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Processing biomass-derived oxygenates in the oil refinery: Catalytic cracking (FCC) reaction pathways and role of catalyst

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Abstract

The catalytic cracking of glycerol and sorbitol, as representative of biomass-derived oxygenates, was studied at 500–700 °C with six different catalysts, including a fresh fluid catalytic cracking (FCC) catalyst (FCC1), an equilibrium FCC catalyst with metal impurities (ECat), a mesoporous Al_2O_3, a USY zeolite (Y), a ZSM5-based FCC additive (ZSM5), and an inert silicon carbide (SiC). In this process, oxygen is removed from the feed as H_2O, CO, or CO_2. Repeated dehydration and hydrogen transfer allows the production of olefins, paraffins, and coke. Aromatics (in yields up to 20 molar carbon%) are formed by Diels–Alder and condensation reactions of olefins and dehydrated species, and the different reaction pathways are discussed. Sorbitol and glycerol gave similar product distributions, with the primary difference being that sorbitol produces more CO than glycerol. Glycerol can also be converted when fed together with vacuum gasoil without significantly altering the product selectivity, suggesting that biomass-derived products can be co-fed with petroleum-derived streams in an industrial FCC reactor. When glycerol is fed together with a vacuum gasoil, interactions between the hydrocarbon components and the glycerol reaction intermediates occur, resulting in final selectivities better than those calculated by considering a simple additive effect.

Keywords: Biomass; Catalytic cracking; Glycerol; Zeolites; Biofuels; Biochemicals

1. Introduction

Declining petroleum resources, combined with an increasing demand for petroleum by emerging economies as well as political and environmental concerns about fossil fuels, are spurring the search for new sources of liquid fuels. In this respect, plant biomass is the only current sustainable source of organic carbon, and biofuels (fuels derived from plant biomass) are the only current sustainable liquid fuels [1–3]. Biofuels produce significantly less greenhouse gas emissions than fossil fuels and can even be greenhouse gas neutral if efficient methods for biofuels production are developed [1,4–6]. According to the European Biomass Industry Association (EUBIA), Europe, Africa, and Latin America could produce 8.9, 21.4, and 19.9 EJs of biomass per year with an energy equivalence of 1.4×10^9, 3.5×10^9, and 3.2×10^9 boe, respectively [7]. The current cost of delivered biomass is significantly cheaper than crude oil in many nations. The cost of biomass per boe in the European Union ranges from $11 for solid industrial residues to $39 for energy crops, such as rapeseed [7]. In the United States, it has been estimated that the cost of lignocellulosic biomass is $5 to 15/boe [1,2], which is significantly below the current cost of crude oil of $56/bbl (average cost in 2005) [8].

One option for biofuel production is to use biomass-derived feedstocks in a petroleum refinery. Petroleum refineries are already built, and using this existing infrastructure for biofuel production would require little capital cost investment. The European Commission has set a goal of 5.75% of transportation fuels in the EU as biofuels by 2010; co-feeding biomass-derived molecules into a petroleum refinery could rapidly decrease our dependence on petroleum feedstocks. In contrast to petroleum-derived feedstocks, biomass-derived compounds

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contain large amounts of oxygen, and their conversion into liquid fuels requires oxygen removal. Carbohydrates, which compose approximately 75 wt% of cellulosic biomass, have a C-to-O ratio of 1:1. Water-soluble biomass-derived oxygenates (including carbohydrates, polysaccharides, furfural, and lignin-derived compounds) can be produced from cellulosic biomass by acid hydrolysis, pyrolysis, or liquefaction [2,9–14]. Bio-oils, produced by fast pyrolysis or liquefaction from biomass, are a mixture of more than 300 highly oxygenated compounds. Bio-oils are thermally unstable and must be upgraded if they are to be used as fuels. Glycerol also can be produced from biomass through fermentation of sugars or transesterification of vegetable oils during biodiesel production. Glycerol is a valuable byproduct of biodiesel production, with a current refined value of around \$1.10/kg. As biodiesel production increases, the cost of glycerol is projected to decrease significantly; the cost of glycerol has already dropped by almost half over the last few years [15]. Bray has estimated that the cost of refined glycerol could drop to as low as \$0.77/kg [16]. Werpy and Peterson have estimated that the cost of unrefined glycerol could decrease to \$0.44/kg [17], or close to 150 \$/boe.

Fluid catalytic cracking (FCC) is the most widely used process for conversion of the heavy fraction of crude oil into gasoline and other hydrocarbons in oil refineries [18]. The FCC process comprises two main reaction zones coupled together. In a first transported bed reactor, a hot particulate catalyst is contacted with the hydrocarbon feedstock, thereby producing cracked products and spent coked catalyst. After the cracking reaction, the catalyst is largely deactivated by coke. The coked catalyst is separated from the cracked products, stripped of residual oil by steam, and then regenerated by burning the coke from the deactivated catalyst in a regenerator. The regeneration process occurs at 650–760 °C and a pressure of around 2 atm. The hot catalyst is then recycled to the riser reactor for additional cracking.

The major challenge with all biomass conversion strategies is how to efficiently remove the oxygen from the hydrophilic biomass-derived feedstock and convert it into a hydrophobic molecule with the appropriate combustion or chemical properties. In this respect, FCC catalysts are very effective at removing oxygen from biomass-derived molecules. Oxygen can be removed as CO, CO_2 or H_2O through the following reaction:

$$C_6O_6H_{12} \rightarrow aC_xH_{2x+2}O_y + bCO_2 + cH_2O + dCO + eC. \quad (1)$$

Chen et al. [19] studied the conversion of carbohydrates over ZSM5 catalysts and found coke, CO, hydrocarbons, and CO_2 as the major products. These authors found that the major challenges in biomass conversion were removing oxygen from the biomass and increasing the hydrogen content of the hydrocarbon product. They presented an effective hydrogen-to-carbon ratio (H/C_{eff}) as defined in Eq. (2), which we use in the present work to help understand the chemistry involved in the conversion of biomass-derived oxygenates during catalytic cracking. The H/C_{eff} ratio of biomass-derived oxygenates is lower than that of petroleum-derived feedstocks due to the high oxygen content of biomass-derived molecules. The H/C_{eff} ratios of carbohydrates, sorbitol, and glycerol (all biomass-derived compounds) are 0, 1/3, and 2/3 respectively. The H/C_{eff} ratio of petroleum-derived feeds ranges from ∼2 for highly paraffinic feeds to slightly >1 for highly aromatic residues. In this respect, biomass can be viewed as a hydrogen-deficient molecule compared with petroleum-based feedstocks,

$$H/C_{eff} = \frac{H - 2O - 3N - 2S}{C}, \quad (2)$$

where H, C, O, N, and S are the mol of hydrogen, carbon, oxygen, nitrogen, and sulfur respectively.

Conversion of bio-oils and model bio-oil compounds have been investigated using zeolites as catalysts [20–27]. Bio-oils are a complicated mixture of more than 300 different oxygenated compounds [9,13] produced by fast pyrolysis or liquefaction. Bio-oils have a higher H/C_{eff} factor than carbohydrates because some of the oxygen is removed from the biomass during bio-oil production. Bakhshi and co-workers studied zeolite upgrading of wood-derived fast-pyrolysis bio-oils [20–24]. They tested five different catalysts (ZSM5, H-Y-zeolite, H-mordenite, silicalite, and silica alumina) for bio-oil upgrading in a flow reactor at temperatures of 290–410 °C and 30 min of catalyst residence time and found that ZSM5 produced the highest amount (34 wt% of feed) of liquid organic products [21]. The products in the organic carbon were mostly aromatics for ZSM5 and aliphatics for SiO_2–Al_2O_3. The zeolite catalysts had higher hydrocarbon yields than the silica–alumina and silicalite catalysts. Mixtures of ZSM5 with silica–alumina were also tested [22]. Gaseous products included CO_2, CO, light alkanes, and light olefins. Large amounts of coke (6–29 wt% of feed), char (12–37 wt% of feed), and tar (12–37 wt% of feed) were formed during zeolite upgrading.

The reactivity and reaction pathways for model bio-oil compounds using ZSM5 catalysts have been studied by Gayubo and co-workers [25–27]. Alcohols convert into olefins at temperatures around 200 °C and then to higher olefins at 250 °C, followed by paraffins and a small proportion of aromatics at 350 °C [25]. Phenol has a low reactivity on HZSM5 and produces only small amounts of propylene and butanes [25]. 2-Methoxyphenol also has low reactivity to hydrocarbons and thermally decomposes, generating coke [25]. Acetaldehyde has a low reactivity on ZSM5 catalysts and also undergoes thermal decomposition, leading to coking problems [26]. Acetone, which is less reactive than alcohols, is first dehydrated to isobutene at 250 °C and then converts to C_{5+} olefins at temperatures above 350 °C. These olefins are then converted into gasoline-range paraffins, aromatics, and alkenes. Acetic acid is first converted to acetone, which reacts further. Products from zeolite upgrading of acetic acid and acetone produce considerably more coke than products from alcohol feedstocks. Thus different molecules in the bio-oils have a significant difference in reactivity and coke formation rates.

In the present work, we investigated how FCC of biomass-derived oxygenates—more specifically glycerol and sorbitol—can be used alone or co-fed with vacuum gasoil to produce olefins, aromatics, H_2, CO, and process heat. We report the products obtained and the most likely reaction routes to ex-

Table 1
Catalytic properties of catalysts used in this study

Catalyst	Si/Al	BET surface area (m^2/g)	Particle size (mm)	Micropore volume (cm^3/g)
FCC1	13	290	0.1	0.087
ECat	20	156	0.1	0.050
ZSM5 additive	50	70	0.1	0.027
Al_2O_3	0	150	0.2–0.4	0
Y-Zeolite	12	400	0.2–0.4	0.122
Silicon carbide (SiC)	–	<1	0.4–0.8	<0.001

Table 2
Properties of the vacuum gas oil

Density 288 K (g/cm^3)						0.9081
Sulfur (wt%)						0.35
N_2 (ppm)						1614
Carbon Conradson (wt%)						0.15
Average molecular weight (g/mol)						464
K_{UOP}						12.11
Distillation curve D-1160:						
vol%	5	10	30	50	70	90
K	638	673	704	729	763	824

plain the formation of those products. We studied the influence of the catalyst by working with a range of materials with different pore sizes and acidity distributions and found that the impact of the biomass-derived product when cracked together with commercial feeds can have a positive impact on product formation.

2. Experimental

2.1. Materials and reactants

The physicochemical characteristics of the six solids used in this study—a fresh commercial FCC catalyst containing Y-zeolite in a silica–alumina matrix (Precision 1% Rare Earth, supplied by BASF, tag FCC1), a commercial equilibrium FCC catalyst with V and Ni impurities (supplied by BP, tag ECat), Al_2O_3 (Aldrich), a pure USY zeolite (tag Y) with an area of 400 m^2/g and an UCS of 24.28 Å, a ZSM5 FCC additive (supplied by InterCat, tag ZSM5), and a low–surface area inert silicon carbide (tag SiC, supplied by Aldrich Chemicals)—are presented in Table 1. The Ecat had a metal content of 4400 ppm V and 1600 ppm Ni. The FCC1 catalyst was laboratory-deactivated over 4 h at 1089 K under a steam-vapor atmosphere and had no metal content. The Y-zeolite is CBV500, steamed for 4 h at 1089 K. The ZSM5 zeolite was mixed with a clay binder to around 15 wt%.

A glycerol solution was prepared with 99.5 wt% glycerol (Aldrich Chemicals) diluted at a 1:1 weight ratio with distilled water. A sorbitol solution was prepared with 99% sorbitol and the same water dilution. Vacuum gasoil corresponds to an Arabian Light supplied by CEPSA, and its characteristics are given in Table 2.

2.2. Microactivity tests

Experiments described in this paper were performed in a microactivity test (MAT) reactor [28]. The reaction zone and product recovery system were designed in accordance with ASTM D-3907. Before each experiment, the MAT system was purged with a 50-mL/min N_2 flow for 30 min at the reaction temperature. All MAT reactions reported herein were done with 30 s time on stream. After reaction, stripping of the catalyst was carried out for 15 min using a N_2 flow of 40 mL/min. During the reaction and stripping steps, the liquid products were collected in the corresponding glass receivers located at the exit of the reactor and kept at 278 K by means of a computer-controlled bath. Meanwhile, the gaseous products were collected in a gas burette by water displacement. After stripping, the catalyst was regenerated at 813 K for 3 h in a 100-mL/min stream of air. The reaction gases were analyzed using a Varian 3800 gas chromatograph equipped with three detectors, two thermal conductivity detectors (TCDs) for analysis of H_2 and $CO/CO_2/N_2$, separated on a 2-m molecular sieve 5A column and a 2.5-m molecular sieve 13X column, respectively, and a flame ionization detector (FID) for C_1–C_6 hydrocarbons separated on a 50-m Plot/Al_2O_3 column. Liquid samples were analyzed on a Varian 3900 gas chromatograph equipped with a Petrocol-100 fused silica column connected to a FID detector following the PIONA procedure. The different products were then grouped into oxygenates and hydrocarbons. Simulated distillation of vacuum gasoil (VGO) cracking samples were carried out using a Varian 3800 gas chromatograph according to the ASTM-2887-D86 procedure; cutpoints were set at 489.3 K for gasoline and 632 K for light cycle oil (LCO). The CO_2 formed during the regeneration step was monitored and quantified by means of an IR cell. The carbon yields reported herein are defined as the mol of carbon in each product divided by the carbon in the feed. To compare carbon selectivities when VGO was injected, we considered a carbon content of the VGO of 88 wt%. We calculated the hydrogen yield as mol of hydrogen produced divided by mol of potential hydrogen. The mol of potential hydrogen were defined as the mol of hydrogen that would be produced if all of the carbon was converted to CO plus the mol of CO_2 obtained experimentally. When glycerol and sorbitol are used as feeds, the conversion is defined as the conversion to gases, coke, and aromatics. When VGO or VGO mixtures are used as feeds, the conversion is defined as the conversion to gases, coke, and the gasoline liquid fraction.

3. Results and discussion

3.1. Effect of catalyst on catalytic cracking of glycerol

Six different catalysts (FCC1, ECat, Al_2O_3, Y, ZSM5, and SiC) were tested for catalytic cracking of an aqueous 50 wt% glycerol, as shown in Figs. 1–3. The products for the FCC1 catalyst include coke, gas, and liquids. Between 30 and 50% of the carbon in the glycerol feed was converted into coke with the FCC1 catalyst (Fig. 1). The coke yield increased while the aromatic yield decreased with increasing conversion, which can be

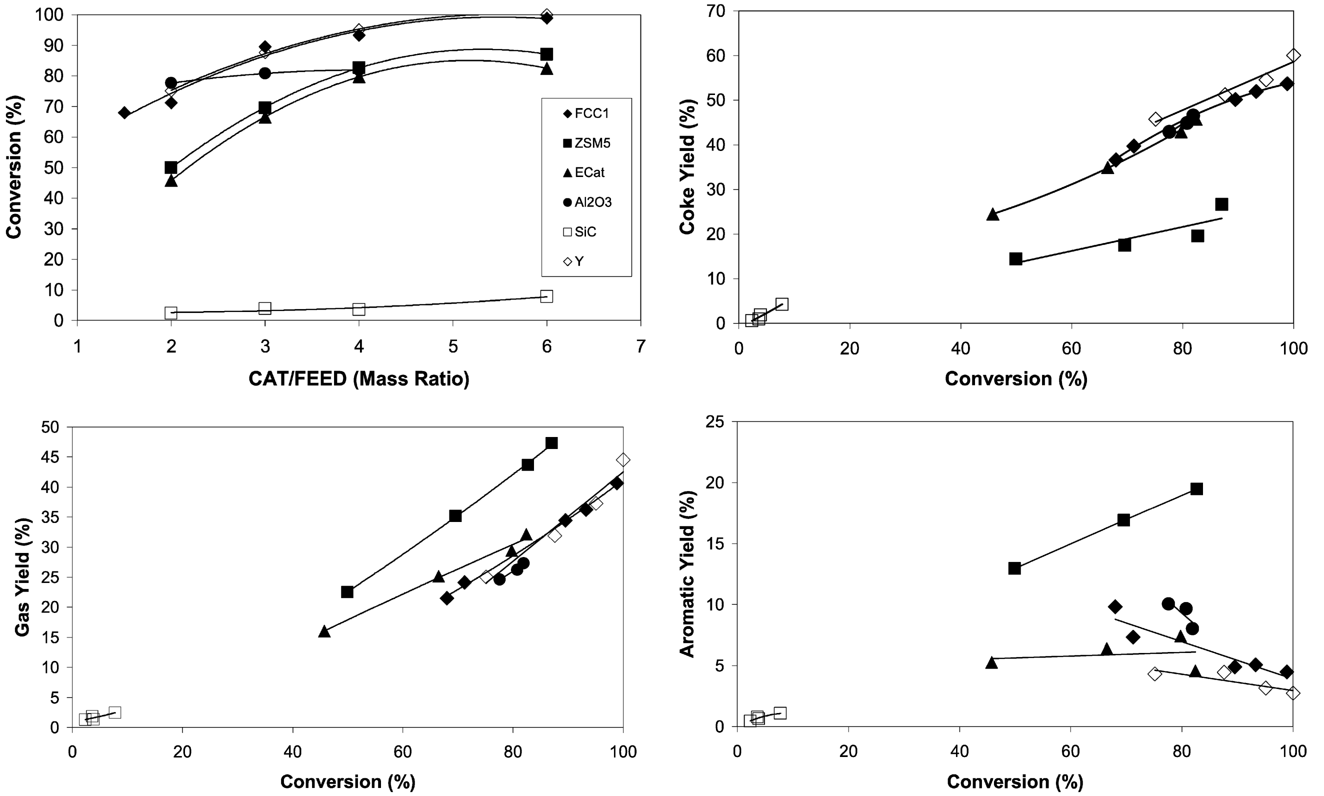


Fig. 1. Effect of catalyst composition on catalytic cracking of 50 wt% glycerol–water solution in MAT reactor at 500 °C and TOS 30 s. ((◆) FCC1, (■) ZSM5, (▲) ECat, (●) Al_2O_3, (□) silicon carbide, (◇) Y-zeolite. Glycerol feed into reactor as a 50 wt% glycerol–water mixture. Yields are based on carbon molar selectivity. Conversion includes coke + gases + aromatics.)

explained by the formation of coke from aromatic compounds. The yield of gases decreased in the following order: CO > propene > CO_2 > ethene > butene > methane > ethane > propane > *n*-butane (Fig. 2).

Because alkanes and olefins are produced in this process, it indicates that under typical FCC conditions, metal catalytic site are not necessary for the hydrogen-transfer processes that lead to alkanes and olefins from the oxygenated dehydrated species. H_2 was also produced, indicating that not all the hydrogen present in the reactants is used for producing alkane or olefin products. The C_3 and C_4 olefin-to-paraffin ratio for FCC1 is >10, as shown in Fig. 3, much higher values than observed when feeding vacuum gasoil. The results obtained when cracking glycerol with fresh FCC catalysts clearly show that it is possible through this process to obtain yields of olefins and aromatics >40 wt%. However, the large amount of coke formed already indicates the convenience of cracking glycerol together with FCC feeds in a commercial unit. Nevertheless, the behavior of glycerol should be studied with an equilibrium catalyst to obtain more realistic values of the conversion and products formed. Therefore, we also studied the cracking of glycerol with an equilibrium catalyst (ECat) that besides having a reduced surface area ($\sim$150 m^2/g) also contains V and Ni. As expected, this catalyst has a lower activity than the fresh FCC1 catalyst (see Fig. 1). The FCC1 and ECat catalysts have very similar product selectivity, demonstrating the minor role played by the metal impurities on the catalyst during the cracking of biomass-derived products. To test the thermal stability of glycerol, we used an "inert" SiC material; the low activity observed with this material demonstrates that glycerol has a high thermal stability.

FCC catalysts generally contain an Al_2O_3 matrix and a Y zeolite as active components. Thus, we tested pure γ-Al_2O_3 and USY zeolite as catalysts separately (Fig. 1). The γ-Al_2O_3 catalyst had a high activity for glycerol conversion, and gave a similar gas and coke yield as the FCC1 and ECat catalysts. The gas yields for γ-Al_2O_3 also were similar to those of FCC1 and Ecat, with the exception that γ-Al_2O_3 gave higher H_2 and ethane and lower propylene, *n*-butane, butane, and aromatic yields. γ-Al_2O_3 exhibited lower thermal/hydrothermal stability during catalyst regeneration than the other catalysts.

USY zeolite presented similar catalytic activity to FCC1. The high activity of the USY zeolite, γ-Al_2O_3, and FCC1 catalysts shows that dehydration reactions can occur readily on both Brönsted and Lewis acid sites. The coke yield was slightly higher for USY zeolite than for FCC1 catalyst, as is generally observed when zeolite is dispersed in a matrix. The USY zeolite had lower aromatic and CO_2 yields and higher C_1–C_4 alkane and H_2 yields than the FCC1 catalyst. Olefin yield was similar in the USY-zeolite and FCC1 catalysts; thus, the olefin-to-paraffin ratio was lower in the USY zeolite compared with FCC1, in agreement with the differences observed for the production of CO, CO_2, H_2, and coke.

Because ZSM5 is a well-known additive for FCC catalysts, we also tested its activity for the catalytic cracking of glycerol.

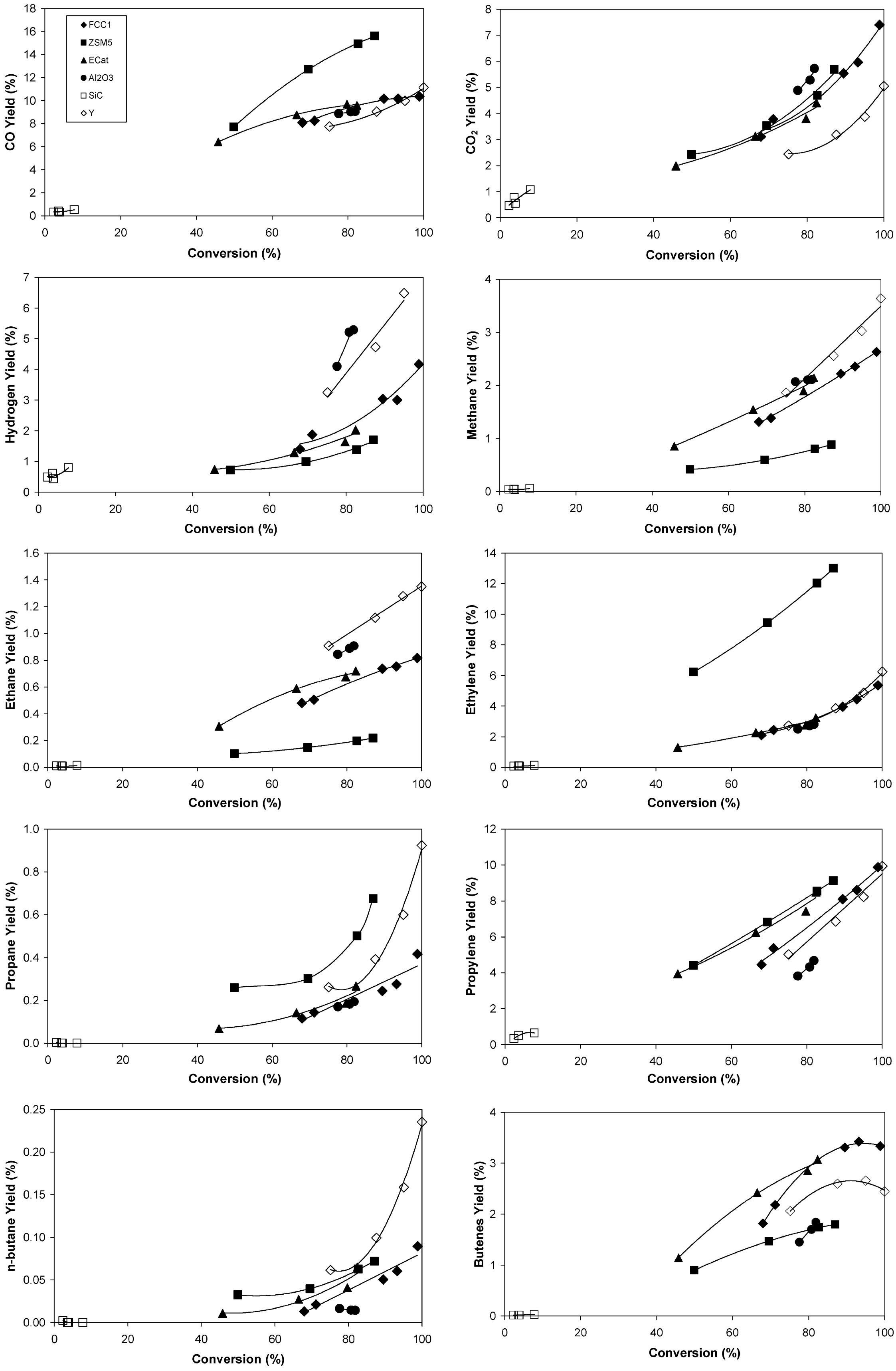


Fig. 2. Effect of catalyst composition on gas-phase yields for catalytic cracking of 50 wt% glycerol–water solution in MAT reactor at 500 °C and TOS 30 s. ((◆) FCC1, (■) ZSM5, (▲) ECat, (●) Al_2O_3, (□) silicon carbide, (◇) Y-zeolite. Glycerol feed into reactor as a 50 wt% glycerol–water mixture. Yields are based on carbon molar selectivity. Conversion includes coke + gases + aromatics.)

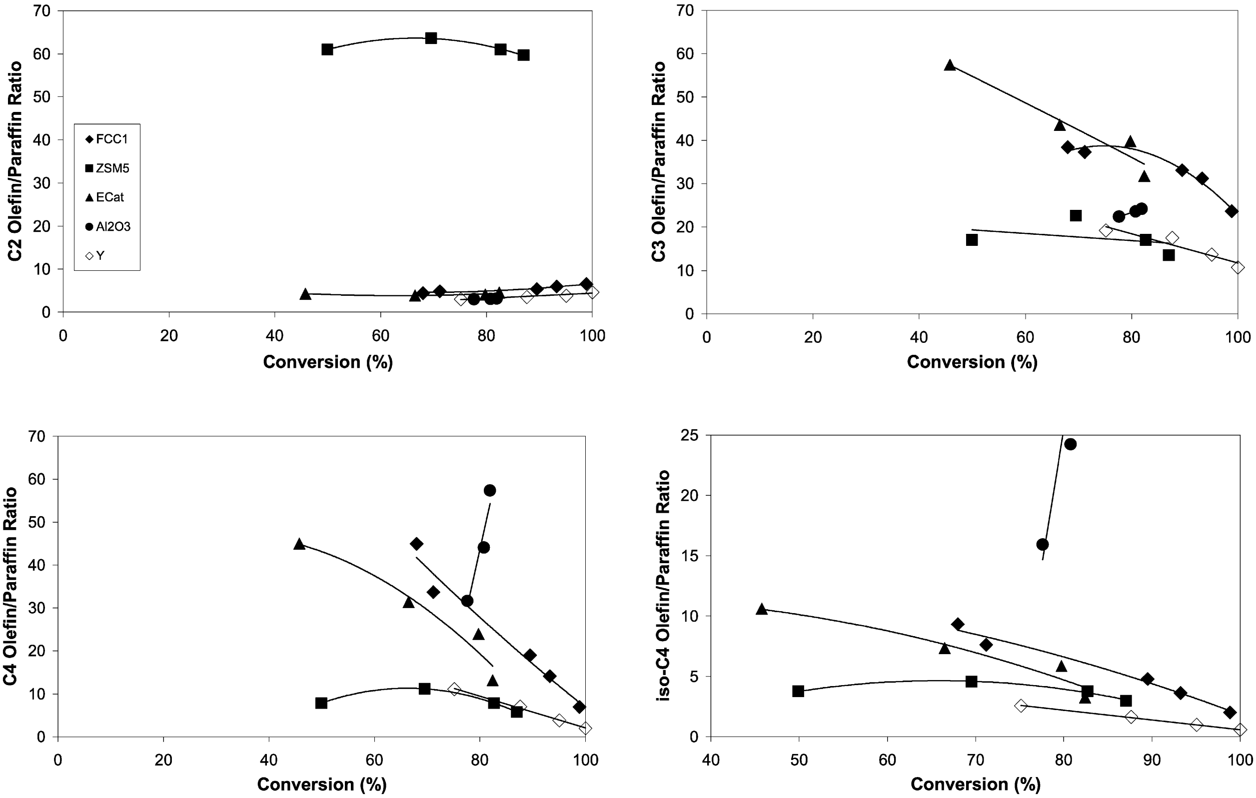


Fig. 3. Effect of catalyst composition on olefin-to-paraffin ratio and isobutene-to-isobutane ratio for catalytic cracking of 50 wt% glycerol–water solution in MAT reactor at 500 °C and TOS 30 s. ((◆) FCC1, (■) ZSM5, (▲) ECat, (●) Al_2O_3, (□) silicon carbide, (◇) Y-zeolite. Glycerol feed into reactor as a 50 wt% glycerol–water mixture. Yields are based on carbon molar selectivity. Conversion includes coke + gases + aromatics.)

The major difference between ZSM5 and the other catalysts tested is that ZSM5 gives less coke, more gases, and more aromatics. This is due to this zeolite's smaller pore size, making it difficult for larger aromatic coke precursors to form into the small ZSM5 pores. The activity of the catalysts (in terms of total conversion to gases, coke, and aromatics) decreased in the following order: Y ~ FCC1 > Al_2O_3 > ZSM5 > ECat ≫ SiC. The gas yields decreased in the order ZSM5 ≫ ECat > FCC1 > Al_2O_3 ~ Y.

The aromatic yield increased linearly with conversion for ZSM5 catalyst, but decreased with increasing conversion for FCC1, Y, ECat and Al_2O_3 catalysts. It has been shown that for hydrocarbon cracking, the small ZSM5 zeolite pore channels make it difficult to form polyaromatic products that act as coke precursors. Thus, higher yields of coke are seen on the Y, Ecat, and FCC1 catalysts due to the larger cage diameter of the Y zeolite. The carbon yields to gases for ZSM5 decreased in the order CO > ethene > propene > CO_2 > butene > methane > ethane > propane > *n*-butane.

The ZSM5 had a higher ethene yield and lower methane yield than the other catalysts, possibly indicating that ethene on ZSM5 may be formed through decarbonylation of an oxygenated intermediate rather than by cracking of longer-chain hydrocarbons. It also has been shown that ethene can be formed from alkylaromatics.

The olefin-to-paraffin ratio for these catalysts is >10 in most cases (Fig. 3). The olefin-to-paraffin ratio for C_2 compounds is extremely high (e.g., >60) for the ZSM5 catalyst. For the ECat and FCC1 catalysts, the C_3 and C_4 olefin-to-paraffin ratios decrease with increasing conversion. The C_3 and C_4 olefin-to-paraffin ratio remains constant for the ZSM5 catalyst. Two explanations for the decreasing olefin-to-paraffin ratio with increasing conversion can be given. One is that the olefins are hydrogenated as the conversion increases, consistent with the increased yield of butane and propane; the other is that the olefins react to form aromatics, which also can lead to coke, as the conversion increases.

3.2. *Effect of temperature on catalytic cracking of glycerol*

Figs. 4–6 show the effect of temperature on the catalytic cracking of glycerol with ZSM5. As can be expected, the activity for cracking of glycerol increased with temperature, as shown in Fig. 4. As temperature increased, coke yield decreased significantly (Fig. 4) and CO and H_2 yields increased (Fig. 5). Similar temperature effects were observed for catalytic cracking of glycerol with FCC1. At 500 °C, the coke yield increased linearly with conversion, whereas at 600 and 700 °C, coke yield did not increase with conversion. The aromatics also increased linearly with conversion at 500 °C, but decreased linearly with conversion at 600 and 700 °C. These results can be explained based on thermodynamics that predict a lower extension of the exothermic oligomerization and hydrogen transfer (both reactions are required to form aromatics and coke) with increasing temperature [29].

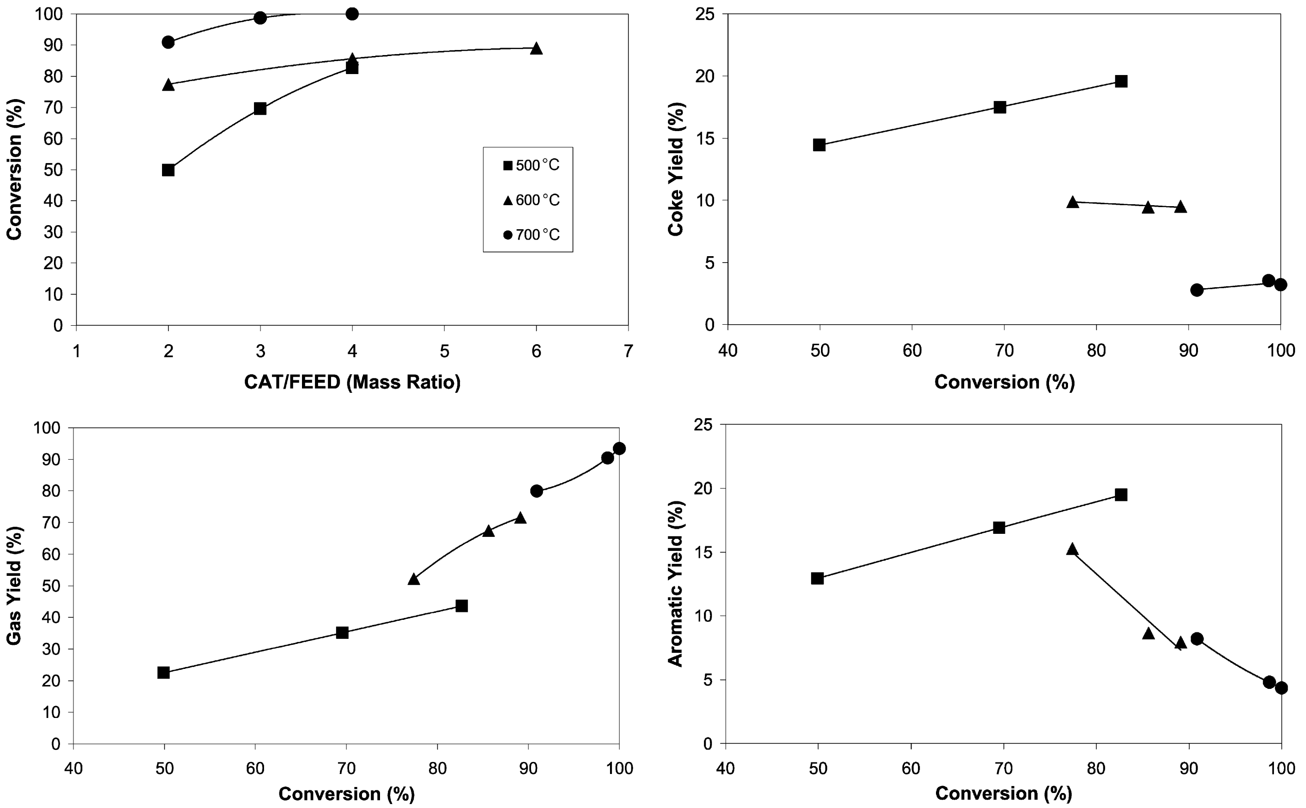


Fig. 4. Effect of temperature on catalytic cracking of 50 wt% glycerol–water solution with ZSM5 catalyst in MAT reactor, TOS 30 s. ((■) 500 °C, (▲) 600 °C, (●) 700 °C. Glycerol feed into reactor as a 50 wt% glycerol–water mixture. Yields are based on carbon molar selectivity. Conversion includes coke + gases + aromatics.)

3.3. Effect of water and glycerol partial pressure on catalytic cracking of glycerol

Biomass-derived feeds usually contain large amounts of water; Figs. 7 and 8 show the effect of water and N_2 dilution on the catalytic cracking of glycerol. For these experiments, we used 50 wt% glycerol in water (16 mol% glycerol), 100 wt% glycerol diluted with N_2 during the cracking experiment (16 mol% glycerol), and pure glycerol without N_2 dilution as feeds. Dilution of the feed with either H_2O or N_2 decreased conversion as corresponds to a non-zero-order kinetics for decarboxylation, dehydration, and cracking reactions (Fig. 7). The gas and coke yields for all feeds were similar, whereas the pure glycerol had a slightly higher yield of aromatics than the diluted feed. This can be due to a decrease in the bimolecular condensation reaction rates for diluted feeds. The main differences between the aqueous–glycerol and pure glycerol feeds are that the former gives higher CO_2 and H_2 yields and a lower CO yield compared with the latter. The CO_2 yield is lowest for the feed diluted with N_2. This indicates that the CO_2 is produced by the water–gas shift (WGS) reaction, and decreasing the water partial pressure decreases the CO_2 yield. The C_1–C_3 alkane yields are slightly higher for the pure glycerol solution, whereas the C_2–C_4 olefins yields are similar for all of the feedstocks. The increase in propane and butane with pure glycerol is likely due to hydrogen-transfer reactions, which are favored by a higher partial pressure of hydrocarbons. The increase in methane and ethane with pure glycerol may be due to a decreased gas residence time with the diluted glycerol feeds, which leads to decreased thermal cracking.

3.4. Sorbitol as a feed

To test the catalytic cracking of other biomass-derived oxygenates, we also reacted sorbitol with ZSM5 and SiC. Importantly, sorbitol has a lower H/C_{eff} ratio than glycerol. Figs. 9–11 show the results obtained when reacting aqueous solutions of 50 wt% sorbitol and 50 wt% glycerol feeds in the MAT reactor. At low catalyst-to-feed ratios, sorbitol has higher activity than glycerol (Fig. 9); however, at higher catalyst-to-feed ratios, glycerol has a higher activity than sorbitol. The thermal stability of glycerol is greater than that of sorbitol, as shown in Fig. 9. Surprisingly, however, even though sorbitol and glycerol have different H/C_{eff} ratios, they give similar coke, gas and aromatic yields.

The gas-phase yields for glycerol and sorbitol are shown in Fig. 10. The main differences between the two feeds are that sorbitol gives a higher CO yield than glycerol feeds with the ZSM5 catalyst. The CO and CO_2 yield is also higher for the thermal sorbitol reaction (1–2% CO yield at conversions of 4–18%) than for glycerol (0.3–0.5% CO yield at conversions of 2–8%). More hydrogen is required to convert sorbitol into a paraffin or olefin than to convert glycerol; therefore, hydrogen-producing reactions (such as CO production) should be greater for sorbitol than for glycerol at similar olefin and paraffin yields in the hydrocarbon fraction. Sorbitol also has a lower ethylene

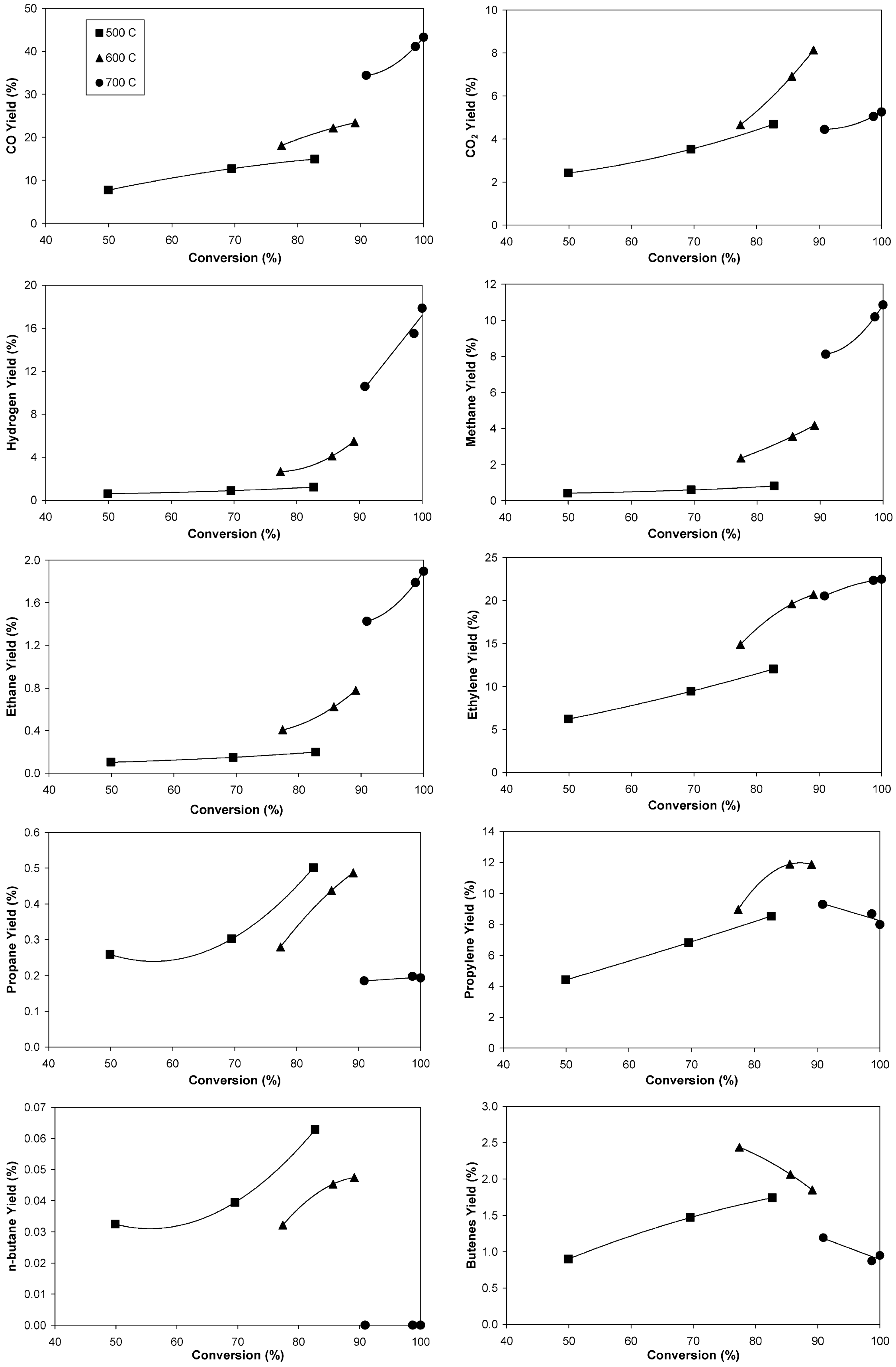


Fig. 5. Effect of temperature on gas-phase yields for catalytic cracking of 50 wt% glycerol–water solution with ZSM5 catalyst in MAT reactor, TOS 30 s. ((■) 500 °C, (▲) 600 °C, (●) 700 °C. Glycerol feed into reactor as a 50 wt% glycerol–water mixture. Yields are based on carbon molar selectivity. Conversion includes coke + gases + aromatics.)

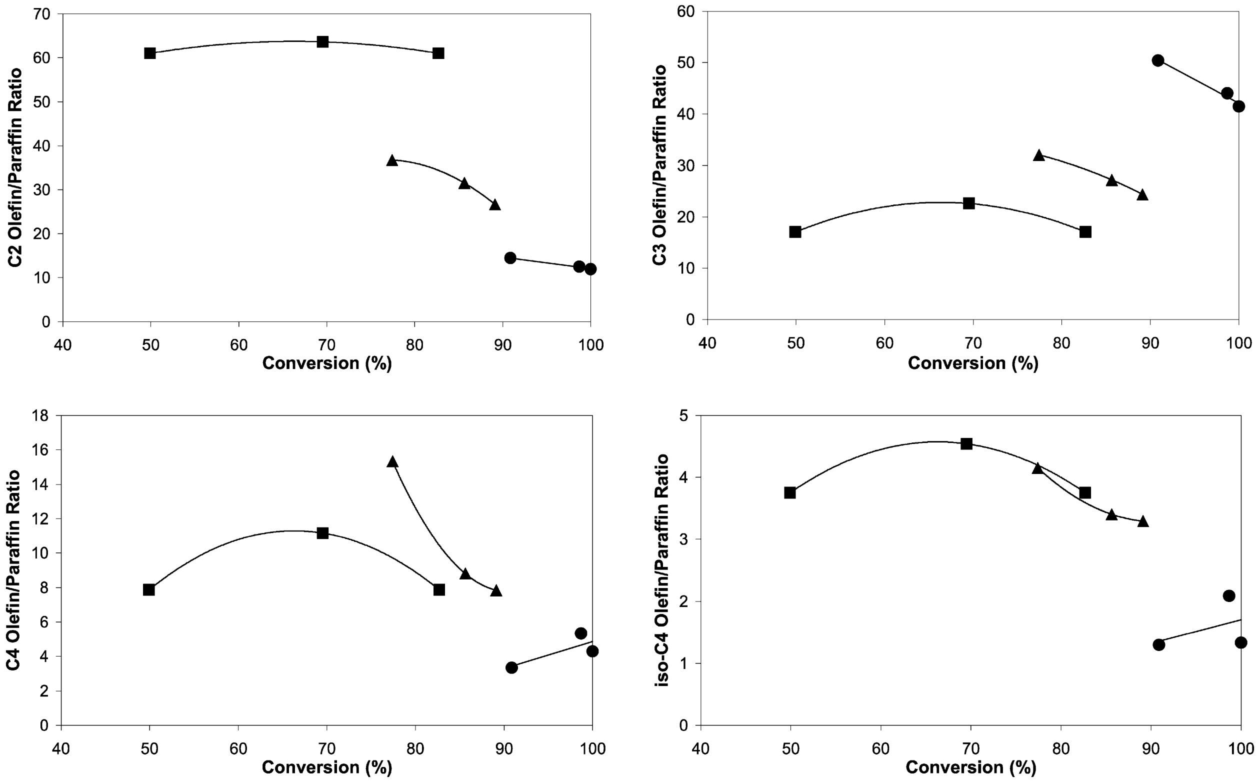


Fig. 6. Effect of temperature on olefin-to-paraffin ratio for catalytic cracking of 50 wt% glycerol–water solution with ZSM5 catalyst in MAT reactor, TOS 30 s. ((■) 500 °C, (▲) 600 °C, (●) 700 °C. Glycerol feed into reactor as a 50 wt% glycerol–water mixture. Yields are based on carbon molar selectivity. Conversion includes coke + gases + aromatics.)

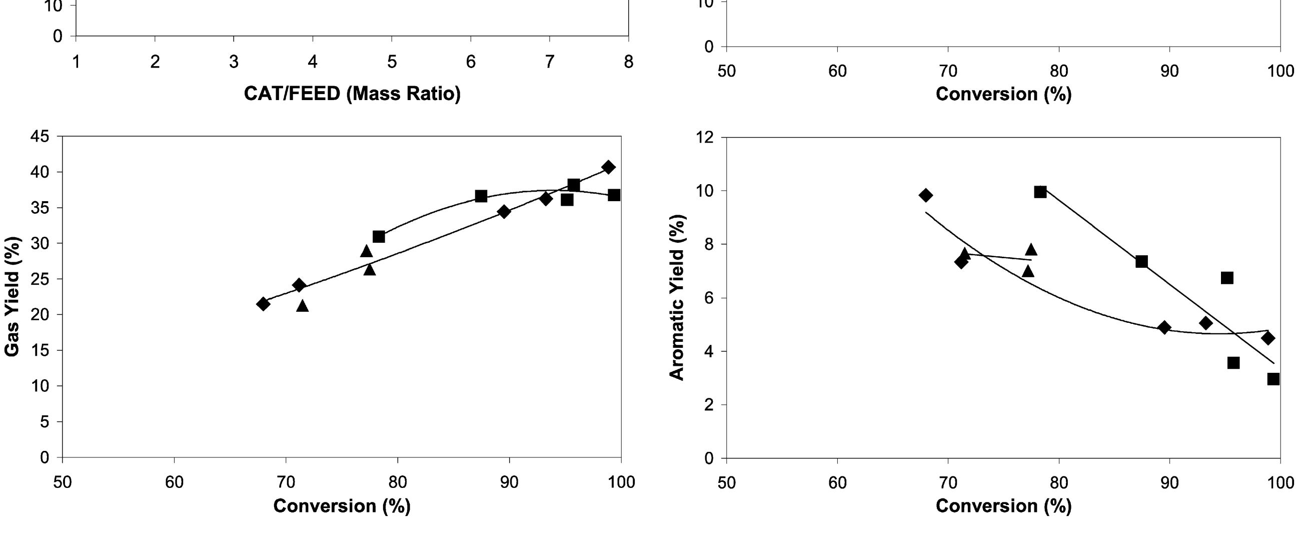


Fig. 7. Effect of water and dilution on catalytic cracking of 16 mol% glycerol–water, pure glycerol, 16 mol% glycerol–N_2 with FCC1 catalyst in MAT reactor at 500 °C and TOS 30 s. (16 mol% glycerol–water corresponds to 50 wt% glycerol–water. (◆) 16 mol% glycerol–water, (■) pure glycerol, and (▲) 16 mol% glycerol–N_2.)

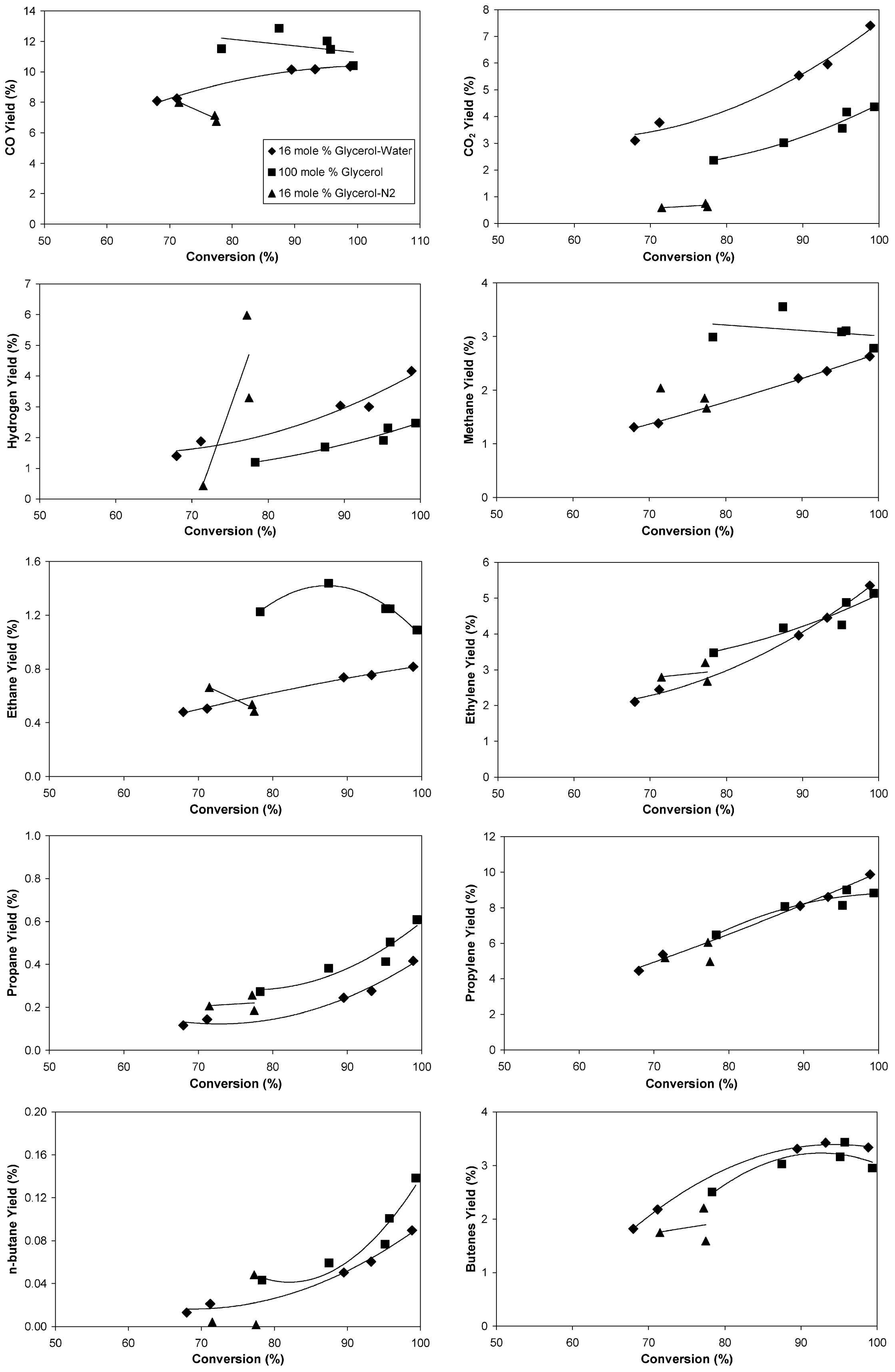


Fig. 8. Effect of water and dilution on gas-phase yields for catalytic cracking of 16 mol% glycerol–water, pure glycerol, 16 mol% glycerol–N_2 with FCC1 catalyst in MAT reactor at 500 °C and TOS 30 s. (16 mol% glycerol–water corresponds to 50 wt% glycerol–water. (◆) 16 mol% glycerol–water, (■) pure glycerol, and (▲) 16 mol% glycerol–N_2.)

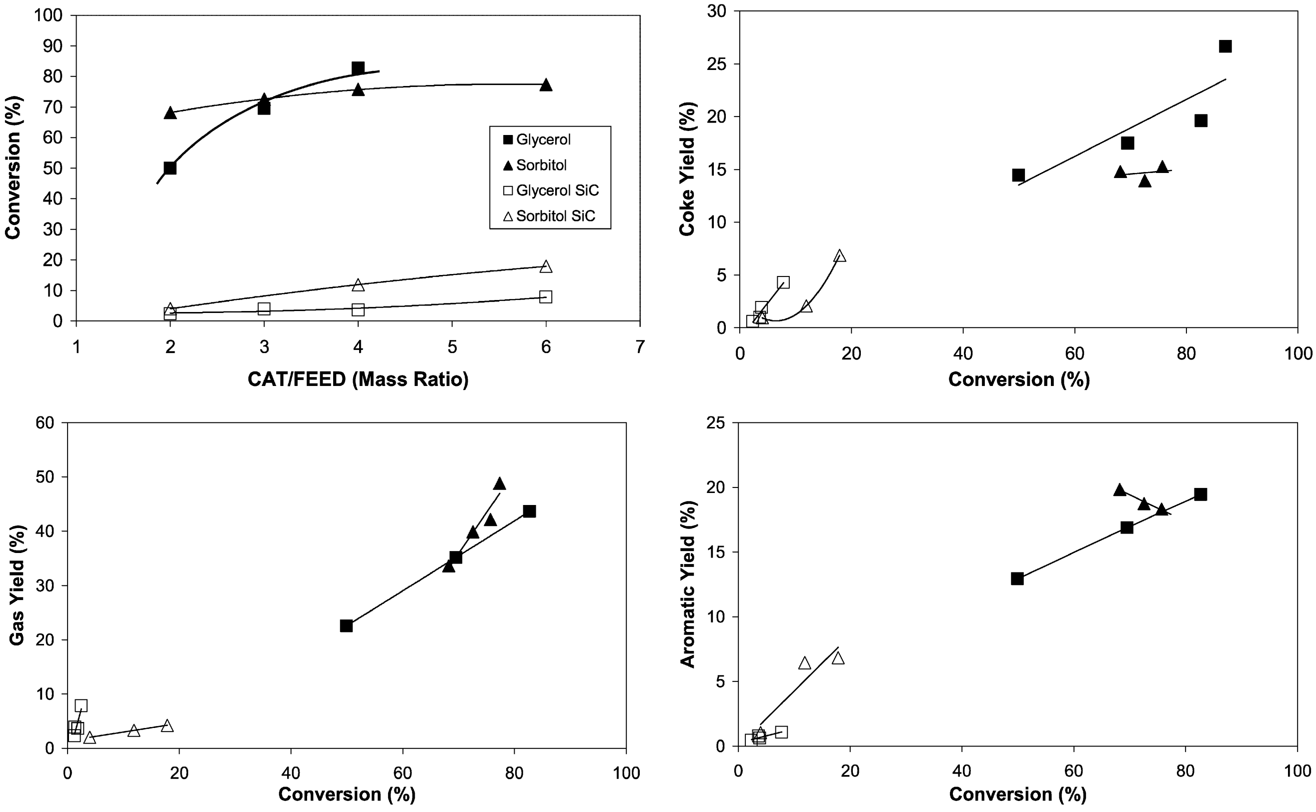


Fig. 9. Catalytic cracking of 50 wt% glycerol and 50 wt% sorbitol aqueous solutions using ZSM5 and silicon carbide catalysts in MAT reactor at 500 °C and TOS 30 s. ((■) Glycerol with ZSM5, (▲) sorbitol with ZSM5, (□) glycerol with SiC, (△) sorbitol with SiC. Conversion includes coke + gases + aromatics.)

yield than glycerol; the yields of the other hydrocarbons are fairly similar.

3.5. A global reaction network

Oxygen must be removed and hydrogen added to biomass-derived molecules, such as carbohydrates and glycerol, to convert them into liquid fuels. In this respect, biomass-derived oxygenates can be viewed as hydrogen-deficient molecules. As we demonstrated earlier, the FCC process is very effective at removing oxygen from the biomass-derived oxygenates; however, the process does not always remove the oxygen by the optimal pathway. The process is also able to produce hydrogen. This H_2 can be produced through steam-reforming reactions or by direct dehydrogenation of the carbohydrates and hydrocarbons, the WGS reaction, and decarbonylation of partially dehydrated species or the feedstock (Fig. 12). The occurrence of these reactions will be consistent with the formation of CO, CO_2, graphitic coke, and H_2 that have been observed experimentally. On the other hand, the H_2 produced in these reactions can be consumed in reactions that increase the H/C_{eff} ratio of the products, as shown in Fig. 13, leading to olefins and alkanes. Hydrogen will be exchanged through hydrogen-transfer reactions between two hydrocarbon/carbohydrate chains or through consecutive dehydrogenation/hydrogenation reactions. The hydrocarbons formed through these first reaction steps will then undergo the traditional oligomerization cracking chemistry of hydrocarbons.

Aromatics and larger products can form by other reactions, including condensation and the Diels–Alder reaction. This reaction scheme is supported by the nature of the oxygenate compounds detected; 2-hydroxyacetone and acrolein are formed by glycerol dehydration, whereas propen-2-ol and acetone are formed by acrolein after addition of hydrogen. The formation of methyl vinylketone (4 carbons), as well as a large number of C_9–C_{10} aromatic isomers demonstrates that additional/cracking reactions also contributed to the formation of products (Table 3). Larger oxygenated molecules, like sorbitol, also can be broken apart by retro-aldol condensation reactions. At lower temperatures, sorbitol is known to break into smaller fragments [30]. Retro-aldol condensation of glucose produces dihydroxyacetone and glyceraldehydes [31]. It is likely that these reactions occur with sorbitol-based feeds, thereby converting sorbitol into smaller oxygenated fragments, which are then converted through similar pathways as glycerol. From the above findings, we can conclude that selective production of olefins and aromatics requires a proper balancing of dehydration, hydrogen-producing, and hydrogen-transfer reactions by selecting the adequate catalyst and reaction conditions.

During the catalytic cracking of oxygenated compounds, dehydration reactions occur on acid sites, producing water and a dehydrated compound. The H/C_{eff} ratio does not change during the dehydration process. Dehydration of glycerol has been shown to produce acetol and then acrolein, as shown in Fig. 12 [32–34]. We found the formation of relatively large amounts of acrolein during MAT experiments with glycerol. Further

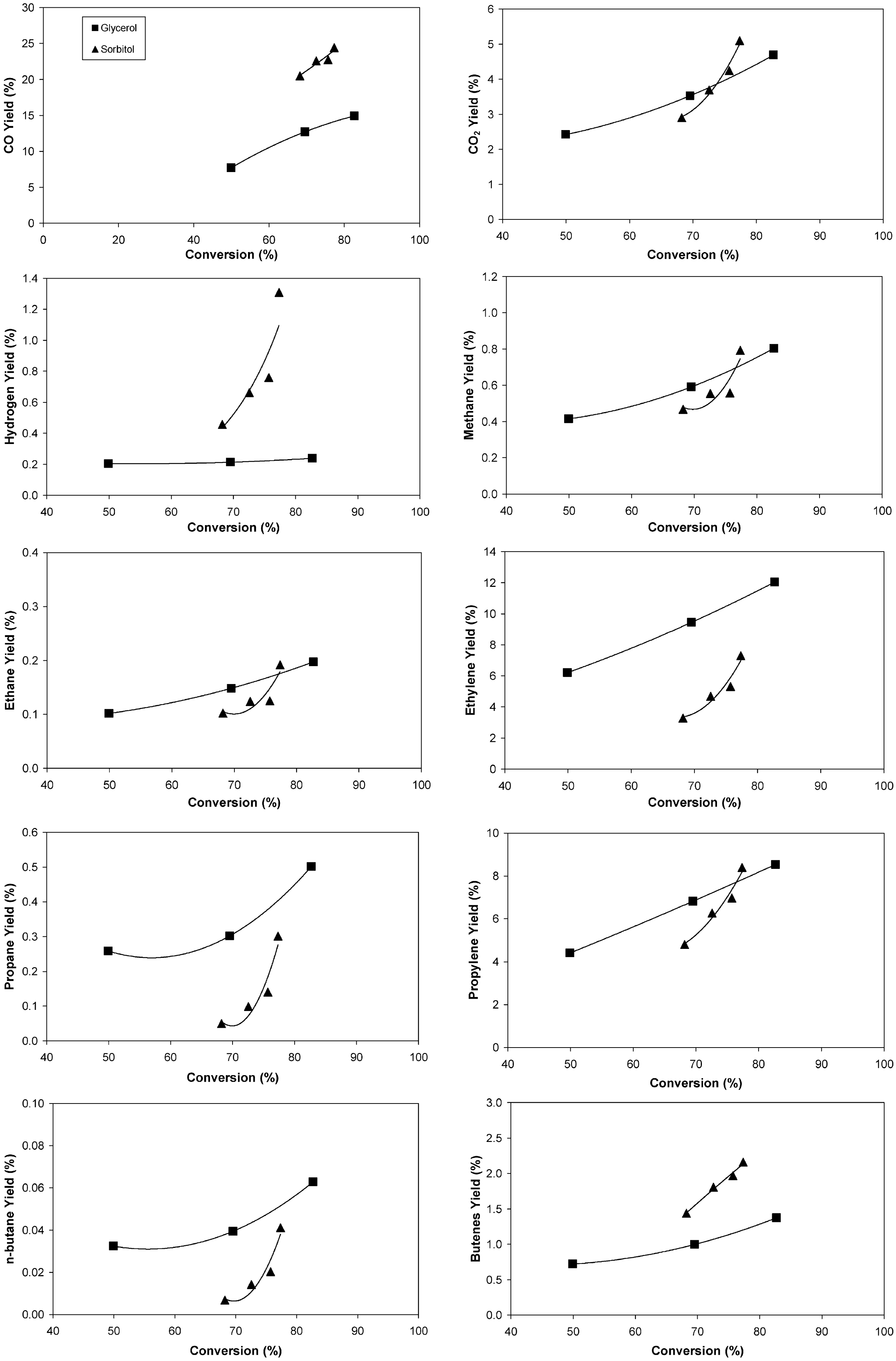


Fig. 10. Gas-phase yields of 50 wt% glycerol and 50 wt% sorbitol aqueous solutions for catalytic cracking using ZSM5 catalyst in MAT reactor at 500 °C and TOS 30 s. ((■) Glycerol, (▲) sorbitol. Conversion includes coke + gases + aromatics.)

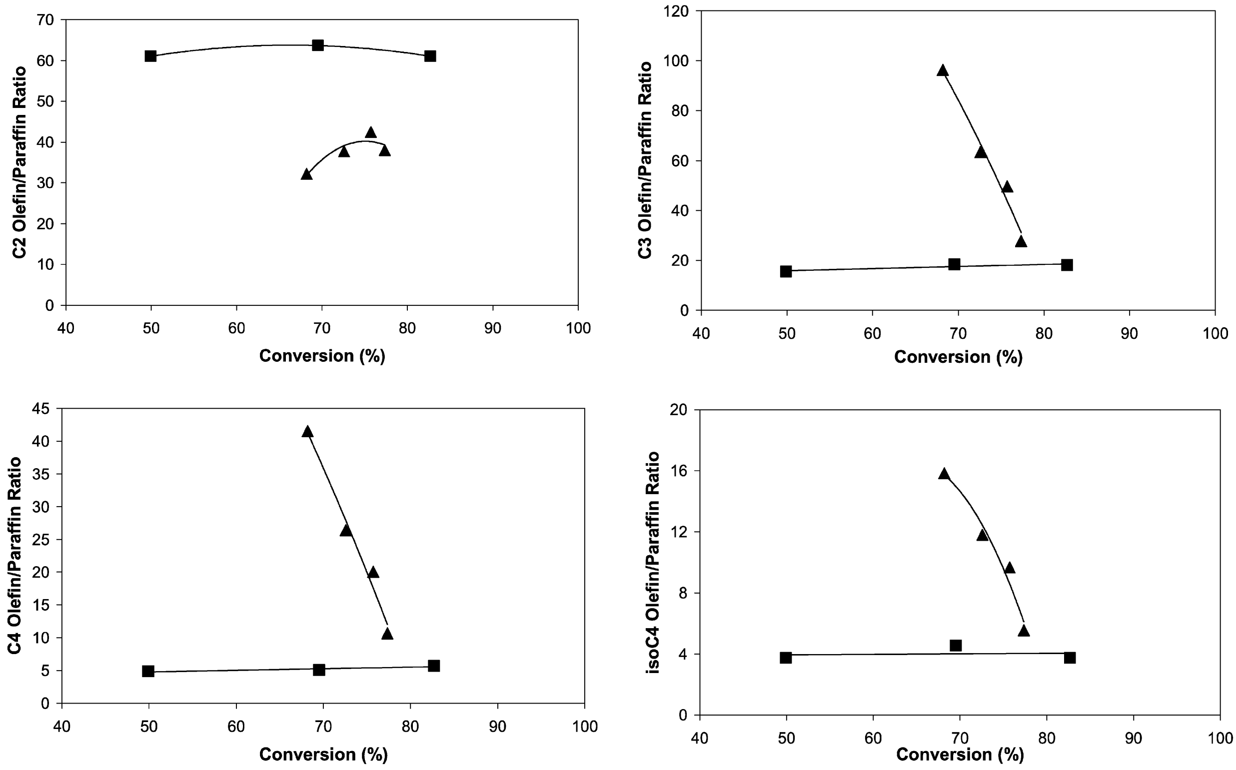
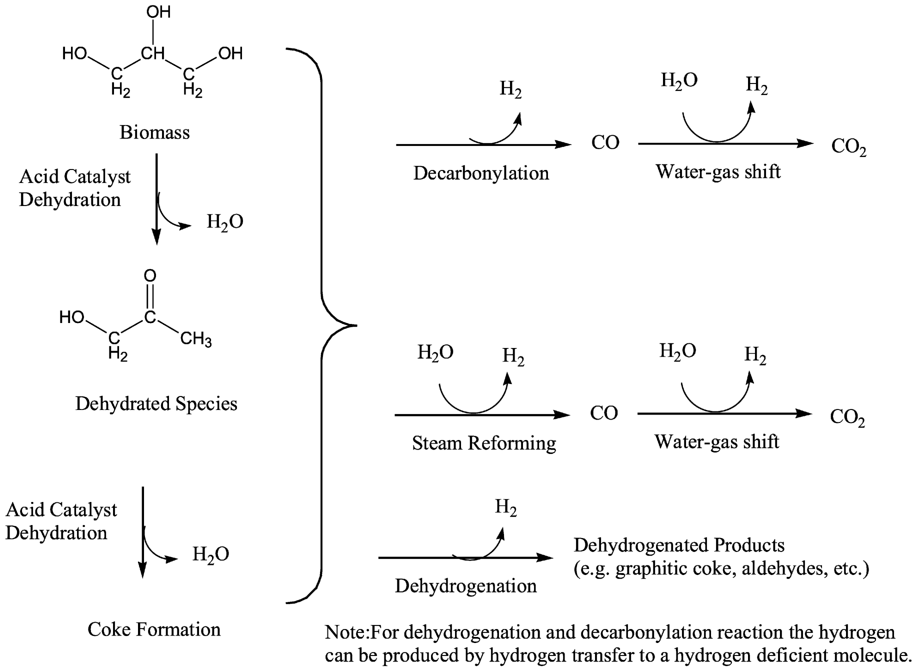


Fig. 11. Olefin-to-paraffin ratio for 50 wt% glycerol and 50 wt% sorbitol aqueous solutions for catalytic cracking using ZSM5 catalyst in MAT reactor at 500 °C and TOS 30 s. ((■) Glycerol, (▲) sorbitol. Conversion includes coke + gases + aromatics.)



Note:For dehydrogenation and decarbonylation reaction the hydrogen can be produced by hydrogen transfer to a hydrogen deficient molecule.

Fig. 12. Hydrogen producing reactions for catalytic cracking of biomass.

dehydration of acrolein would lead to coke species. Cyclic ether species with C–O–C linkages also may form during dehydration reactions [32,34]. Dehydrated glycerol species, such as acetol, also can oligomerize to form polyglycerol species, which may lead to coking reactions, and water may decrease the amount of oligomers [35]. Conversion of acetaldehyde over zeolite catalysts has been shown to produce large amounts of coke by polymerization of oligomers from acetaldehyde [25,26].

Steam reforming of dehydrated species produces CO and H_2, as shown in Fig. 12. The WGS reaction can be used to produce more H_2, and, as we have shown, increasing the partial

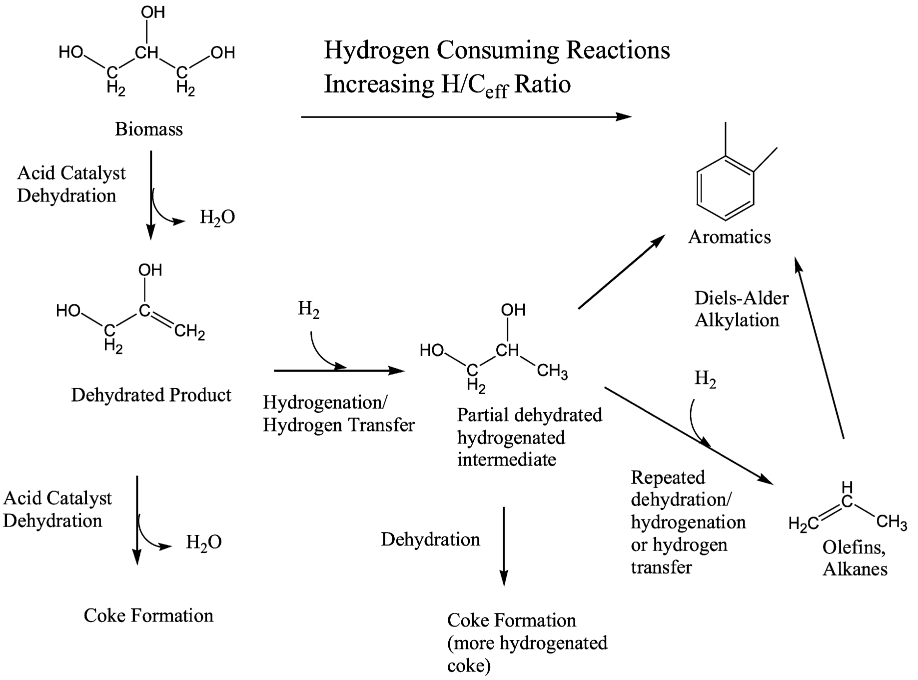


Fig. 13. Hydrogen consuming reactions for catalytic cracking of biomass.

Table 3
Oxygenates and Cl_{5+} hydrocarbons distribution obtained with ZSM5 catalyst by cracking of 50/50 wt% glycerol/water solution

Compound	Carbon balance	% in fraction
Oxygenates	wt%	% in oxygenates
Acrolein	0–10	40
Ethanal	0–10	40
Methylvinylketone	0–1	4
Propen-2-ol/acetone	0–1	4
2-Hydroxyacetone	0–1	4
Acetic acid	0–0.5	2
Propenoic acid	0–0.5	2
Furans	0–1	4
Hydrocarbons	wt%	% in C_{5+} hydrocarbons
Benzene	0–0.2	1
Toluene	0–0.5	4
Xylenes	0–3	25
C_9–C_{10} aromatics	0–8	70

pressure of water increases the rate of the WGS reaction. The dehydrated species can react with the hydrogen via hydrogen-transfer reactions to produce olefins and aromatics. Decarbonylation reactions also may occur and will produce ethylene and CO from acrolein. Larger aromatic and olefin compounds are probably formed by Diels–Alder and aldol condensation reactions of olefins and aldehydes.

Our findings and the reaction schemes that we propose also are in agreement with the results obtained by Chen et al., who studied the conversion of carbohydrates (including 50 wt% aqueous solutions of xylose, glucose, starch, and sucrose) over ZSM5 catalysts in a flow reactor at 500 °C [19,36,37]. They observed that 40–66% of the carbon left the reactor as coke when xylose, glucose, starch, and sucrose were fed over a ZSM5 catalyst at 500 °C at a residence time of 10 min, and that frequent regenerations were required. Other products formed included hydrocarbons (light alkanes, olefins, and aromatics), CO, and CO_2. Mixing the aqueous–carbohydrate streams with methanol led to lower levels of coke and higher levels of hydrocarbons. Testing ZSM5 in the MAT reactor resulted in lower levels of coke (15–20% yields; see Fig. 1) than Chen et al. found with ZSM5 and carbohydrate-based feeds. This difference may be due to shorter time on stream in our case (30 s) compared with 10 min in the study of Chen et al. Another reason for the difference may be that Chen et al. worked with glucose, which has a low thermal stability, whereas our work was done with sorbitol and glycerol.

3.6. Hydrogen-producing reactions

A number of H_2-producing reactions can occur in the FCC of biomass-derived oxygenates, including steam reforming, WGS, dehydrogenation, and decarbonylation. Some reactions produce more H_2 per carbon than others (Fig. 13). The pathway producing the highest amount of H_2 per mol of carbon feed is reacting the feed with water to produce CO_2 and H_2, as shown in Eq. (3). If glycerol is the feedstock, then 7/3 mol of H_2 are produced per mol of carbon. If the glycerol molecule is decomposed to syngas via a decarbonylation/decomposition pathway [Eq. (4)], then 4/3 mol of H_2 are produced per mol of carbon feedstock. Glycerol can be thermally decomposed into CO and H_2 with Pt catalysts at low temperatures (300–450 °C) [38]. If the carbon in the glycerol is converted to coke, followed by a dehydrogenation pathway to produce H_2 from the coke [Eq. (5)], then 1 mol of H_2 is produced per mol of carbon feedstock. This reaction produces the least amount of H_2 per carbon atom. Therefore,

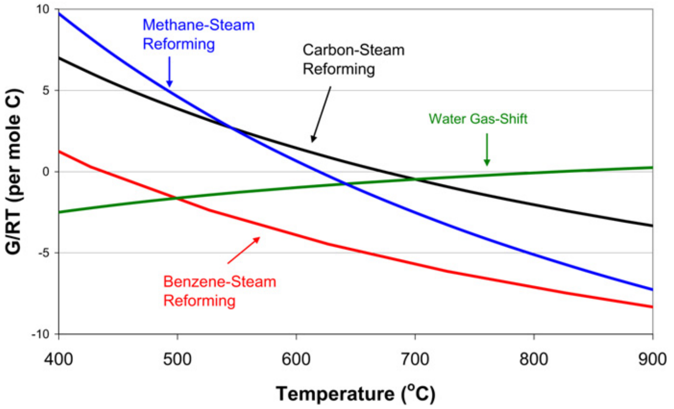


Fig. 14. Thermodynamics for reactions involving steam reforming. Blue lines—methane steam reforming, red lines—benzene steam reforming, green lines—water–gas shift, and black lines—carbon-graphite steam reforming. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the amount of H_2 produced increases when the carbon of glycerol is converted into $C < CO < CO_2$:

$$C_3O_3H_8 + 3H_2O \rightarrow 3CO_2 + 7H_2, \tag{3}$$

$$C_3O_3H_8 \rightarrow 3CO + 4H_2, \tag{4}$$

$$C_3O_3H_8 \rightarrow 3C + 3H_2O + H_2. \tag{5}$$

The coke formed in reaction (5) can be converted into H_2 by steam reforming. Because large amounts of coke are formed during the catalytic cracking process, one option may be to steam reform the coke to produce syngas. The steam reforming of coke, benzene, and methane is shown as Eqs. (6), (7), and (8), respectively. Fig. 14 shows the standard Gibbs free energy (G/RT) for these reactions, in which all values are normalized per mol of carbon. H_2O and reforming of carbon (represented as graphite in Fig. 14) is thermodynamically favorable at temperatures above 700 °C. Reforming of benzene is thermodynamically favorable at temperatures above 450 °C. The thermodynamics of benzene are probably similar to those of hydrogenated coke species on the catalyst surface. The results of the present study show that increasing the reaction temperature decreases the coke yield and increases CO and H_2 yield. This may be due to increased steam reforming of partially dehydrated species at the higher temperatures. Steam reforming and the WGS are known to occur over metal catalysts, such as Ni and Pt, and one should take into account that in many cases, low amounts of Ni are deposited on the catalyst surface during catalytic cracking of vacuum gasoil and residues. One way to improve these reactions may be to add metals to the catalyst.

The WGS reaction is also very desirable in catalytic cracking of biomass because it can increase the effectiveness of H_2 production. The WGS reaction, shown as Eq. (9), is an exothermic reaction that is favorable at temperatures below 700 °C (Fig. 14):

$$C + H_2O \rightarrow CO + H_2, \tag{6}$$

$$C_6H_6 + 6H_2O \rightarrow 6CO + 9H_2, \tag{7}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2, \tag{8}$$

$$CO + H_2O \rightarrow CO_2 + H_2. \tag{9}$$

Aldehydes, ketones, and acids can undergo a decarbonylation reaction to produce CO and a molecule with an increased H/C_{eff} ratio. Thus, the decarbonylation reaction can also be considered to produce and consume H_2 by internal hydrogen transfer. For example, the decarbonylation of acrolein produces ethylene and CO:

$$C_3H_3OH \rightarrow CO + C_2H_4. \tag{10}$$

Decarbonylation and carbonylation reactions occur with zeolite-based catalysts at low temperatures [39]. Other researchers have shown that ketones can undergo decarbonylation reactions on zeolite catalysts; for example, acetone undergoes decarbonylation/condensation reactions to form CO and iso-butene [26,40]. This last mechanism offers another way of producing hydrocarbon products with longer carbon chains than the feed, similar to the dimerization cracking mechanism that has been identified in the cracking of paraffins to explain longer-chain products [18].

3.7. Hydrogen-consuming reactions

Hydrogenation, hydrogen transfer, and decarbonylation are the key reactions that can enrich the H/C_{eff} ratio of the products. Hydrogenation reactions usually occur on metal surfaces where H_2 is dissociated and then reacted. Metal or metal oxide impurities on the zeolite surface may dissociate H_2, which could then be used for hydrogenation reactions. However, experimental and recent theoretical results have shown that hydrogenation reactions also can occur with acid catalysts [41–44]. Alkenes, aromatics, aldehydes, and ketones have been hydrogenated with acid catalysts [42,44]. The key step in the mechanism is the reaction between a carbenium ion and molecular hydrogen. Hydrogenation of aromatics requires an aliphatic solvent for hydrogen transfer, because protonated benzene does not react with H_2 directly [42,44]. Gas-phase H_2 is observed under our reaction conditions; however, the H_2 partial pressure is typically low, indicating that most of the H_2 produced is consumed in the reaction.

Hydrogen-transfer reactions are also known to occur in FCC. The typical reaction involves a hydrogen donor (e.g., a naphthene) and a hydrogen acceptor (e.g., an olefin) [18]. Under our reaction conditions, we have few naphthenes to act as hydrogen donors; thus, we need another hydrogen source. Hydrogen transfer could occur from coke species transferring hydrogen to other dehydrated species, while the coke forms a graphitic dehydrogenated species. The ZSM5 catalyst contains low levels of coke (yield <20%), indicating that hydrogen transfer from coke does not need to be a hydrogen-consuming reaction. Decreasing the H/C_{eff} ratio of the feedstock will decrease the amount of hydrogen that can be produced from the coke, and carbohydrates will not produce any hydrogen if they produce coke.

Decarbonylation reactions are both hydrogen-consuming and hydrogen-producing. Ethylene can be produced directly from acrolein (doubly dehydrated glycerol), as shown in Eq. (10). Catalytic cracking of glycerol shows high levels of ethylene, indicating that this decarbonylation is probably a reaction pathway. However, decarbonylation of dehydrated glycerol species does not produce propylene, whereas propylene is observed in high yields when glycerol feedstocks are used. This indicates that decarbonylation cannot be the only pathway for hydrogen-consuming reactions.

3.8. Selectivity considerations

Olefins and aromatics are the most valuable products from catalytic cracking of biomass-derived molecules. During the production of olefins, the oxygen is removed as CO_2, CO, or H_2O, and hydrogen is produced and consumed in a series of reactions. Here we use propylene to represent the desired product molecule and glycerol to represent that of biomass-derived oxygenates. The highest theoretical yield of propylene from glycerol is a 77% carbon yield according to Eq. (11). In this reaction, the oxygen is removed as CO_2 and H_2O. The hydrogen-producing reactions are steam reforming and WGS of the glycerol according to Eq. (3), and the hydrogen produced from this reaction is used to convert another glycerol molecule into propylene and water. If oxygen is removed from the glycerol as CO and H_2O [Eq. (12)], then the maximum theoretical carbon yield of propylene is 66%. If oxygen is only removed as water by dehydration [Eq. (13)], then the maximum carbon theoretical yield of propylene is 33%. Therefore, to increase the maximum theoretical yield of propylene, the oxygen should be rejected as both CO_2 and H_2O and the coke levels should be minimized. A similar analysis can be done for aromatics if they are the targeted product. The maximum theoretical yield for olefins also decreases when feeds with lower H/C_{eff} ratios are used. For example, the maximum carbon theoretical yield of propylene for the sorbitol feedstock is 72% according to Eq. (14), lower than that for the glycerol-based feedstock (77%):

$$(9/7)C_3O_3H_8 \rightarrow C_3H_6 + (6/7)CO_2 + (15/7)H_2O, \quad (11)$$

$$1.5C_3O_3H_8 \rightarrow C_3H_6 + 1.5CO + 3H_2O, \quad (12)$$

$$3C_3O_3H_8 \rightarrow C_3H_6 + 6C + 9H_2O, \quad (13)$$

$$(9/13)C_6O_6H_{14} \rightarrow C_3H_6 + (15/13)CO_2 + (24/13)H_2O. \quad (14)$$

The maximum yield of olefins + aromatics versus coke yields at 500 °C that we obtained experimentally is shown in Fig. 15. None of these yields approaches the maximum theoretical yield of 77% as defined in Eq. (11). The ECat, FCC1, and Al_2O_3 catalysts all have similar olefin and aromatic yields, which approach 25% as the coke level approaches 60%. These yields approach the maximum theoretical olefin yield of 33% according to Eq. (13). The coke yield with these catalysts (60%) also approaches the yield of 72% according to Eq. (13). ZSM5 produces a lower level of coke and a higher level of olefins + aromatics, approaching 45%. However, the olefin and aromatic yield for ZSM5 is still significantly lower than the maximum theoretical yields of 77% according to Eq. (11) and 66% according to Eq. (12). This suggests that future improvements can be made to further improve the olefin and aromatic yields. Future catalysts and reactors should be designed to maximize CO_2 production by increasing the WGS reaction and to minimize coke formation.

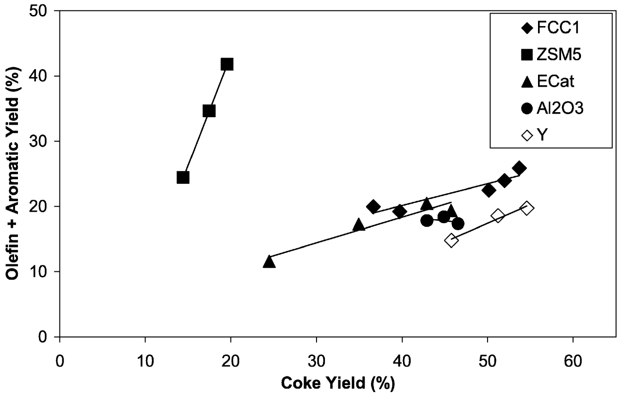


Fig. 15. Olefin + aromatics yields vs coke yields for catalytic cracking of 50 wt% glycerol–water solution in MAT reactor at 500 °C and TOS 30 s. ((◆) FCC1, (■) ZSM5, (▲) ECat, (●) Al_2O_3, (□) silicon carbide, (◇) Y-zeolite. Glycerol feed into reactor as a 50 wt% glycerol–water mixture. Yields are based on carbon molar selectivity. Conversion includes coke + gases + aromatics.)

3.9. Catalytic cracking of glycerol with hydrocarbon mixtures

In a petroleum refinery, biomass-derived oxygenates could be co-fed into a FCC reactor with petroleum-derived feedstocks. To simulate this, we processed mixtures of VGO with glycerol and pure VGO as feedstocks in the MAT reactor with FCC1 catalyst at 500 °C, as shown in Figs. 16–18. In all of the mixtures, a 50 wt% glycerol in water solution was used. The mixed feeds consisted of 9:1 and 2:1 VGO-to-glycerol solution volumetric mixtures, corresponding to VGO-to-glycerol molar carbon ratios of 31:1 and 7:1, respectively. The conversion in these figures includes the gases, coke, and gasoline fraction for VGO and VGO mixtures. For the pure glycerol feed, the conversion, as weight percent of solution fed, includes gases, coke, and aromatics. The catalyst-to-feed ratio in Fig. 16 includes the weight of both the glycerol solution and the VGO in calculating the feed weight.

As shown in Fig. 16, the glycerol solution gives a lower conversion to gas, aromatics, and coke than VGO, and increasing the amount of glycerol in the VGO–glycerol mixtures decreases the conversion slightly. Selectivity effects are barely seen with the 9:1 VGO–glycerol mixture, because the amount of biomass is too small to produce significant changes in the different yields. However, the 2:1 VGO–glycerol mixture introduces an important dilution of the VGO feedstock (at least a 3/1 molar ratio between VGO feed molecules and the glycerol/water mixture) and has a significant effect on gas and coke yields; thus, we now focus on the 2:1 glycerol–VGO mixture. Shown as dashed lines in Figs. 17 and 18 are the product yields when glycerol addition to VGO is purely additive (which we call the "additive effect"). This effect was calculated by adding the yields obtained with glycerol solution and VGO runs with respect to the mass ratio of both feeds and normalizing to 100%.

One major difference between VGO and glycerol is that glycerol produces more coke than VGO. Adding glycerol to VGO significantly increases the amount of coke, but in a smaller proportion than what would be observed as an addi-

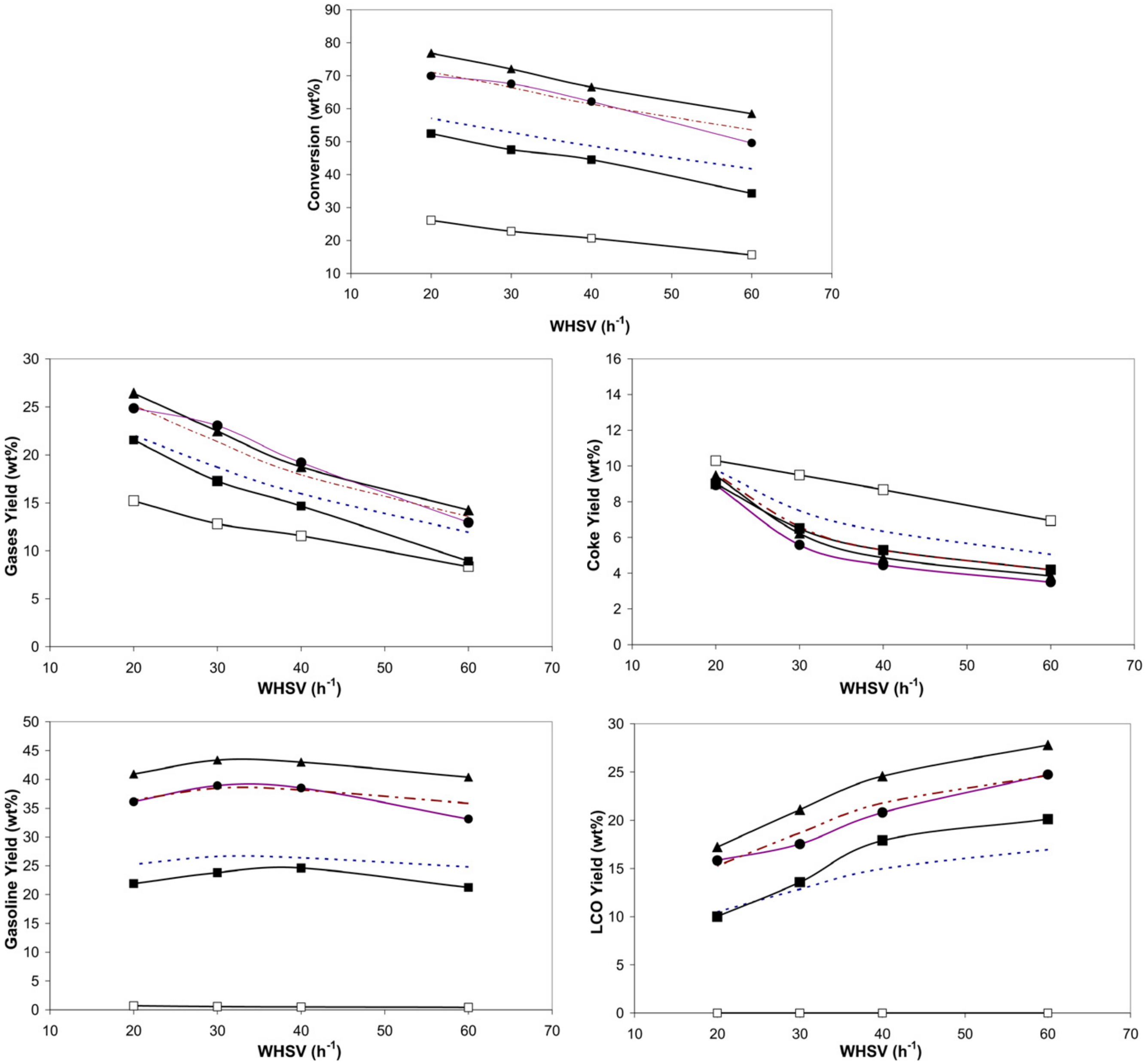


Fig. 16. Catalytic cracking of mixtures vacuum gas oil (VGO) with 50 wt% glycerol using FCC1 catalyst in MAT reactor at 500 °C and TOS 30 s. ((□) Glycerol, (■) glycerol–VGO 1–2 volume mixtures, (●) glycerol–VGO 1–10 volume mixtures, and (▲) VGO. Dotted lines ((- - -) 2:1 and (- · -) 10:1) represent yields if an additive effect of glycerol and VGO were observed. Glycerol feed into reactor as a 50 wt% glycerol–water mixture.)

tive effect. Addition of glycerol to VGO decreases the gasoline yield while it increases slightly the LCO yield due to a dilution effect with the glycerol feed, which is also a cause to the observed decrease in the conversion. The gas selectivity decreased with the amount of glycerol solution added to the VGO. The gas yield obtained from the glycerol–VGO mixture was lower than what would have occurred due to a mere additive effective of glycerol and VGO, as shown in Fig. 16. This indicates the presence of some synergetic effect between glycerol and VGO, which has various effects on the different gas yields. The yields of the different gas-phase products do change with feedstocks, as shown in Fig. 17. Compared with the VGO, glycerol cracking produced significant amounts of CO and CO_2, a similar yield of hydrogen, more methane and ethylene but less ethane, more propylene but less propane, and much less butanes and more butenes. Moreover, the olefin-to-paraffin ratios were much higher with glycerol cracking.

The synergetic effect of the glycerol–VGO mixture includes the following features:

- The hydrogen yield of glycerol–VGO was lower than that of either the pure VGO or glycerol cracking, indicating that either the H_2 was consumed in a synergetic reaction or H_2 production was inhibited.
- CO and CO_2 selectivities were lower than expected for glycerol–VGO.

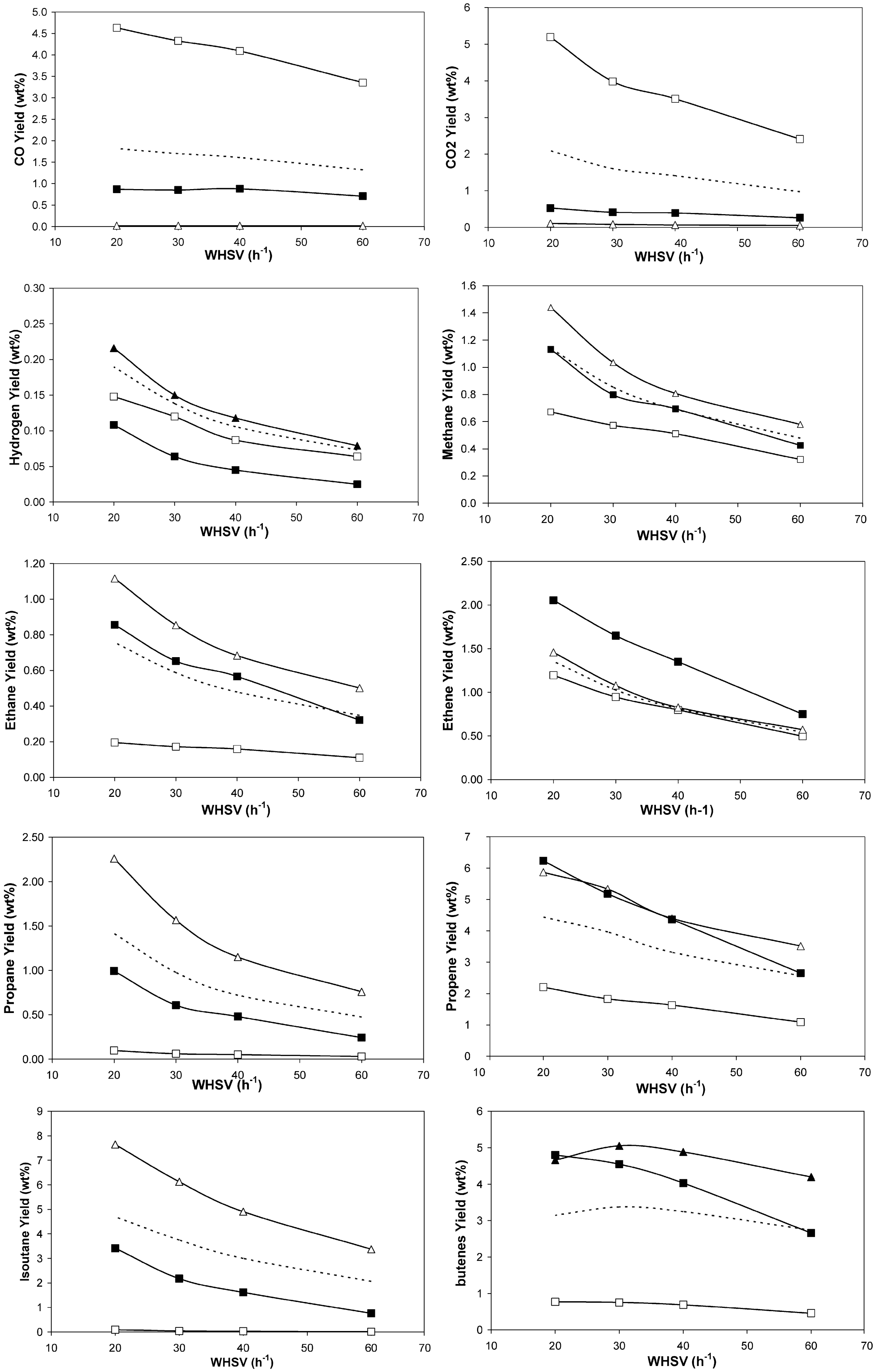


Fig. 17. Gas-phase yields and micromoles H_2 produced for catalytic cracking of mixtures vacuum gas oil (VGO) with 50 wt% glycerol using FCC1 catalyst in MAT reactor at 500 °C and TOS 30 s. ((□) Glycerol, (■) glycerol–VGO 1–2 volume mixtures, and (▲) VGO. Glycerol feed into reactor as a 50 wt% glycerol–water mixture. (- - -) represents yields if an additive effect of glycerol and VGO were observed.)

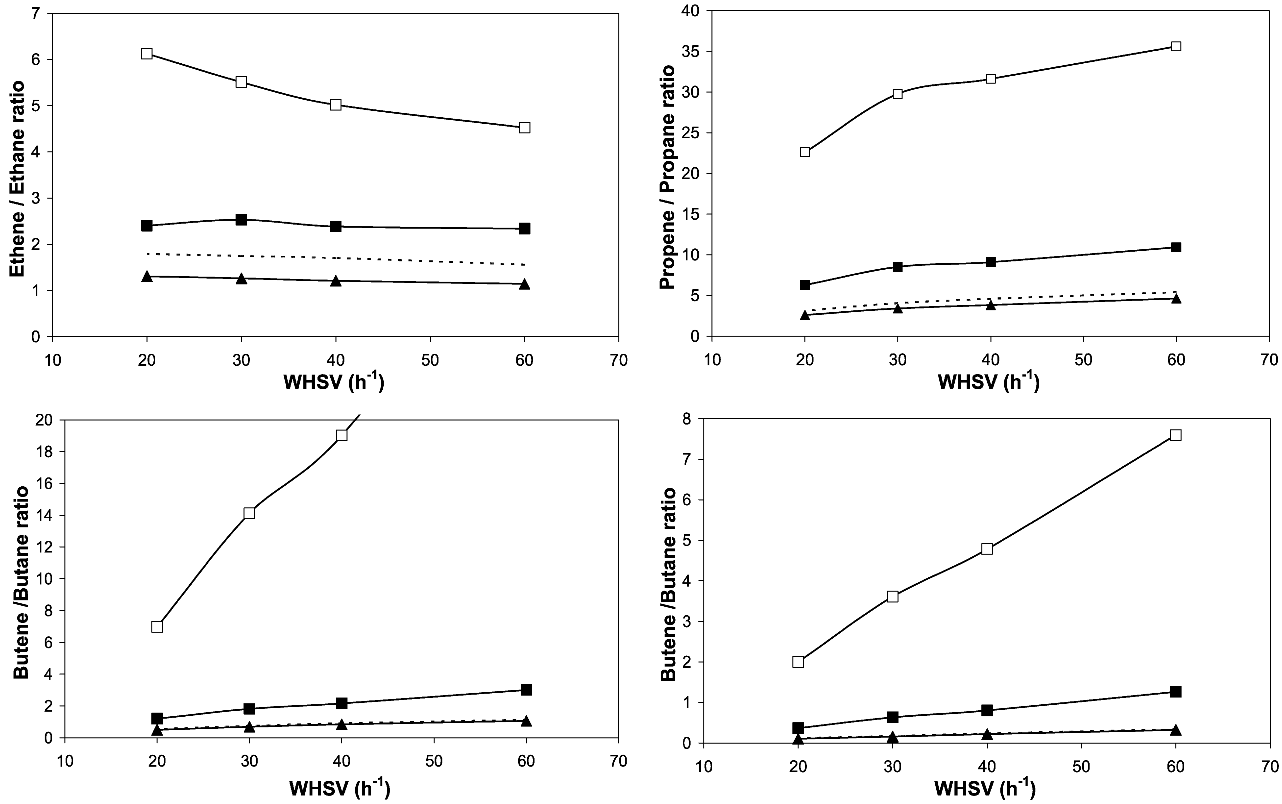


Fig. 18. Olefin-to-paraffin ratios for catalytic cracking of mixtures vacuum gas oil (VGO) with 50 wt% glycerol using FCC1 catalyst in MAT reactor at 500 °C and TOS 30 s. ((□) Glycerol, (■) glycerol–VGO 1–2 volume mixtures, and (▲) VGO. Glycerol feed into reactor as a 50 wt% glycerol–water mixture.)

- Ethene, propene, and butene selectivities were higher for glycerol–VGO mixture cracking than expected by additive mixing, with propene and butene selectivities higher than those obtained with VGO cracking at a space velocity of $20\ \mathrm{h}^{-1}$.
- Propane and butane selectivities were lower than expected for glycerol–VGO.

Importantly, adding glycerol to VGO increased the olefin-to-paraffin ratio of C_2–C_4 hydrocarbons, as shown in Fig. 18. Our results show that the co-feeding of glycerol may not have no significant synergetic effect on the chemistry of gasoil cracking other than a dilution effect. The coke yield of glycerol cracking added to the gasoil cracking coke yield. However, the gas olefins yields for glycerol–VGO mixtures were higher than what would be expected from an additive mixture, indicating that some synergetic effect was occurring for the glycerol cracking.

Note that the heat balance also depends on the dilution of the glycerol solution. Extra water added with the glycerol solution could act as an effective heat sink in the FCC, because water has a high heat of vaporization. Inversely, the glycerol solution may be used as atomization medium to spare process water. One option for further improving the olefin and aromatic yields for co-feeding of glycerol and petroleum-derived feedstocks into an FCC reactor might involve adding ZSM5 to the FCC catalyst, because ZSM5 produced more olefins and less coke than the FCC1 catalyst.

Table 4
Conversion of 50 wt% aqueous glycerol solution in MAT reactor at 500 °C and TOS 30 s with fresh FCC catalyst, regenerated and coked

Catalyst	Coked	Coked	Regen.	Regen.	Regen.	Regen.
Cat/feed	4.0	8.0	1.5	2.0	3.0	4.0
Conversion (wt%)						
To gas	19.9	25.4	21.5	24.1	34.4	36.2
To coke	19.0	10.6	36.6	39.7	50.2	52.0
To aromatics	9.1	3.7	9.8	7.3	4.9	5.1
Carbon yields (wt%)						
CO	7.54	8.54	8.09	8.25	10.15	10.16
CO_2	2.40	1.16	3.11	3.77	5.54	5.96
Methane	1.30	1.91	1.31	1.38	2.22	2.36
Ethane	0.49	0.64	0.48	0.50	0.74	0.75
Ethylene	1.87	3.25	2.10	2.44	3.96	4.45
Propane	0.11	0.17	0.12	0.14	0.24	0.28
Propylene	4.19	6.58	4.44	5.36	8.10	8.60
n-Butane	0.02	0.03	0.01	0.02	0.05	0.06
Iso-butane	0.04	0.04	0.03	0.04	0.12	0.18
Butenes	1.91	3.00	1.8	2.2	3.3	3.4
H_2 yield	1.2	2.9	1.4	1.9	3.0	3.0

3.10. Catalytic cracking of glycerol on precoked catalyst

Biomass-derived feedstocks may be injected into the FCC reactor before, with, or after VGO injection. In this study, we simulated injection before and with VGO. We also conducted experiments for biomass injection on a precoked catalyst. We cracked a 50 wt% glycerol solution in a MAT reactor on FCC1 with coke deposited before the test, as shown in Table 4. The

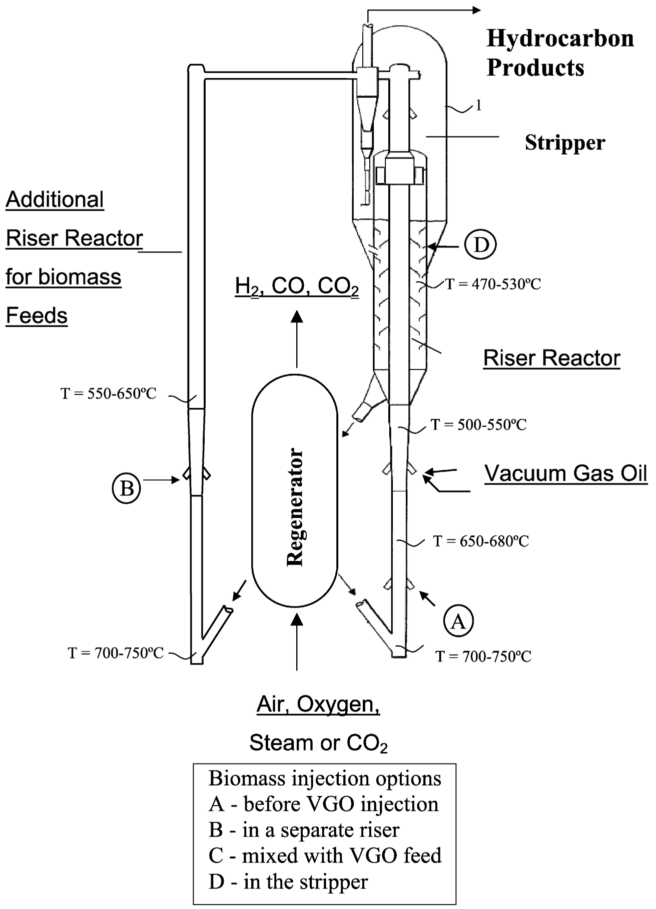


Fig. 19. Flow diagram of a modified FCC process for co-feeding biomass-derived oxygenates with petroleum feedstocks.

coke was deposited on the catalyst through a MAT run with heavy gasoil using the procedure described in Section 2.2 (but obviating the regeneration step) before passing the glycerol solution. The coke content of the catalyst before the test was 2.0 wt%. Coked catalyst is known to retain a significant cracking activity [45].

The precoked catalysts gave lower coke yields than the fresh catalysts, as shown in Table 4, but their activity is also lower. The gas yields with the coked and fresh catalysts were similar when compared at similar levels of conversion. Yields of the different gas fractions were quite similar for the hydrocarbons, whereas more CO and less CO_2 were produced on the coked catalyst. Aromatic selectivity also was quite similar for both the fresh and coked catalysts. Thus, one way to reduce coke selectivity in an FCC reactor is to inject in biomass-derived feeds after injection of VGO.

3.11. *Injection of glycerol in FCC*

Glycerol (or other biomass-derived feedstocks) also can be injected in various locations in the FCC process to take advantage of different operating conditions (Fig. 19). Before the VGO injection point, very severe cracking conditions (i.e., high temperature, high catalyst-to-oil ratio) may be encountered. After the VGO injection point, or in the stripper, very soft cracking conditions (i.e., moderate temperature, coked catalyst with reduced activity) are available. Finally, injection of glycerol in a parallel reactor to VGO cracking allows for intermediate operation. As shown by our results, the higher the cracking temperature, the higher the yields of CO, H_2, and ethylene. Moreover, coke selectivity from glycerol decreased with increasing reaction temperature. The higher dry gas production may be a drawback, because it might overflow the FCC unit compressor. Another option would be to crack the biomass-based stock before the VGO injection, providing an increase in small olefin yields, acting as a heat sink because of the extra water injected in the unit, and increasing the VGO cracking selectivity with precoked catalyst. Basic calculations of heat requirements for the biomass processing show that it could be possible to process a flow of glycerol solution as high as 20 wt% of the VGO flow in the FCC riser. Based on the coke yield of glycerol cracking at 700 °C (i.e., contacting the glycerol with the catalyst before contacting with the hydrocarbon feed [3% of the carbon in the glycerol solution]) will lead to a $<0.02\%$ increase of coke on the catalyst.

4. Conclusion

Sorbitol and glycerol were used as feeds in a MAT reactor to study the catalytic cracking of biomass-derived oxygenates. Six catalysts were used for this study: FCC1, ECat, Al_2O_3, ZSM5, USY, and SiC. Products from this reaction include olefins (ethylene, propylene, and butenes), aromatics, light paraffins (methane, ethane, propane), CO, CO_2, H_2, and coke. The activity of the catalysts (in terms of total conversion to gases, coke, and aromatics) for conversion of glycerol decreased in the order USY $\sim$ FCC $>$ Al_2O_3 $>$ ZSM5 $>$ ECat $\gg$ silicon carbide. The major difference between these catalysts is that ZSM5 gave low levels of coke ($<20\%$), whereas the other catalysts had high coke yields (30–50%). The coke yields decreased and the CO yield increased with increasing temperature. The ZSM5 catalyst had the highest level of olefins and aromatics. The gas-phase carbon yields for the fresh FCC, ECat, USY, and Al_2O_3 catalysts decreased in the following order: CO $>$ propene $>$ CO_2 $>$ ethene $>$ butene $>$ methane $>$ ethane $>$ propane $>$ n-butane. The gas-phase carbon yields for ZSM5 decreased in the order CO $>$ ethene $>$ propene $>$ CO_2 $>$ butene $>$ methane $>$ ethane $>$ propane $>$ n-butane. ZSM5 had a higher ethylene yield and lower methane yield than the other catalysts.

Sorbitol had a similar product selectivity as glycerol, the major difference being that sorbitol produced higher yields of CO. Water has an inhibiting effect on the reaction. Increasing the water partial pressure increased the CO_2 yield, probably by increasing the rate of the WGS reaction. Glycerol can be co-fed to an FCC unit with heavy gasoil (VGO). The addition of glycerol to VGO did not significantly change the product distribution of the final products.

A complex pathway of reactions is involved in the catalytic cracking of biomass. Gas-phase products, including olefins, CO, CO_2, H_2, and paraffins, are formed by three main catalytic pathways: dehydration reactions, hydrogen-producing reactions, and hydrogen-consuming reactions. A balance between these three pathways is needed to produce desired olefins from biomass-derived molecules. Aromatics are formed by condensation and Diels–Alder reactions of olefins and dehydrated species. Hydrogen-producing reactions include steam-reforming, WGS, decarbonylation, and dehydrogenation reactions. The hydrogen produced is transferred to dehydrated molecules by hydrogenation, hydrogen-transfer, and decarbonylation reactions. We believe that future advances in understanding this complex chemistry, followed by improved catalysts and reactor design, will lead to improved processes for the conversion of biomass-derived oxygenates into fuels and chemicals via catalytic cracking.

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