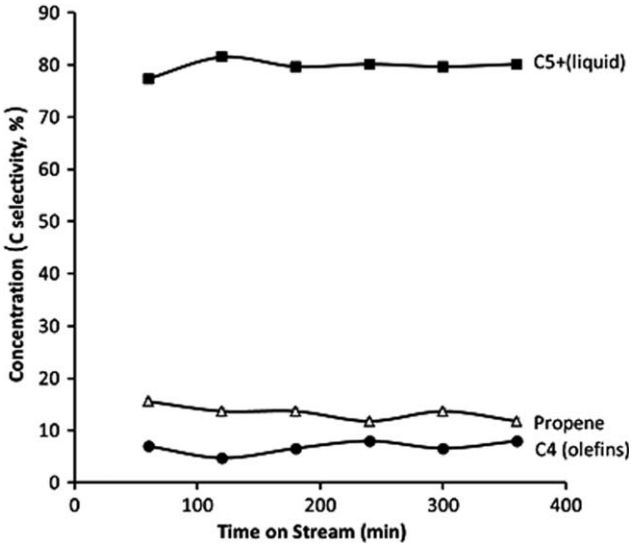

Figure 10. Product distribution of gases and liquids for the mixed alcohol reaction over HZSM-5 (280), T=370°C, WHSV=1.31 h^{-1}, P=101 kPa (abs).

Effect of varying WHSV

Figure 13 illustrates the gas product distribution at different WHSV at T=370°C. Between 0.5 and 11.23 h^{-1}, dehydration is the dominant reaction because linear olefins are the most abundant species (~95%). The product distribution is not affected by changing WHSV. In this WHSV range, the amount of gases (C3–C4) is negligible.

Figure 14 illustrates the liquid carbon distribution of the liquid products at different WHSV. In this WHSV, the most abundant components are C7 to C9. The product carbon distribution is not affected by changing WHSV.

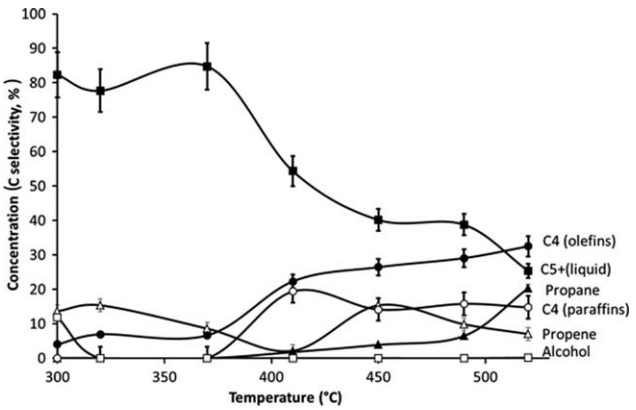

Figure 11. Product distribution of gases and liquids for mixed alcohol reaction over HZSM-5 (280), WHSV=1.31 h^{-1}, P=101 kPa (abs). (Error bars are ±1σ).

Liquid product distribution

Table 2 shows the most abundant compounds in the liquid-phase product at 300–410°C and WHSV=1.31 h^{-1}. Linear olefins are abundant because dehydration in these variable ranges is the only reaction that occurred. For higher temperatures (450–520°C), oligomerization occurs and the compounds are similar to isopropanol products shown in Table 1.

Coke deposition

Transformation of alcohols to hydrocarbons can be limited by catalyst deactivation. Catalyst activity can be determined by the stability of the product distribution during time on stream and the amount of coke produced. During all the experiments with isopropanol and mixed alcohol, the product distribution did not vary during the 360-min time on stream;

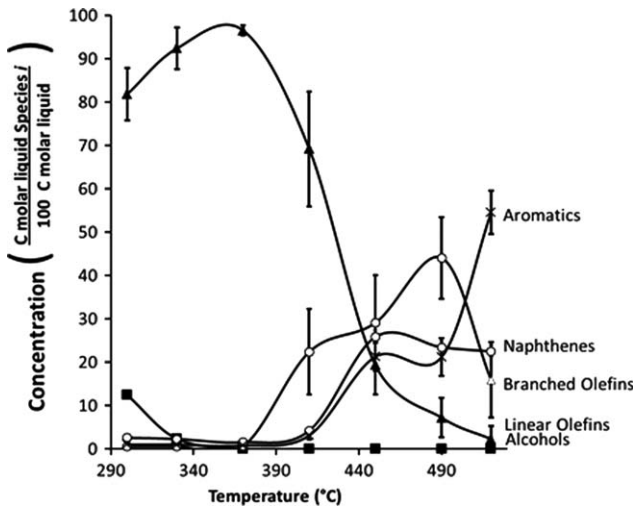

Figure 12. Liquid product distribution of mixed alcohol reaction over HZSM-5 (280), WHSV=1.31 h^{-1}, P=101 kPa (abs). (Error bars are ±1σ).

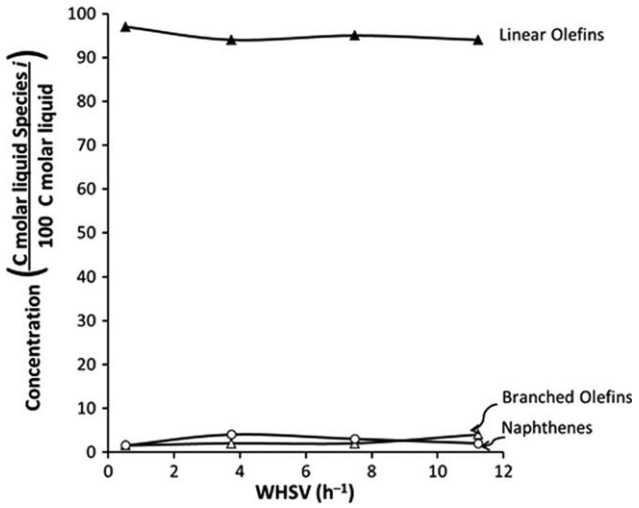

Figure 13. Product distribution of gases and liquids for mixed alcohol reaction over HZSM-5 (280), T=370°C, P=101 kPa (abs). (Error bars are±1σ).

however, the catalyst coked. The coke is characterized by the coke yield, which is defined as the weight of coke produced per total weight of feed injected in the reactor.

$$\text{Coke Yield (wt \%)} \equiv \frac{\text{Coke}_{\text{produced}}}{\text{Feed}_{\text{total}}} \times 100$$

where

$\text{Coke}_{\text{produced}}$=coke produced (g)

$\text{Feed}_{\text{total}}$=Total feed mass (g)

For example, if the coke weight is 0.6 g and 100 g of alcohol was injected during a period of time, the coke yield is 0.6 wt %.

Table 3 shows the amount of coke deposited in the catalyst. For isopropanol, the coke yield at low temperature (320°C) is low (0.31 wt %); whereas, at high temperature (410°C), the coke content doubled to 0.65 wt %. For mixed alcohol, the coke content increased with temperature as well. For example, the coke yield at low temperature (320°C) is low (0.59 wt %); whereas, at high temperature (410°C), the coke content increased to 0.63 wt %.

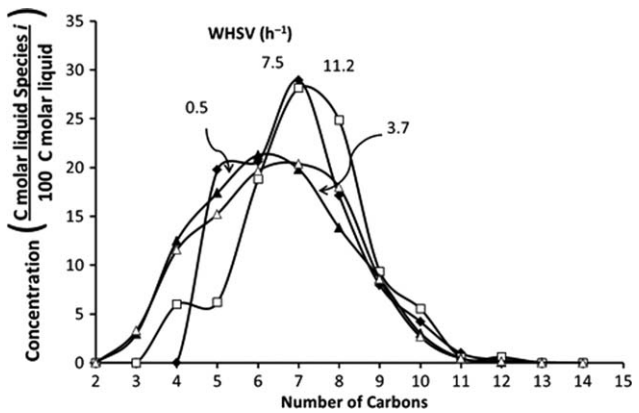

Figure 14. Liquid product distribution of mixed alcohol reaction over HZSM-5 (280), T=370°C, P = 101 kPa (abs).

Table 2. Most Abundant Liquid Compounds for the Mixed Alcohol Reaction over HZSM-5, T=300–420°C, WHSV=1.31 h^{-1}, P=101 kPa (abs)

Olefins	Concentration Range (mol %)
2-Pentene	6.0–17.0
1-Hexene	1.5–1.7
2-Hexene	2.0–11.3
2-Heptene	3.8–29.7
3-Heptene	2.5–12.8
2-Octene	2.8–4.2
3-Octene	7.6–9.1
4-Octene	1.4–2.3
4-Nonene	9.1–19.3
3-Decene	1.5–1.6
4-Decene	3.5
4-Undecene	4.6–8.4
5-Undecene	1.5
4-Dodecene	1.5–1.9

Table 3. Coke Yield for Different Reactants and Temperatures

T (°C)	Feed	Time on Stream (min)	Coke Yield (wt %)
320	Isopropanol	360	0.31
370	Isopropanol	360	0.58
410	Isopropanol	360	0.65
320	Mixed alcohol	360	0.59
370	Mixed alcohol	360	0.55
410	Mixed alcohol	360	0.63

Conclusions

This study investigated the conversion of isopropanol and mixed alcohols to hydrocarbons using HZSM-5 at 101 kPa (abs). For both isopropanol and mixed alcohols during the first 360 min, there was no catalyst deactivation during the oligomerization reaction.

For isopropanol, higher temperatures (410 to 450°C) produced more gaseous products and aromatics whereas the olefins decreased. High WHSV gives high concentrations of C6+ olefins whereas low WHSV gives high concentrations of C9 aromatics.

For mixed alcohols, the amount of liquid produced was much greater than isopropanol. Between 300 and 410°C, dehydration occurs producing only linear olefins. Above 410°C, the linear olefins are transformed into branched olefins, naphthenes, and aromatics. Isoparaffins were not observed as reaction products from mixed alcohols. Varying WHSV did not affect product distribution; only dehydration products were observed.

Although the catalyst formed coke, it did not affect the product distribution during the isopropanol and mixed alcohol experiments. Higher temperatures produced more coke for both feeds. For isopropanol and mixed alcohol, the coke produced was very similar.

Acknowledgments

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Literature Cited

1. Pham V, Holtzapple M, El-Halwagi M. Techno-economic analysis of biomass to fuel conversion via the MixAlco process. *J Ind Microbiol Biotechnol*. 2010;37(11):1157–1168.
2. Holtzapple M, Davison R, Ross M, Aldrett-Lee S, Nagwani M, Lee C-M, Lee C, Adelson S, Kaar W, Gaskin D, Shirage H, Chang N-S, Chang V, Loescher M. Biomass conversion to mixed alcohol fuels using the MixAlco process. *Appl Biochem Biotechnol*.1999; 79(1):609–631.
3. Granda C, Holtzapple M, Luce G, Searcy K, Mamrosh D. Carboxylate platform: the MixAlco process part 2: Process economics. *Appl Biochem Biotechnol*. 2009;156(1–3):107–554.
4. Holtzapple M, Granda C. Carboxylate platform: the MixAlco process part 1: comparison of three biomass conversion platforms. *Appl Biochem Biotechnol*. 2009;156(1–3):95–536.
5. Agler M, Wrenn B, Zinder S, Angenent L. Waste to bioproduct conversion with undefined mixed cultures: the carboxylate platform. *Trends Biotechnol*. 2011;29(2):70–78.
6. Agbogbo F, Holtzapple M. Fermentation of rice straw/chicken manure to carboxylic acids using a mixed culture of marine mesophilic microorganisms. *App Biochem Biotechnol*. 2006;132 (1–3):997–1014.
7. Aiello-Mazzarri C, Coward G, Agbogbo F, Holtzapple M. Conversion of municipal solid waste into carboxylic acids by anaerobic countercurrent fermentation—effect of using intermediate lime treatment. *Appl Biochem Biotechnol*. 2005;127(2):79–93.
8. Domke S, Aiello-Mazzarri C, Holtzapple M. Mixed acid fermentation of paper fines and industrial biosludge. *Bioresour Technol*. 2004;91(1):41–51.
9. Thanakoses P, Mostafa N, Holtzapple M. Conversion of sugarcane bagasse to carboxylic acids using a mixed culture of mesophilic microorganisms. *Appl Biochem Biotechnol*. 2003;105:523–546.
10. Kalghatgi-Gautam T. U.S. Patent 6,565,617, 2003.
11. Taco-Vasquez S, Holtzapple M. Transformation of Acetone and Isopropanol to Hydrocarbons. Berlin: LAP LAMBERT Academic Publishing, 2012:76–84.
12. Mayfield H. JP-8 Composition and Variability Report. Tyndall AFB Florida: Armstrong Laboratories, 1996.
13. Chang C, Silvestri A. The conversion of methanol and other O-compounds to hydrocarbons over zeolite catalysts. *J Catal*. 1977;47:249–259.
14. Stocker, M. Methanol-to-hydrocarbons: catalytic materials and their behavior. *Microporous Mesoporous Mater*. 1999;29(1–2):3–48.
15. Wu X, Abraha M, Anthony R. Methanol conversion on SAPO-34: reaction condition for fixed-bed reactor. *Appl Catal. A, General*. 2004;260(1):63–69.
16. Chang C. Hydrocarbons from Methanol, 2nd ed. New York: Marcel Dekker, Inc., 1983.
17. Frerich J.K. Review: Methanol-to-hydrocarbons: process technology. *Microporous Mesoporous Mater*. 1999;29(1–2):49–66.
18. Meisel S.L. Gasoline from methanol in one step. *Chemtech*. 1976;6(2):86–89.
19. Fuhse J, Bandermann F. Conversion of organic oxygen compounds and their mixtures on HZSM-5. *Chem Eng Technol*. 1987;10:323–329.
20. Aguayo A, Gayubo A, Tarrio A, Atutxa, A, Bilbao J. Study of operating variables in the transformation of aqueous ethanol into hydrocarbons on an HZSM-5 zeolite. *J Chem Technol Biotechnol*. 2002;7(2):211–216.
21. Behrens M. The scientific bases for the preparation of heterogeneous catalysts. In: Gaigneaux E, editor. Proceedings of the 10th International Symposium, July 11–15, 2010, Louvain-la-Neuve, Belgium, July, 1st ed. Amsterdam, 2010.
22. Yoon J.W, Chang J, Lee H, Kim T, Jhung SH. Trimerization of isobutene over a zeolite beta catalyst. *J Catal*. 2007;245(1):253–256.
23. Gayubo A, Aguayo A, Atutxa A, Aguado R, Bilbao J. Transformation of oxygenated components of biomass pyrolysis oil on a HZSM-5 zeolite. I alcohols and phenols. *Kinet Catal React Eng*. 2004;43:2610–2618.

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