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Catalytic cracking of glycerol to fine chemicals over equilibrium fluid catalytic cracking catalyst

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Abstract

Effective conversion of glycerol into fuels and chemicals is an emerging field in terms economic viability of first generation bio-fuels development. In the present work the refinery fluid catalytic cracking (FCC) process is used to convert the biomass-derived glycerol into possible fine chemicals through a series of reactions like dehydration, cracking and hydrogen transfer. The catalytic cracking of biomass–derived glycerol have been carried out using industrially available fluid catalytic cracking equilibrium catalyst (E-CAT) in an advanced cracking evaluation (ACE-R) FCC unit for temperatures ranging from 350 to 550 ^{0}C. The catalyst-to-oil (C/O) ratio was kept constant at 5 wt.%. At higher temperatures (430-550 ^{0}C) 100% glycerol conversion and 50% of acetaldehyde yield was obtained with E-CAT. The maximum yield of acrolein was found to be 7.61% at 430 °C temperature; whereas the yield of acetaldehyde was increased with increase in temperature and it was higher at 550 °C. The gas and liquid products have been analyzed using gas chromatography (GC) and nuclear magnetic resonance (NMR) spectroscopy techniques, respectively. Carbon dioxide produced in the regeneration process was analyzed using infrared (IR) spectroscopy. Further in the liquid product, in addition to acetaldehyde and acrolein, light olefins and aromatics were also found.

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Keywords: Glycerol; acetaldehyde; acrolein; ACE-R; fluid catalytic cracking; E-CAT.

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1. Introduction

The growing demands of energy sources from fossil fuels lead to search for alternative energy resources. Increasing demand of fossil fuels and limitation of their resources has led to development of bio-fuels, such as biodiesel, ethanol, bio-oils, etc., made from renewable feedstock. Biodiesel is a first generation biofuel. The global production capacity of biodiesel has reached up to 11930 million liters (in 2012) [1]. Biodiesel is being produced from transesterification reaction of vegetable oils (edible or non-edible oils) with methanol in the presence of a catalyst. During the transesterification reaction the significant amount (~10 wt.%) of glycerol is produced as a byproduct. Glycerol has been the raw material for the production of several fine chemicals, such as: acrolein via dehydration [4]; 1,2 propanediol via hydrogenolysis [6]; 1,3 propanediol via fermentation [7]; glycerol carbonate via carboxylation [8]; glycerides via esterification [9]; syngas via reforming [3]; dihydroxyacetone via oxidation [5]. Till date there are more than 1500 direct applications of glycerol have been reported in food, cosmetics and pharmaceutical industries worldwide [2]. The major application of acrolein is in the production of a nutritional supplement, dl-methionine for animal feed and sodium ployacrylate for super-absorbent polymer. The acetaledehyde is generally used as a chemical intermediate in the synthesis of other chemicals.

In recent years, the dehydration of glycerol over acid catalysts in liquid and gas phase has received a huge attention [11]. During the acrolein polymerization and liquid phase dehydration of glycerol, the glycerol conversion is limited by the by-product formation and the catalyst deactivation due to coke formation. However these limitations can be accounted by the catalyst that can be easily regenerated. This problem can be easily addressed by adopting the conventional refinery fluid catalytic cracking reactor (circulating fluidized bed reactor), where there is possibility of continuous regeneration along with reaction. Corma et al. [10] carried out catalytic conversion of glycerol aqueous solution mixture in a micro downer (FCC type) reactor over H-ZSM-5 zeolite-based catalyst. They observed increase in the acetaldehyde yield with increase in temperature from 350 to 500 ^0C, and obtained 58wt.% acrolein yield at 350 $^\circ$C temperature. Kartryniok et al. [11] reported that the dehydration of glycerol in gas phase over zeolite (H-ZSM-5, H-ZSM-11 and H-b) catalysts give acrolein selectivity in the range of 70–83% at lower temperatures, ranging from 330 to 360 $^\circ$C. The parallel reaction pathways for glycerol dehydration over heterogeneous catalyst towards hydroxyacetone or acrolein or acetaldehyde/formaldehyde was reported by Yadav et al. [12]. Zhao et al. [13] reported that higher temperatures lead to increase in higher yields of acetaldehyde.

The present study aimed to convert the biomass–derived glycerol into possible fine chemicals (such as acetaldehyde, acrolein, etc.). The glycerol conversion is carried out by operating conventional fluid catalytic cracking process in a block operation mode at various temperatures and at constant catalyst-to-oil ratio. The gas and liquid products were analyzed with gas chromatography and nuclear magnetic spectroscopy.

2. Materials and methods

In the present work the catalyst used was an industrially available equilibrium catalyst, E-CAT. E-CAT is comprised of Y-zeolite in a silica-alumina matrix mixed with a clay binder and a FCC additive based on ZSM5 zeolite. Table 1 show the properties of the E-CAT used in the present work. The biomass-derived glycerol used was laboratory grade glycerol (98%, Sigma-Aldrich Chemicals). All chemicals (such as tetramethylsilane, DMSO, etc.) used in GC and NMR analysis were of analytical grade. The experiments for catalytic cracking of glycerol were carried out on an Advanced Cracking Evaluation (ACE-R) unit fabricated by M/s. Kayser Technology Texas (USA). The schematic diagram and experimental setup of ACE-R unit is shown in Figures 1 and 2, respectively. The experimental facility was equipped with an automated fixed-fluidized bed reactor. For each experiment a constant amount of catalyst (~9 g) was loaded. The catalyst-to-oil ratio was maintained by adjusting the injection times of feedstock.

The catalytic cracking of biomass-derived glycerol was carried out at atmospheric pressure and temperature ranging from 350 to 550 $^\circ$C. The catalyst was stripped off by nitrogen for a period of multiple of 7 times of injection time. During the catalytic cracking and stripping process the liquid product was collected in a glass receiver, which was located at the end of the reactor exit and was maintained at –10 $^\circ$C temperature.

The gaseous products were collected in a gas receiver by water displacement method. The gas products were analyzed using a refinery gas analyzer (GC Agilant 7890A) equipped with three detectors, a flame ionization detector (FID) and two thermal conductivity detectors. After the completion of stripping process, the in-situ catalyst regeneration was carried out in the presence of air at 700 ^0C temperature to measure the amount coke deposited on the catalyst surface. The carbon monoxide was converted into carbon dioxide in a catalytic converter, which was operated

at 540 ^{0}C temperature. The coke deposited on the catalyst is burned with air in regeneration mode. The resulted total carbon dioxide was analyzed using IR spectroscopy.

Table 1. Properties of equilibrium fluid catalytic cracking catalyst.

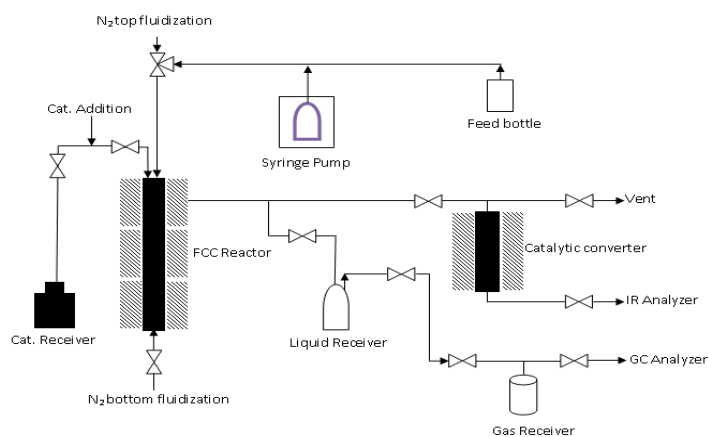| Properties	E-CAT
SiO_2 (wt.%)	39.05
Al_2O_3 (wt.%)	20.8
Na_2O (wt.%)	0.3124
Ni (ppm)	762
V (ppm)	57
Fe (ppm)	4182
Cu (ppm)	459
Surface area, m^2/g	171

Fig. 1 Schematic diagram of advanced cracking evaluation (ACE-R) FCC unit

Fig. 2 Experimental setup for fluid catalytic cracking (ACE-R) unit

Chemito 1000 gas chromatography equipped with polar column HP INNOWAX (15m×0.53mm i.d×1.0μm film

thickness) was used to measure the liquid products. The liquid samples were also characterized by a set of NMR experiments like ^{1}H, ^{13}C, DEPT-45, 90 and135, Quat. To have a detailed understanding about the structural connectivity between groups, two dimensional hetero-nuclear correlation techniques like ^{1}H-^{13}C HMQC, ^{1}H-^{13}C HMBC were used. A Bruker Avance III NMR spectrometer was used to record the ^{1}H and ^{13}C NMR spectra. The NMR spectrometer was equipped with a 5mm-mm BBFO probe resonating at the frequency of 500.13 and 125.7 MHz, for ^{1}H and ^{13}C respectively. The conventional ^{1}H spectra were carried out using 5% w/v sample solutions in DMSO d6 containing 0.03%TMS (99.8% Merck) with a sweep width of 6KHz, 16 number of scans, 13.4-μs $\pi/2$ ptoton pulse and 2-s relaxation delay.

The ^{13}C NMR spectra of the sample were recorded using 30% (w/v) in DMSO –d6 solutions. The quantitative ^{13}C spectra were acquired using NOE suppressed inverse gated proton decoupled technique (Waltz-16) , with a sweep width of 19 KHz. Using a 5–s delay 8K number of scans were collected. Chemical shifts were referenced to tetramethylsilane (TMS; $\delta = 0.00$ppm). The DEPT experiments were carried out at pulse angles of $3\pi/2$, using pulse sequences as reported by Bandall and Pegg [16]. In these experiments $\pi/2$ pulse width used for ^{1}H and ^{13}C were 13.4 and 9.9 μs respectively. J_{CH} values were set to 145 Hz, an intermediate value between aliphatic, aromatic and oxygenated carbons. The relaxation delays are 2 for DEPT experiments, respectively. 2K numbers of transients were acquired for DEPT experiments and 4K number scans were acquired for QUAT spectra.

3. Results and discussion

The conversion of biomass-derived glycerol over equilibrium FCC catalyst was 100 w/w% for the temperatures ranging from 470 – 550 °C. in fluid catalytic cracking unit. However, at lower temperatures, i.e. 350 and 390 °C, unconverted glycerol was found, therefore the conversion decreased at lower temperatures. The coke yield was increased from 7.7 to 10.4 wt.% with decrease in temperature from 550 to 350 °C. The different products formed during the fluid catalytic cracking of biomass–derived glycerol were analyzed using gas chromatographic and are listed in Table 2. Acetaldehyde, acrolein, 1,2-propanediol, and unconverted glycerol were observed in the liquid products, while carbon dioxide, methane, ethane, ethylene, propane and propylene were found in the gas products.

It was observed that the acetaldehyde yield increases from 18 wt.% to 53 wt.% with increase in temperature from 350 to 550 °C. The maximum acrolein yield was observed at lower temperature, i.e. 430 °C. The present experimental results were in good agreement with the experimental findings of Corma et al. [10]. The carbon dioxide yield was also increased from 4.2 to 7.7 wt.% with increase in temperature, which indicates that equilibrium FCC catalyst is also effective for dehydration as well as decarboxylation reactions in addition to cracking. Further the increasing trend of ethylene (from 0.17 to 1.5 wt.%) and propylene (from 0.59 to 2.9 wt.%) yields were observed with increase in temperature.

Table 2. Effect of temperature on product yields based on GC at catalyst–to–oil ratio of 5

Temperature. °C	Glycerol Conversion, %	Coke Yield, wt.%	Yield, wt.% (GC identified)			
			Acetaldehyde	Acrolein	1,2-propanediol	Glycerol
350	94.3	10.4	18.88	3.24	4.35	5.7
390	98.3	9.8	22.38	6.44	3.64	1.7
430	100	9.2	29.36	7.61	2.31	<1
470	100	8.6	50.49	5.09	Nd	<1
510	100	8.2	52.32	4.07	Nd	<1
550	100	7.7	53.33	3.14	Nd	<1

Further, acetaldehyde and acrolein were also identified from 1D 1H, 13C, 1H-1H COSY, 1H-13C HMQC and 1H-13C HMBC NMR, and quantified from quantitative NMR. Figure 3 shows the qualitative analysis of acetaldehyde and acrolein.

Figure 4 shows the acrolien yields analyzed using both gas chromatography as well as 2D nuclear magnetic spectroscopy. I can be seen from Figure 4 that at lower temperature, i.e. at 470 ^{0}C, the deviation between both the analysis was approximately 40%. However, at higher temperature, i.e. 510 and 550 ^{0}C, the deviation in the yield from both the analysis was within ±10%.
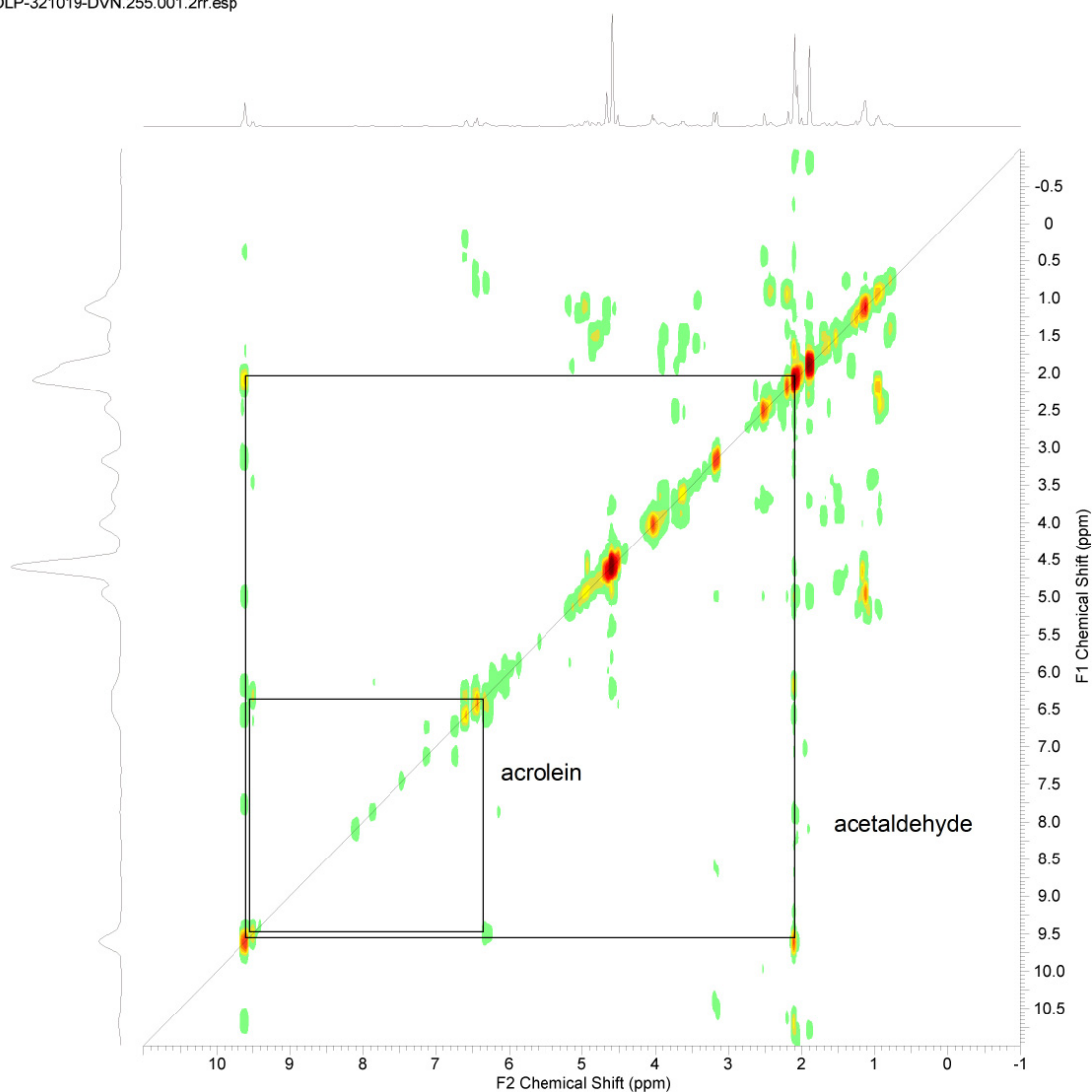
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Fig. 3 Qualitative analysis of acetaldehyde and acrolein at 470°C temperature

4. Conclusion

In the present work the fluid catalytic cracking of biomass-derive glycerol was carried out for temperatures ranging from 350 to 550 ^{0}C. At higher temperatures, 100% glycerol conversion and more than 53% of acetaldehyde yield was achieved by operating a fluid catalytic cracking process in block operation mode. It was observed that the yield of acetaldehyded increases with increase in temperature at catalyst-to-oil ratio of 5wt.%, whereas maximum yield of acrolein, i.e. 7.6%, was obtained at lower temperature, i.e. 430 °C. The yield of acrolein was analyzed using both gas chromatography and nuclear magnetic spectroscopy, and the results were found in good agreement at higher temperatures. The findings from the present work indicated that the existing refinery FCC process can be effectively utilized for the production of acetaldehyde from glycerol using commercial equilibrium FCC catalyst at the cost of higher coke deposition. However, the catalyst deactivation due to coke deposition could be sorted out by regenerating catalyst in a regenerator.
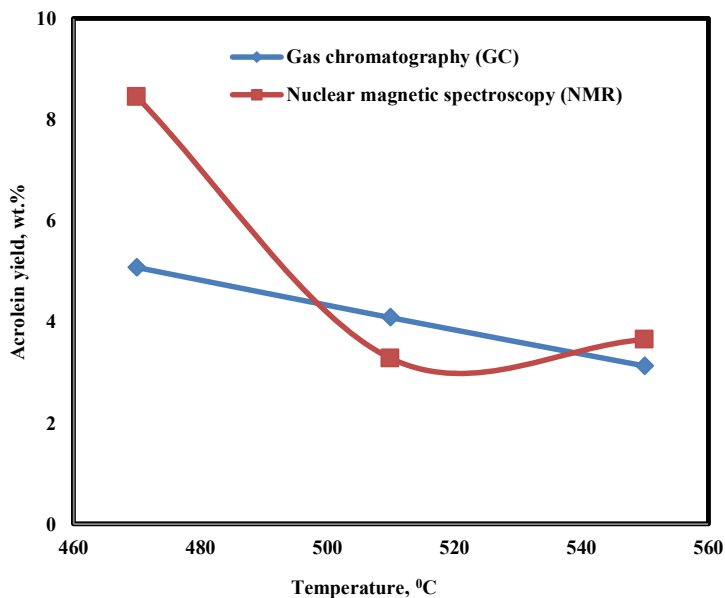
Fig. 4 Comparison of acrolein yield from GC and 2D-NMR

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