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Biomass to chemicals: Catalytic conversion of glycerol/water mixtures into acrolein, reaction network

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ABSTRACT

Acrolein was obtained by reacting gas-phase glycerol/water mixtures with zeolite catalysts. Glycerol was converted through a series of reactions involving dehydration, cracking, and hydrogen transfer and catalyzed by the acid sites of the zeolite. Acrolein was the major product; short olefins, aromatics, acetaldehyde, hydroxyacetone, acids, and acetone also were formed through a complex reaction network.

1. Introduction

Today, there is renewed interest in the conversion of biomass and biomass-derived products into fuels and chemicals [1–6]. Oxygenated petrochemicals are currently produced through the controlled oxidation of hydrocarbons. The conversion of petroleum-derived feedstocks into functionalized oxygenated chemicals involves the high-temperature activation of thermally stable molecules that have low functionality. In contrast, biomass-derived feedstocks with high oxygen content are thermally unstable but can be converted into oxygenated chemicals via deoxygenation processes [7,8]. These oxygenated chemicals can be high-value chemical feedstocks that possibly could replace petroleum-derived products. The deoxygenation process typically involves dehydration reactions to remove the oxygen as water. One example of this is the selective dehydration of fructose and xylose in biphasic mixtures to produce 5-hydroxyfurfural and furfural, respectively, or 2,5-dimethylfuran from fructose [9,10].

Glycerol is currently a valuable byproduct of biodiesel production with a refined value close to 1 $/kg. Biodiesel is currently produced by transesterification of vegetable oils (triglycerides) and methanol, with 1 mol of glycerol produced per mol of triglyceride feed [2,11]. Vegetable oils also can be converted into diesel fuel range alkanes by hydrotreatment [12–14]. It is estimated that approximately 80% of the biofuels in Europe are biodiesel [11]. As biodiesel production increases, the price of glycerol is expected to drop significantly from the actual cost, which has already decreased by half in the last few years [15]. Thus, it has been estimated that the cost of unrefined glycerol could decrease to 0.44 $/kg [16]. Importantly, the economics of biodiesel production are such that a credit of 300 $/ton is given for the reselling of crude glycerol, based on 2010 NREL estimates [17]. Such an inexpensive feed makes the development of processes for the conversion of glycerol into other chemicals desirable.

One of the chemicals into which glycerol can be converted is acrolein. The dehydration of glycerol into acrolein has been known since the nineteenth century. Acrolein is used to produce acrylic acid, acrylic acid esters, superabsorber polymers, and detergents. As early as 1918, Sabatier and Gaudion [18] reported the synthesis of acrolein (10% yield) from glycerol by gas-phase dehydration on Al_2O_3 or UO_2 catalysts at 360 and 350 °C, respectively, with ethanol, water, and allyl alcohol as other products. In 1928, Freund reported that pure acrolein could be produced from glycerol at 180 °C using diatomaceous silica [19]. Twenty years later, Hoyt and Manninen reported a method to produce acrolein from glycerol using solid phosphoric acid catalysts [20]. Heinemann et al. studied the dehydration of organic compounds (including glycerol) with activated bauxite catalysts and observed acrolein yields of up to 42% from glycerol working in gas phase at 430 °C [21]. In 1993,

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Table 1
Physico-chemical characteristics of catalysts

Catalyst	ECat	ZSM-5 additive
Si/Al	20	50
BET surface area (m^2/g)	156	70
Micropore volume (cm^3/g)	0.050	0.027
Zeolite content	11	15
Rare earth content, wt%	1.0	–
Particle size (μm)	40–120	40–120

Degussa reported a process to produce acrolein by dehydration of glycerol in the liquid or gaseous phase with solid acidic catalysts [22]. They claimed that aqueous solutions from 10 to 40 wt% glycerol could be converted to acrolein at 180–340 °C in the liquid phase or 250–340 °C in the gaseous phase. Gas-phase dehydration of glycerol at 300 °C with phosphoric acid supported on alumina gave acrolein yields of 70% and 65% as the concentration of glycerol increased from 10 to 40 wt%; however, the yield to acrolein decreased with increasing glycerol content. Consequently, a process to produce acrolein using aqueous solutions from biodiesel production (∼85 wt% glycerol in water) would be desirable.

Dehydration of glycerol has been conducted in liquid phase with H-ZSM-5, Na-ZSM-5, mordenite, Li_3PO_4 and $FePO_4$ as catalysts. But acrolein yields were lower in liquid phase than in gas phase; the highest liquid-phase yield was 36%. Acrolein also can be prepared from glycerol using subcritical and supercritical water [23–25] or with homogeneous catalysts [26]. The maximum acrolein yield with subcritical and supercritical water was reported to be 37.5% at 360 °C, 25 MPa, and 470 ppm ($g\,g^{-1}$) of zinc sulfate as the catalyst [24]. Most earlier processes involved solid acid catalysts in fixed-bed reactors, because catalyst deactivation with pure, diluted glycerol feeds was considered sufficiently low to support fixed-bed, continuous operation without regeneration for a significant period [22]. Nevertheless, the presence of contaminants—especially basic contaminants from the production of biodiesel and the possible secondary reactions of glycerol cracking products—may produce coke that causes deactivation of the catalyst, which then must be regenerated.

In this paper, we report that glycerol in water can be converted into acrolein, olefins, and acetaldehyde by reaction with zeolites in a continuous fluidized-bed reactor. This reaction system allows better heat and mass transfer than fixed-bed reactors, along with the possibility of performing continuous regeneration if needed. We show that glycerol reacts through a complex reaction network with numerous consecutive and parallel reactions that involve such processes as dehydration, cracking, and hydrogen transfer, all of which are catalyzed by acid sites.

2. Experimental

2.1. Materials and feeds

Table 1 summarizes the physical and chemical characteristics of catalysts used in this study, including a commercial FCC catalysts containing Y-zeolite in a silica–alumina matrix (Precision 1% Rare Earth, supplied by BASF, tag FCC1) and a FCC additive based on ZSM5 zeolite, mixed with a clay binder to ∼15% weight. These equilibrium catalysts were subjected to hydrothermal deactivation (816 °C, 4 h, 100% steam). The same catalyst sample was used to perform all of the tests with different feeds and operating conditions with no noticeable changes in the catalyst parameters or in the original activity or stability. Aqueous solutions of 20, 50, and 85 wt% of glycerol were prepared from 99.5 wt% glycerol (Aldrich Chemicals).

2.2. Laboratory units

2.2.1. Microactivity test (MAT)

Some of the experiments described herein were performed in a fixed microactivity test (MAT) reactor. The reaction zone and product recovery system were designed in accordance with ASTM D-3907 [27]. Before each experiment, the MAT system was purged with a 50 cc/min N_2 flow for 30 min at the reaction temperature. All MAT reactions reported herein were conducted at 30 s time on-stream. After the reaction, stripping of the catalyst was done using a N_2 flow of 40 cm^3/min for 15 min. During the reaction and stripping steps, the liquid products were collected in the corresponding glass receivers located at the exit of the reactor, 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 in a 100-cm^3/min stream of air for 3 h.

2.2.2. Microdowner reactor

Hardware and detailed operation of the Microdowner unit has been described previously [28]. The unit's main features are a catalyst preheater in which the catalyst is stored before testing, a once-through reactor in which the feed and the preheated catalyst are fed continuously during the test at a very short residence time (0.3–2 s), and a separator that stores the catalyst used during the test for regeneration and coke determination. The unit simulates a steady-state regime during the test, which usually takes 1–2 min. The catalyst separated from the reaction products is continuously stripped during the reaction and for 60 s after the end of the reaction. Liquids and gaseous products are recovered by known methods (cold traps and water displacement burette). As in many tests, both an aqueous phase and a hydrocarbon phase appeared in the traps. Acetone was used to dilute both phases, to allow extraction of a single sample from each trap. The catalyst was regenerated after the test with 500 cm^3/min of air at 850 K for 3 h. Alternatively, the coked catalyst could be withdrawn from the unit after the stripping step, thus ignoring the regeneration step. A flow of nitrogen was used for solid transportation and feed dispersion.

2.2.3. Analysis of the reaction products

The reaction gases were analyzed with a Varian 3800-GC gas chromatograph equipped with three detectors, two thermal conductivity detectors (TCDs) for analyzing 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 to C_6 hydrocarbons separated on a 50-m Plot/Al_2O_3 column. Liquid samples were analyzed with a Varian 3900-GC gas chromatograph equipped with a Petrocol-100 fused silica column connected to a FID following the PIONA procedure. Gas chromatography–mass spectroscopy (Agilent Technologies 5973 and 6890N, with a 20-m HP1 column) was used to identify the main oxygenates appearing in analyses of the gas and liquid samples. 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. The conversion presented is the conversion of the feedstock. The conversion toward gas (carbon oxides, hydrogen, and C1 to C4) plus hydrocarbons in liquids plus coke (i.e., excluding the oxygenated products) is also presented in addition to the traditional conversion.

3. Results and discussion

3.1. Conversion of glycerol at temperatures from 500 to 700 °C

Table 2 gives the results of converting a 50% aqueous glycerol solution at 500–650 °C with a commercial USY-based equilibrium

Table 2
High temperature glycerol conversion in Microdowner (MD) and Microactivity test (MAT) reactors (50 wt% glycerol aqueous solution)

Laboratory unit	MD	MD	MD	MD	MD	MAT	MAT
Test no.	1	2	3	4	5	6	7
Catalyst	ECat	ECat	ZSM5	ZSM5	ZSM5	ZSM5	ECat
Operating conditions							
Temperature (°C)	500	650	500	500	650	700	720
Catalyst to feed ratio	12	51	11	48	45	4	6
Residence time (s)	0.7	0.7	0.7	1.4	0.7	30	83
WHSV (h^{-1})	396	108	431	55	121	30	7
Glycerol conversion, wt%	100	100	100	100	100	100	100
Molar carbon selectivity (%)							
Carbon monoxide	6.8	23.6	6.2	9.7	18.0	42.0	51.0
Carbon dioxide	5.0	9.2	4.2	6.3	8.8	5.1	8.8
C_1–C_4 alkanes	0.8	6.6	0.2	0.5	3.3	12.9	12.5
Ethylene	1.2	6.6	2.4	4.5	10.5	21.8	13.1
Propylene	4.2	7.5	2.4	4.3	6.1	7.8	4.9
Butenes	1.3	2.5	1.6	1.9	3.5	0.9	0.4
Acetaldehyde	23.6	13.3	24.9	15.2	20.7	1.0	0.5
Acrolein	18.3	6.0	39.0	23.2	11.0	0.4	0.1
Acetone	6.1	3.5	3.6	3.2	3.6	0.2	0.2
2-Propenol	0.1	<0.1	<0.1	<0.1	<0.1	0.0	0.0
Acetol	0.2	<0.1	<0.1	<0.1	<0.1	0.0	0.0
Acids	2.4	0.4	0.9	1.3	0.2	0.0	0.0
C_5 + BTX	1.7	2.8	2.8	6.7	6.2	1.7	1.0
Others CHO	5.2	2.8	5.4	5.5	2.4	0.2	0.1
Coke	23.0	15.3	6.2	17.7	5.7	3.2	7.3

catalyst (ECat) and ZSM5-based additive in a Microdowner reactor. The Microdowner unit was operated with catalyst residence times close to 1 s and catalyst-to-feed (CTF) ratios of 12–51 to simulate adiabatic mixing of the glycerol solution (100 °C) and the catalyst (close to 700 °C from an industrial regenerator). A test at 500 °C with a CTF ratio of 48 using a ZSM5-based catalyst was also conducted to study the effect of CTF ratio on product selectivity. These reaction conditions were chosen to be representative of the operation conditions encountered at the several possible injection points of glycerol in a FCC unit, as depicted in Fig. 1.

In all tests, the glycerol conversion was 100%. The main products of the reaction with both catalysts were CO, CO_2, ethylene, propylene, butenes, oxygenates, acrolein, acetaldehyde, acids (including acetic acid, propionic acid, and acrylic acid), C_5^+ hydrocarbons, and coke. Acetone/propanal and 2-hydroxyacetone (acetol) were present at very low yields at 500 °C and above. The C_5^+ hydrocarbons present included pentenes, benzene, toluene, and xylenes. A series of products grouped under the label "other CHO" included hydrocarbons (hexanes and higher-boiling point components) and oxygenated products, including methacrolein, methyl vinyl ketone, butanone, cyclopentanone, and methylcyclopenenone. No alcohols were found as products in these tests. Propane and butane yields were very low in all cases, whereas methane, ethane, and butadiene yields were significant at 650 °C due to thermal cracking. Ethyne and propyne were not found as products, in contrast to the steam cracking operation, in which they are obtained in significant amounts.

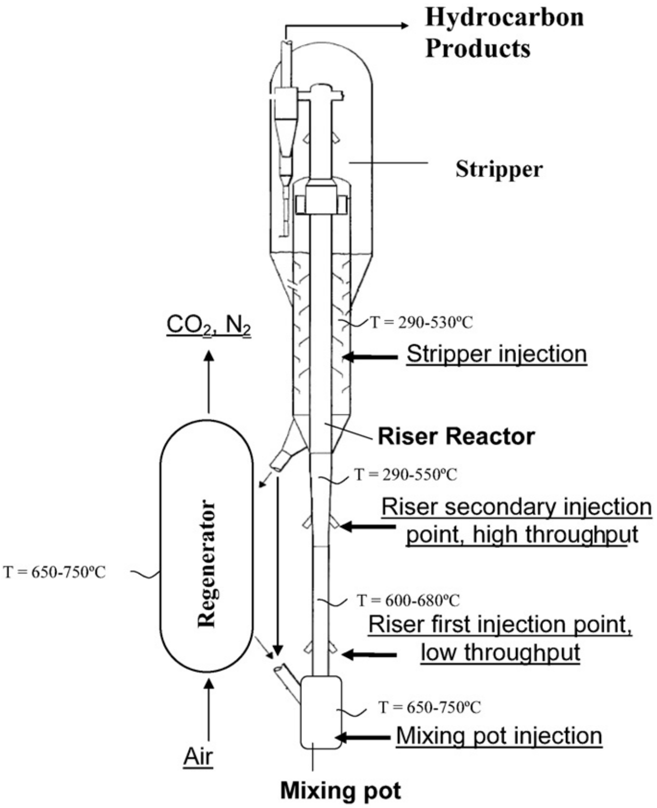

Fig. 1. Injection of glycerol into FCC type reactor.

Table 3
Comparison of glycerol conversion at 700 °C and naphtha steam cracking at 800 °C for the production of olefins, carbon yield basis

	Glycerol cracking, carbon wt% yield	Naphtha steam cracking, carbon wt% yield
Carbon monoxide	42	–
Carbon dioxide	5.1	–
Methane	10.5	15.7
Ethane	1.8	3.3
Ethylene	21.8	30.8
Propane and butanes	0.6	0.6
Propylene	7.8	14.0
Butenes	0.9	3.8
C_2–C_4 alkynes		6.5
Acrolein	<2	–
Other oxygenates		–
C_5^+ hydrocarbons	4.2	19.3
Fuel oil	–	5.2
Coke	3.2	–

With increasing reaction temperature, the yields of CO, CO_2, light olefins, methane, and C_5^+ hydrocarbons increased, whereas the yields of the other major products, coke and oxygenates, decreased. Yields of acrolein and organic acids decreased faster than those of acetaldehyde and acetone with increasing temperature. This general pattern was seen regardless of the two catalysts used. These findings indicate that the high-temperature operation is not the ideal operating condition for oxygenate production as it is for light-olefin production [29]. Conversion toward light olefins can be further increased by increasing the temperature and decreasing the space velocity. We simulated these conditions by performing MAT testing at 700 °C with long residence times (20–80 s). At such a high temperature, the conversion of oxygenated products was almost complete with both the ZSM5 and Y catalysts, whereas ethylene yield increased to nearly 22% and propylene yield remained around 8% (based on feed carbon content) with the ZSM5 catalyst. The CO yield was very high and coke yield was low with both catalysts. We note that coke-on-catalyst was 10-fold higher in the MAT reactor (fixed bed) than in the MD reactor (transported bed), due to the different residence times in the two reactors. The ethylene yields were similar to those obtained with steam cracking of naphtha at 800 °C, as shown in Table 3, but with lower yields of methane, dienes, and liquids in the former. High levels of CO also were produced with glycerol conversion, which could be used to produce additional hydrogen via the WGS reaction.

Table 4
Optimal conditions of temperature, glycerol dilution and space time for best acrolein yield. Catalyst based on ZSM5 zeolite, operation in Microdowner unit

Laboratory unit	MD	MD	MD	MD	MD	MD
Test no.	8	9	10	11	12	13
Operating conditions						
Temperature (°C)	290	350	350	350	350	350
Catalyst to feed ratio	12.6	5.6	10.7	11.5	5.4	9.9
Residence time (s)	1.0	0.5	1.0	0.9	0.5	0.9
WHSV (h^{-1})	282	1243	360	335	1315	388
Feed dilution (wt% glycerol)	50	50	50	20	85	85
Glycerol conversion, wt%	98	89	100	100	86	97
Molar carbon selectivity (%)						
Carbon monoxide	2.8	1.8	2.6	2.3	1.6	2.2
Carbon dioxide	0.6	0.1	0.8	1.1	0.5	0.7
C_1–C_4 saturates	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ethylene	0.3	0.4	0.6	0.5	0.4	0.5
Propylene	0.8	0.6	0.9	0.5	0.7	1.0
Butenes	0.2	0.2	0.3	0.2	0.2	0.3
Acetaldehyde	4.6	8.9	8.5	10.9	6.2	5.9
Acrolein	58.8	58.9	58.8	62.1	59.1	58.6
Acetone	2.4	2.0	3.3	1.5	1.4	2.1
2-Propenol	1.2	0.2	0.7	0.1	1.2	0.9
Acetol	0.9	4.0	2.7	0.5	2.6	1.8
Acids	2.0	2.4	3.9	1.6	2.2	2.0
C_5 + BTX	0.6	0.5	0.6	1.2	0.7	0.9
Others CHO	4.2	12.3	4.1	2.4	13.2	6.8
Coke	20.6	7.8	12.2	15.0	10.1	16.2

Comparing the behavior of the two catalysts under the same operating conditions shows lower amounts of CO, CO_2, and coke and greater amounts of oxygenates and olefins with the ZSM5-based catalyst. C_5^+ hydrocarbon yield was higher with the ZSM5 additive.

When the CTF ratio was increased at constant temperature, the yields of CO, CO_2, coke, olefins, and C_5^+ hydrocarbon increased, whereas the yield of oxygenates decreased. Acrolein and acetaldehyde yields were decreased, probably because they were converted mainly to olefins, CO, and coke with increasing CTF ratio. Clearly, the yield to acrolein and other oxygenates was maximized at higher space velocities and lower temperatures.

3.2. Low-temperature conversion of glycerol

As demonstrated by the previous results, high space velocities and low temperatures are the best conditions for acrolein production. Consequently, we performed several tests at 290–350 °C and space velocities close to 400 h^{-1} and 1200 h^{-1}. To attain these space velocities, we used catalyst residence times of 0.5–1 s and CTF ratios of 5–12. The results, given in Table 4, show that the acrolein yield increased with decreasing temperature. Acrolein selectivities of 58–62% were obtained. The acetaldehyde and acetone yields were decreased at 290–350 °C compared with operation at 500 °C, whereas the acid yield increased slightly. 2-Propenol and acetol also were observed at these lower temperatures. Interestingly, no saturated alcohols (1- and 2-propanol) were detected. Methacrolein and methyl vinyl ketone were present in minor amounts. The production of CO, CO_2, olefins, and C_5^+ hydrocarbons also decreased, whereas coke yield increased. This latter finding may be due to product desorption problems in the same way as Vacuum gasoil produces high coke yield when poorly vaporized in the riser reactor or when the processing temperature is too low [30]. This effect was particularly significant when the reaction temperature approached the temperature of glycerol vaporization (290 °C), and a noticeable increase in the coke yield was seen when the temperature was decreased from 350 to 290 °C. The yields of acetol, acid, acetaldehyde also decreased, possibly due to the lower extent of secondary reactions resulting from the lower temperature and the greater amount of glycerol and/or intermediates trapped on the catalyst. Surprisingly, the acrolein yield was hardly affected by the temperature decrease, possibly indicating a different formation pathway for acrolein and acetol, acids, and acetaldehyde. At a temperature of 290–350 °C and space velocity of 300–400 h^{-1}, the conversion of glycerol was still nearly complete, with a minimum conversion of 97% at 290 °C (Table 4, test 8).

When the space velocity was increased to 1200 h^{-1} (by decreasing the residence time and CTF ratio), glycerol conversion decreased to 89%, as shown in Table 4. This had no significant effect on the selectivity to acrolein or acetaldehyde; however, coke yield decreased significantly due to the lower CTF ratio, whereas the yields of acetol and the unidentified carbohydrates/hydrocarbon increased. This demonstrates that acetol is a primary but unstable product, and that acetone, 2-propenol, and acids are secondary products. In addition, many of the nonidentified products had a boiling point in the range of that of glycerol, suggesting that other minor intermediates besides acetol and 3-hydroxypropionaldehyde were formed from glycerol and were rapidly converted as severity increased. We discuss the possible formation of these intermediates in Section 3.4.

The results of tests 10, 11, and 13 in Table 4 demonstrate the effect of the dilution of glycerol in water on the product distribution. This was little affected by the change in the glycerol dilution, whereas the overall conversion was slightly lower with the 85% glycerol solution (97% vs 100% at lower glycerol concentrations). The acrolein selectivity remained between 58 and 62%, slightly higher with the highest dilution. The hydrocarbon yield did not change with the dilution. The coke yield was lowest with the 50% glycerol solution. This can be explained by the higher product concentration of the 85% glycerol solution, which promotes the hydrogen transfer reaction that produces coke; and the higher catalyst-to-carbon ratio for the most diluted solution, which proportionally increases the coke yield through the strong adsorption of feed or products by the strongest acid sites. Among the oxygenates, the larger molecules (i.e., acetol, other CHO) were favored by higher glycerol concentrations, whereas the acetaldehyde yield was the greatest at lower glycerol concentrations. Lower glycerol concentrations may favor the monomolecular cracking of larger molecules, whereas higher glycerol concentrations may favor bimolecular condensation reactions. A test carried out at high space velocity and 85% glycerol concentration (test 12) showed very similar results as were found with 50% glycerol solutions: decreased glycerol conversion (86%) and coke yield and increased CHO yield.

These results demonstrate that it is possible to produce acrolein as a bulk chemical from glycerol using commercial glycerol solution from biodiesel plants with a carbon selectivity >60%.

3.3. Comparison of MD and MAT units for glycerol processing at low temperature

Fig. 2 compares the processing of a glycerol solution (50% glycerol) at the same temperature (350 °C). The MAT operating conditions were adapted from the standard test conditions so that the space velocity in these tests did not differ significantly from the space velocity in the Microdowner tests (Table 5). In particular, TOS and the CTF ratio were reduced so that space velocity in MAT ranged from 360 to 90 h^{-1}, compared with 20 to 60 h^{-1} in the standard test. As a result, Fig. 2 shows that the conversion obtained at a space velocity of 90 h^{-1} was very close to the MD conversion at 360 h^{-1}. Moreover, the product distribution shown in Fig. 2 also was very similar, whereas some significant differences were found in the acetaldehyde, acetol, CHO, and coke yields for the MAT test at 90 h^{-1}. This difference is probably due to the amount of coke on the catalyst (CoC), which is higher with MAT than with MD testing (typically 1% vs 0.2%). It has been demonstrated [31–33] that

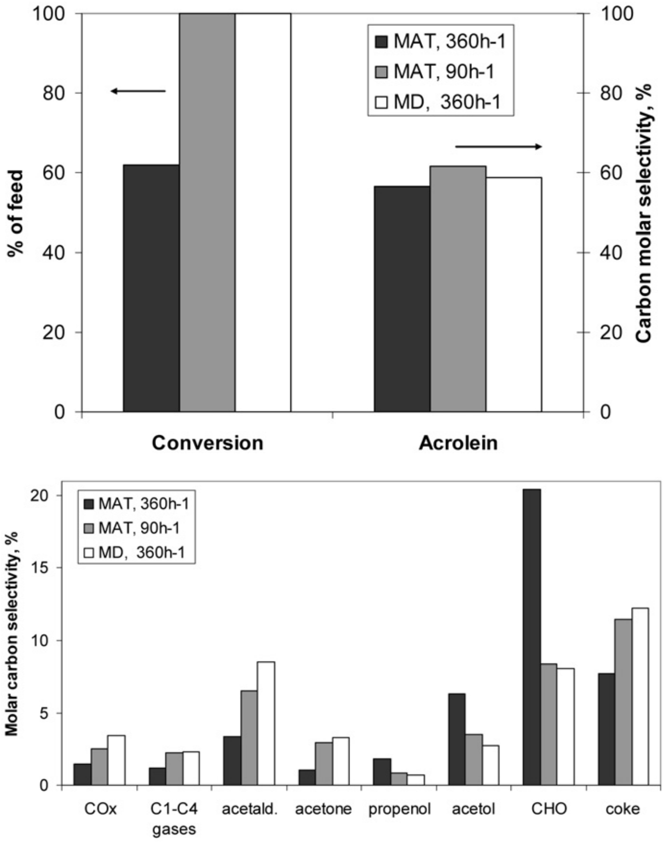

Fig. 2. Comparison between MD and MAT units for glycerol processing, low temperature.

Table 5
Standard MAT operating conditions and modifications for glycerol conversion

Operating conditions	Standard, VGO	Glycerol cracking
Time on stream (s)	30	20
Catalyst to feed ratio	2–6	0.5–2
WHSV (h^{-1})	20–60	90–360
Temperature (°C)	500–550	350

catalyst activity is decreased by a factor of 2–4 for each 1% CoC for typical hydrocarbon cracking reactions. This would explain the difference between the two units in the space velocity required to reach the same conversion. Notwithstanding the differences in the two laboratory units, the MAT unit can give a sufficiently good product selectivity pattern to perform catalyst screening or to explore the main conversion routes of the glycerol reagent and its reaction products.

3.4. *Chemistry of glycerol conversion*

3.4.1. *Oxygenate distribution*

The main oxygenates produced by glycerol conversion, excluding acrolein, were acetaldehyde, acetone, 2-propenol, and 2-hydroxyacetone (acetol). Methacrolein and methyl vinyl ketone were detected in trace amounts. No traces of propanol were detected, and only trace amounts of methanol and ethanol, as well as a number of unidentified compounds with 1 to 3 oxygen atoms and 2 to 4 carbon atoms, were found. These oxygenated compounds, plus acetol, were present at low levels (combined <5 wt%) at 500 °C and above, whereas at lower reaction temperatures, they can represent >10% of the carbon balance.

Table 6
Product selectivity in the conversion of several main products obtained from the glycerol processing. Tests in MAT and MD units with ZSM5-based catalyst, 50 wt% aqueous solutions

Laboratory unit	MAT	MAT	MAT	MAT	MD
Reactant	Acetol	Acetol	Acetone	Acetone	2-Propenol
Operating conditions					
Temperature (°C)	350	500	350	500	500
Catalyst to feed ratio	2	2	2	2	11.9
residence time or TOS (s)	20	20	20	20	0.9
WHSV (h^{-1})	90	90	90	90	391
Feed dilution (wt% glycerol)	50	50	50	50	50
Feed conversion, wt%	23	86	14	35	99
Molar carbon selectivity (%)					
Carbon monoxide	1.2	11.6	0.2	1.2	1.4
Carbon dioxide	0.7	3.1	0.7	7.3	1.0
C_1–C_4 alkanes	<0.1	0.5	0.3	0.7	0.6
Ethylene	0.1	6.1	0.4	1.5	6.7
Propylene	0.3	4.8	1.7	7.6	22.2
Butenes	0.2	2.7	27.9	47.2	4.5
Acetaldehyde	1.4	8.0	0.6	1.0	0.7
Acrolein	0.1	0.2	0.0	0.0	5.0
Acetone	4.0	17.1	–	–	11.6
2-Propenol	0.0	0.0	0.0	0.0	–
Acetol	–	–	2.3	0.0	0.0
Acids	9.4	10.3	20.2	11.1	1.3
C_5 + BTX	2.9	4.3	6.6	4.8	8.4
Others CHO	52.0	24.8	7.3	5.0	16.1
Coke	27.7	6.5	31.9	12.4	20.5

Table 7
Product selectivity in the conversion of minor products observed in the glycerol conversion at 350 °C, with ZSM5-based catalyst, and compared with acetol conversion under similar conditions

Laboratory unit	MAT	MAT	MAT
Product	Acetol	1,2-Propanediol	Propionic acid
Operating conditions			
Temperature (°C)	350	350	350
Catalyst to feed ratio	2	1	1.3
Residence time (s)	20	20	20
WHSV (h^{-1})	90	180	142
Feed dilution (wt% glycerol)	50	50	50
Feed conversion, wt%	23	65	39
Molar carbon selectivity (%)			
Carbon monoxide	1.2	0.3	0.3
Carbon dioxide	0.7	0.3	2.0
C_1–C_4 alkanes	<0.1	0.2	0.0
Ethylene	0.1	0.9	0.6
Propylene	0.3	5.1	0.6
Butenes	0.2	2.4	0.4
Acetaldehyde	1.4	1.3	0.9
Acrolein	0.1	0.0	0.0
Acetone	4.0	60.8	2.3
2-Propenol	0.0	0.4	0.0
Acetol	–	0.3	0.0
Acids	9.4	8.4	0.7
C_5 + BTX	2.9	1.5	1.8
Others CHO	52.0	9.4	6.2
Coke	27.7	8.7	84.2

3.4.2. *Product conversion selectivities and reaction network*

To track the primary, secondary, and stable or unstable character of the different products detected in the conversion of glycerol, we fed several of the main products in the MAT and MD units under representative conditions of the previous MD tests (ZSM5-based catalyst, 350–500 °C, space velocity of 100–400 h^{-1}). The aim was to help establish a reaction network. The operating conditions and selectivity results are summarized in Tables 6 and 7.

Dehydration of glycerol has been shown to first produce acetol and acrolein, as shown in Fig. 3 [34–36]. This mechanism has

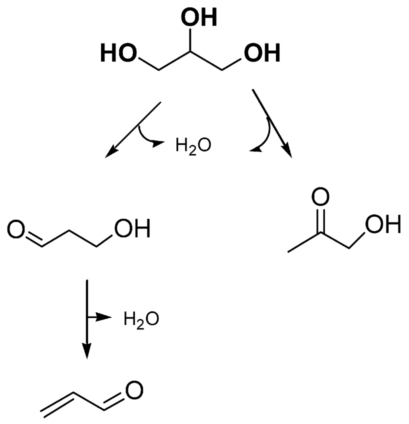

Fig. 3. Glycerol primary products.

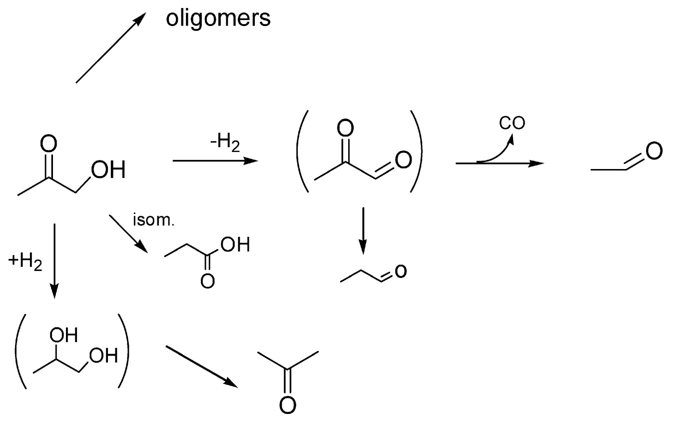

Fig. 4. Acetol conversion scheme.

been observed on a wide variety of catalysts, including base- and acid-supported catalysts and zeolites [37–39]. Similarly, we found the formation of significant amounts of acrolein during the MD experiments with glycerol, as well as significant quantities of acetol at 350 °C and below. But we also found large amounts of subproducts, including acids, acetone, hydrocarbons, and coke, whose formation pathways from glycerol and the primary products formed from glycerol have not yet been described. In addition, it is known that glycerol can form oligomers (polyglycerols), which may lead to coking reactions [40]. (Water may decrease the amounts of oligomers.) The same mechanism is applicable to acetol as well. Coke is also formed from acetaldehyde [41], and probably acrolein; coke can be formed from many sources.

3.4.2.1. Acetol conversion To detect the secondary products rising from acetol, we fed acetol into the MAT unit at 350 and 500 °C and a WHSV close to 90 h^{-1}. The results, presented in Table 6, show that acetol was very reactive; with 86 wt% conversion at 500 °C, but still was less reactive than glycerol. As was the case for glycerol conversion, oxygenate and coke yields decreased and gas and hydrocarbon yields increased with increasing temperature. Nevertheless, the detailed product distribution of acetol conversion was quite different from that of glycerol conversion; whereas coke selectivity was similar or slightly increased at low temperature, acetol yielded more acids and acetone and had unidentified high-molecular-weight oxygenates/hydrocarbons as major products. Meanwhile, acetaldehyde yield was lower, and acrolein was nearly missing as a reaction product. This confirms that glycerol dehydrates through two distinct and independent pathways, one leading to acrolein through 3-hydroxypropenal (a very unstable product) and the other forming acetol, as shown in Fig. 3. The first pathway implies the removal of the central alcohol function in the glycerol molecule, whereas the second implies the removal of one of the two terminal alcohol groups. Statistically, the glycerol would then split into 66% acetol (and subproducts) and 33% acrolein. A selectivity to acrolein of close to 60% was observed at 350 °C, indicating preferential removal of the central alcohol group with ZSM5.

Acetone can be obtained from the hydrodeoxygenation of acetol, as shown in Fig. 4. Whether the reaction proceeds through an intermediate, 1,2-propane diol, which is not observed as a product, or occurs directly in a combined reaction with H_2 or a hydrogen donor in a similar way as in catalytic cracking [42–44] as set in Eq. (1) is not clear.

$$\text{Acetol} + \text{H-donor} \rightarrow \text{acetone} + \text{H-receptor} + H_2O. \tag{1}$$

Coke, olefins, and their acetol species can be H-donor species. The formation of acid can be explained by the isomerization of acetol, forming propionic acid.

3.4.2.2. Acetone and 2-propenol conversion Acetone was fed at 350 °C and 500 °C and a space velocity of 90 h^{-1}, whereas 2-propenol was fed at 500 °C and a space velocity close to 90 h^{-1}. (Propenol was not observed as a product in the conversion of glycerol at 350 °C.) The results, presented in Table 6, indicate that 2-propenol was nearly as reactive as glycerol, whereas acetone was less reactive, with only 30% conversion at 500 °C under the same operating conditions. These two reactants showed high selectivity toward olefins, but 2-propanol was more selective to propene and ethylene, whereas acetone was more selective to butenes, as reported previously for acetone [45]. The conversion of acetone also produced a significant yield of CO_2. Acetic acid also was a major product at 350 °C but not at 500 °C. Some bimolecular mechanism may explain the butene and acid selectivity at low temperature, with the overall stoichiometry

$$2\ \text{Acetone} \rightarrow \text{butene} + \text{acetic acid}. \tag{2}$$

Interestingly, coke selectivity, which usually increases with a bimolecular mechanism, was low in this case. At higher temperatures (>450 °C), acetic acid was converted into CO_2 and hydrocarbons, as was shown by Gayubo et al. [45]. There was a higher coke selectivity with 2-propanol, as well as a higher selectivity toward high-molecular-weight oxygenated components. Production of pentenes and BTX production also was greater. The 2-propenol also could undergo hydrogenation to form propanol, which in turn could undergo dehydration to yield propene. No propanol was found as a product; another donor may exist that leads to propene, similar to the following reaction:

$$\text{propen-2-ol} + \text{H-donor} \rightarrow \text{propene} + \text{H-receptor} + H_2O. \tag{3}$$

As in the case of acetol, such a donor can be coke, an olefin, or another oxygenated oligomer obtained in the conversion of 2-propenol. Aromatics may be formed from small olefins generated during the cracking of acrolein. The aromatics thus formed can then condense with small olefins to form coke, as is well known in the cracking of hydrocarbons [46]. Although acetone and 2-propenol are similar in structure, they have very different conversion networks, as shown in Fig. 5.

3.4.2.3. Propionic acid and propanediol conversion We also fed propionic acid and propanediol into the MAT reactor at 350 °C to check for minor conversion pathways. The findings are compared with those of acetol under similar operating conditions in Table 7. Propanediol exhibited a reactivity similar to that of acetol along with a high selectivity to acetone, obtained by direct dehydration. The propionic acid reactivity was much lower, with a very high selectivity to coke at low temperature and low conversion. The main conversion pathways of these components complete the acetol conversion scheme as shown in Fig. 4.

3.4.2.4. Reaction network Fig. 6 summarizes all of the foregoing findings in a general glycerol conversion scheme. Along with the information included in Figs. 3–5, Fig. 6 presents an additional reaction pathway for the formation of acetaldehyde. Note that acetaldehyde was found as a main product in glycerol conversion and, to a lesser extent, in acetol conversion. No product demonstrated acetaldehyde yields as high as glycerol yields, indicating the formation of acetaldehyde by a different route than that depicted in Fig. 4. Chai et al. [37] and Tsukuba et al. [39], based on a previous computational study [36], proposed that the decomposition of 3-hydroxylpropenal should yield acetaldehyde and formaldehyde by retro aldol condensation. Formaldehyde then may be decomposed into $CO + H_2$ or hydrogenated into methanol. In our study, at 350 °C, formaldehyde was not detected as a product and methanol was present in only trace amounts. Moreover, our hydrogen/CO molar ratio was much lower than 1 at 350 °C, whereas a ratio of 1 should result from formaldehyde decomposition. Acetaldehyde also was found as a reaction product in the conversion of acetol. Consequently, we propose that the mechanism of acetaldehyde formation was coupled with some type of hydrogen-transfer mechanism, with acetaldehyde formed from a dehydrogenated dione intermediate, as shown in Fig. 6. The unstable dione reaction intermediates rapidly decomposed into CO and acetaldehyde, and thus diones were not observed in reaction products.

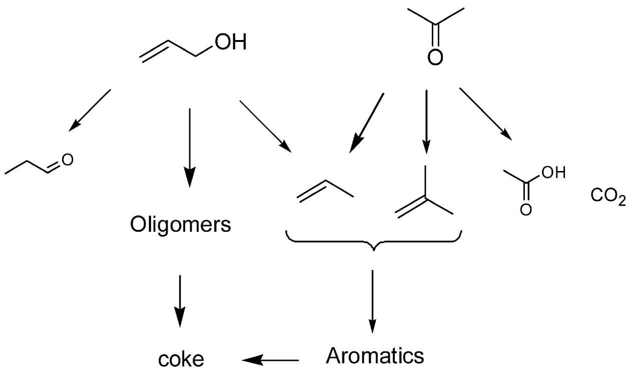

Fig. 5. Acetone and 2-propenol conversion scheme.

Fig. 6 depicts the main conversion pathways for glycerol and subproducts at 350–500 °C. At higher temperatures (above 600 °C), acrolein and other oxygenates may undergo decarbonylation, yielding ethylene and other small olefins as well as CO [47]. These reactions account for the high olefin yield at high temperature in a more direct way than at low temperature, where more oxygenated intermediates are preserved. Finally, steam cracking of glycerol and all of the dehydrated species may produce CO and H_2 at high temperature, and the WGS reaction also can produce more H_2 as well as CO_2. The additional reactions to Fig. 6 that directly produce CO, CO_2, and H_2 are then

$$C_xH_yO_z + (x - z)H_2O \rightarrow xCO + (y/2 + x - z)H_2 \tag{4}$$

and

$$CO + H_2O \rightarrow CO_2 + H_2. \tag{5}$$

3.5. Energy balance for acrolein production

The FCC unit is attractive because the heat necessary for the reaction is generated readily within the process. In state-of-the-art units, 3–5% of the feed is converted to coke, which is burned in the regenerator, generating sufficient heat to vaporize the feed and support the endothermic reaction. Compared with VGO cracking, the processing of glycerol solutions requires that more water to be vaporized per unit of feed, thus increasing the heat requirement (and hence the coke yield) per kg of feed processed.

To calculate the amount of coke that must be burned to maintain the process autothermal, we need the following parameters:

- The heat capacity and the heat of vaporization of the glycerol solution, as well as the temperature of the feed and of the

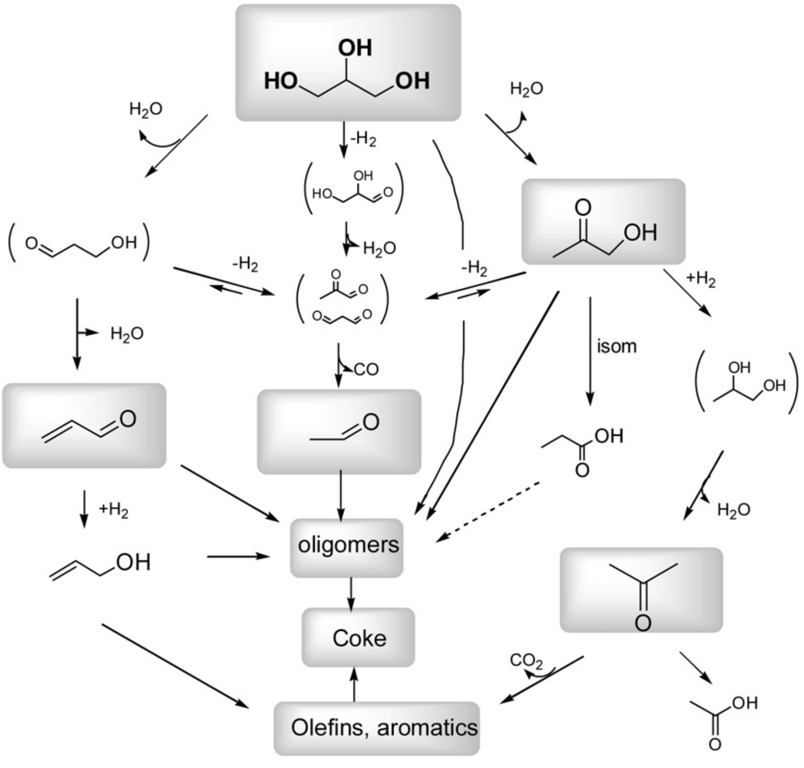

Fig. 6. Proposed general glycerol conversion scheme. Reactant and main reaction products have been highlighted.

Table 8
Coke yield compared with heat balance needs

Glycerol dilution	% coke yield on feed	% coke on carbon in feed
20 wt%	7.9	101
50 wt%	6.3	32
85 wt%	3.7	11

process, to estimate the heat requirement to vaporize and heat up the glycerol solution;

- The heat of combustion of coke;
- The enthalpy of the reaction and the conversion.

We assumed a feed temperature of 70 °C and a reaction temperature of 350 °C. The heat of combustion (complete combustion) is 31,500 kJ/kg for carbon and 115,000 kJ/kg for hydrogen, and we assumed 8 wt% hydrogen in coke. The reaction enthalpy was estimated to be slightly endothermic (10 kJ/mol). In any case, an enthalpy value of 100 kJ/mol would not change the results significantly, because this value is very small compared with the vaporization and heating needs. Finally, the glycerol conversion was considered complete. Calculations based on the foregoing assumptions led to the results presented in Table 8.

We calculated the theoretical coke yield (referred to the amount of feed) needed to maintain the autothermal process for several glycerol concentrations and compared this value to the amount of carbon (39.1% carbon in glycerol) present in the feed. Table 8 shows that processing diluted solutions of glycerol would require burning an amount of coke similar to the amount of carbon present in the feed; thus, to keep the process autothermal, all of the carbon would be converted to coke, and hardly any valuable chemicals would be formed. Consequently, an external heat source is needed in this case. In contrast, with concentrated solutions, such as those produced directly during the transesterification of oils, the autothermal process would require conversion of only 10% of the carbon present in the glycerol to coke, a yield similar to the experimental yield obtained in previous tests at 350 °C with a ZSM5-based catalyst. Thus, the processing of concentrated glycerol solutions obtained from the synthesis of FAME could be carried out in an autothermal process, without the need for external heat.

3.6. Costs, challenges, and future directions

We obtained a 58% carbon acrolein yield, or 28 wt% acrolein yield, with an 85 wt% glycerol feed. Typical yields for acrolein production from propylene oxidation are around 85% mol; that is, ca. 900 kg of propylene (combined with oxygen from air) is needed to obtain 1 ton of acrolein. With feedstock costs of 1000 $/ton for propene and 300 $/ton for glycerol solution, the feed cost for the glycerol-based process (1120 $/ton of acrolein) is close to that for the propene-based process (900 $/ton of acrolein). These calculations show that acrolein production from crude glycerine from a biodiesel plant is already nearly competitive with acrolein produced from propylene oxidation based on feedstock costs, with a safer and less energy-intensive process. The price of acrolein from glycerol can be further improved through further process improvements to achieve higher yields of acrolein (with a theorical maximum of 52 wt% from the raw glycerol solution). Any carbon emission credit obtained from the use of a renewable stock (e.g., glycerol from biomass) can further improve the economics of the process. In addition, significant amounts of acetaldehyde also can be recovered, adding more commercial value. Moreover, the acrolein-to-acetaldehyde ratio can be readily changed by shifting the process temperature.

As shown in Fig. 6, glycerol readily yields acrolein through dehydration; thus, the theorical maximum carbon selectivity is 100%. Increasing the acrolein selectivity requires minimizing any secondary reaction that leads to hydrogenated products or coke—that is, limit the amount of hydrogen transfer.

4. Conclusion

In this paper, we have demonstrated how dehydration on a zeolite-based catalyst in a moving-bed reactor can be used to produce acrolein and other oxygenated chemicals from glycerol. These oxygenated compounds are typically produced from the oxidation of nonrenewable petroleum derived feedstocks. The process is based on standard FCC technology. We used a moving-bed reactor (Microdowner reactor) and a fixed-bed reactor (Microactivity test reactor) to test an equilibrated FCC catalyst (ECat) and a ZSM5-based catalysts at temperatures of 290–650 °C and catalyst residence times of 0.5–30 s. The microdowner reactor simulates the industrial fluid catalytic cracking process. The highest yield of acrolein (55–61% molar carbon yield) was obtained at 350 °C with the ZSM5 zeolite-based catalyst, at low catalyst-to-oil ratios (6–11) and contact times of 0.5–2 s, which correspond to weight hourly space velocities of 300–1300 h^{-1}. Water did not significantly influence the yield of acrolein, and we were able to obtain high yields of acrolein (55% and 62%) with aqueous glycerol solutions ranging from 20 to 85 wt% glycerol. Increasing the temperature from 350 °C and 500 °C caused a partial shift toward the production of acetaldehyde. The advantage of using a moving-bed reactor is that the catalysts can be continuously separated and regenerated while producing the energy to keep the reaction. Future improvements to catalyst and process improvements promise to achieve higher yields of oxygenates.

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