



Conversion of glycerol to light olefins and gasoline precursors



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ABSTRACT

We explore a glycerol-to-olefins process in a reactor containing dehydration, hydrogenation, and upgrading stages in series. Glycerol, co-fed with H₂ over HZSM-5 (1.0 g, Si/Al = 11.5, 400 °C), was first dehydrated to yield a mixture of acetaldehyde, acrolein, and hydroxypropanone. Acrolein was hydrogenated to propanal over a Pd/α-Al₂O₃ catalyst and the effluent was passed to a third stage which served to further upgrade propanal to olefins. Rapid third stage deactivation was observed, although, we obtained a maximum 70% yield of light olefins from a propanal stream reacted over HBEA (0.5 g, 500 °C) with minimal CO production. A decrease in propanal conversion and C_{2–3} olefin yield was observed along with a corresponding increase in C_{4–5} olefin yield as time-on-stream increased to 150 min. We conclude that propanal condensed over Brønsted acid sites to form C_{4–5} olefins, which subsequently cracked at high conversion to form C_{2–3} olefins. Increasing the temperature from 400 to 500 °C also decreased the C_{4–5} olefin yield from 13 to 9% while increasing C_{2–3} olefin yield from 4 to 15%. C–C bond formation occurred during glycerol upgrading in a staged reactor configuration and negligible carbon is lost as CO.

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1. Introduction

Global energy challenges have led to increased interest in the development of renewable carbon-based fuels such as biodiesel as a replacement or supplement for conventional fossil fuels. Process efficiency, however, is limited by the ~10 wt% of crude glycerol that is obtained as a byproduct of conventional biodiesel production processes [1,2]. Supplanting only a small percentage of petroleum diesel usage with biodiesel would result in an oversupply of glycerol [2] creating an economic obstacle that could prevent wide-spread biodiesel production. Significant research has been devoted to finding new markets for glycerol in an attempt to surmount the glycerol surplus obstacle and help make biodiesel production more economically viable [2]. Additionally, glycerol is a simple sugar and can function as a surrogate for glucose in carbohydrate conversion to hydrocarbons research. While new processes are being explored to convert glycerol into products such as ethers [3], ethanol [4], 1,2-propanediol [5], syngas [6], and aromatics [7], one process that has received less attention is olefin production. Light olefins such as ethylene and propylene are common polymer precursors while C_{4–6} olefins can be used in alkylation reactions to produce gasoline-range hydrocarbons through methods such as the Mobil Olefin to Gasoline/Distillate process [8]. Zakaria et al.

obtained a maximum 15% olefin yield from glycerol at 600 °C and 105 h⁻¹ over Cr/HZSM-5 and Cu/HZSM-5 [9]. Corma et al. obtained a maximum 30% yield of ethylene and propylene at 700 °C over HZSM-5 at 30 s on stream in a microactivity test reactor [10], but with 42% of carbon lost as CO. We explore the possibility of developing a tunable process capable of converting glycerol to even higher yields of C_{2–6} olefins with minimal CO production in the interest of finding new pathways for glycerol consumption.

The process we explore utilizes glycerol dehydration and hydrogenation of the ensuing products to form propanal that is further upgraded to olefins by aldol condensation, a reaction that can produce liquid alkanes by C–C bond formation [11]. Glycerol dehydration has been studied in the liquid phase [12,13] and gas phase [7,14,15]. We chose to carry out glycerol dehydration using zeolites because vapor phase glycerol dehydration tends to yield acrolein yields greater than 50% that are stable for more than 2 h on stream [7]. For example, Hoang et al. obtained a 60% yield of acrolein from glycerol at 100% conversion over HZSM-5 at 400 °C, 2 h⁻¹, 2 MPa, and 3 h on stream [7]. The products of glycerol dehydration over HZSM-5 did not react with each other at times on stream greater than 250 min resulting in a stable product output. We have identified experimental conditions to aid us in developing a method of processing glycerol into high yields of olefins at temperatures where dealumination is not as predominant, requiring less frequent catalyst replacement. We demonstrate one such approach using a three-staged reactor. The first stage contained a zeolite such as HZSM-5 which served as a glycerol dehydration catalyst, producing stable yields of acrolein and acetaldehyde. A second stage containing a noble metal catalyst, operating at a lower temperature, served

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as a hydrogenation catalyst to convert acrolein to propanal. A third stage containing HBEA catalyzed the propanal aldol condensation. We also show that a propanal stream in the absence of acetaldehyde fed to HBEA can be converted to ethylene and propylene with yields of up to 70%. Thus, we demonstrate a prototypical tunable system capable of converting glycerol \rightarrow propanal \rightarrow olefins assuming removal of acetaldehyde at low temperatures with higher yields.

2. Materials and methods

2.1. Catalyst preparation

The catalysts used were prepared in the same manner as described previously [16,17]. The zeolites used were HBEA (CP814E*; Si/Al = 12.5) and HZSM-5 (CBV 2314; Si/Al = 11.5). Samples of 1 wt% Pt and Pd were prepared from H_2PtCl_6 (8 wt% in H_2O , Sigma Aldrich) and PdNO_3 (4.1 wt% in H_2O , Sigma Aldrich) respectively on $\gamma\text{-Al}_2\text{O}_3$ (Alfa Aesar) and $\alpha\text{-Al}_2\text{O}_3$ (Mager Scientific) supports. Pd and Pt on both $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ were prepared by identical incipient wetness techniques as discussed previously [16,17].

2.2. Apparatus and analytical methods

The three-stage reactor system was constructed, as shown in Fig. 1, from three quartz tubes (10 mm OD) connected in series. Catalyst particles were situated in each tube between a back-face ceramic foam monolith ($\alpha\text{-Al}_2\text{O}_3$, 80 pores per linear inch) and a quartz wool plug front-face. The first stage catalyst contained HZSM-5 (1.0 g), the second stage contained either Pt or Pd impregnated on either $\alpha\text{-}$ or $\gamma\text{-Al}_2\text{O}_3$ pellets (1.0 g). The third stage contained 0.5 g of HBEA. The entire assembly was wrapped with heating tape and 1/16" thermocouples (Omega K-type Inconel) were inserted at the back-faces of each catalyst stage and used to control the temperature with Omega CSC32 Benchtop Controllers. The first and second stage thermocouples were sealed to prevent leakage while the third stage thermocouple was inserted through the reactor outlet. N_2 and H_2 were fed at 1.5 and 0.5 standard liters per minute (SLPM) respectively through a stainless steel nebulizer consisting of concentric 1/8" and 1/16" tubes by mass flow controllers (MKS Mass-Flo) along with $40\ \mu\text{L}\ \text{min}^{-1}$ of glycerol by a Valco M50 pump. The nebulizer was inserted through a quartz annulus and 0.2 SLPM of Ar was fed from upstream of the annulus to prevent flow of glycerol vapor back through the

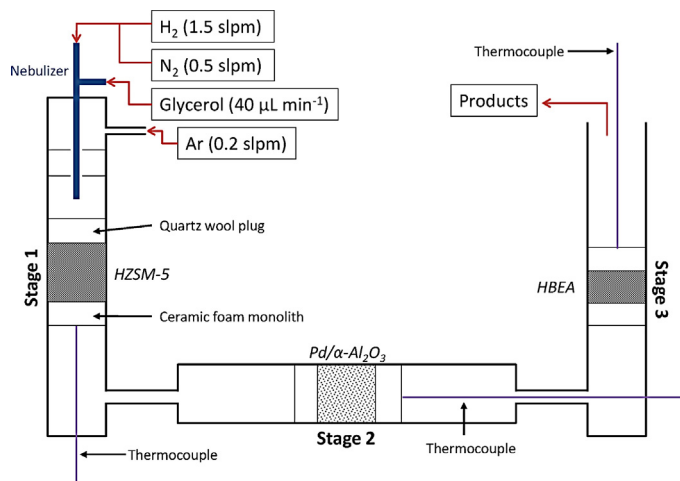


Fig. 1. Staged reactor schematic used for a glycerol feed.

reactor. A reactor configuration identical to the one used by Blass et al. [16] was used for experiments using a pure propanal feed ($57.3\ \mu\text{L}\ \text{min}^{-1}$) with an additional 0.2 SLPM of CH_4 fed as an internal standard. Staged reactor product analysis was carried out on a HP 6890 gas chromatograph (GC) equipped with a HP PLOT/Q column ($30 \times 0.32 \times 20$) and TCD and FID detectors in series. Product identification was aided by a GC/mass spectrometer (HP 5890 GC/5970 MSD, He carrier). Experiments with a pure propanal feed were analyzed on a HP 5890 GC containing an Alltech Heliflex capillary AT-1 column ($60 \times 0.32 \times 1.0$) and an FID detector. Mass balances closed to within 15%.

2.3. Experimental procedure

As glycerol was fed to the first stage, samples were analyzed on a GC at 20 min intervals until 160 min on stream. For experiments with two stages, the first stage was aged for 20 min with glycerol prior to introducing additional stages to ensure a steady state production of acrolein and acetaldehyde without aromatics formation that occurs at smaller times-on-stream. After aging, the glycerol feed was turned off and restarted after the additional stages were connected and heated. Hydrogenation of glycerol dehydration products was carried out over Pt or Pd on $\alpha\text{-}$ or $\gamma\text{-Al}_2\text{O}_3$ from 100 to $300\ ^\circ\text{C}$ at 10 and 30 min on stream. The product spectrum was analyzed at the end of each experiment to ensure that the first stage remained at steady state throughout the duration of the experiment. After each experiment, the second stage was removed from the apparatus and separately regenerated at $500\ ^\circ\text{C}$ with 1.0 SLPM of N_2 and 0.1 SLPM O_2 for 30 min to burn off any coke that formed. The O_2 feed was replaced with 0.1 SLPM of H_2 for an additional 30 min to reduce the catalyst. The first and third stage catalysts containing zeolites were replaced and not regenerated after deactivation.

3. Results and discussion

3.1. Glycerol dehydration (one stage)

Previous attempts to convert glycerol to olefins have not produced olefins with yields greater than 30%. As described above, Corma et al. obtained a 30% yield of ethylene and propylene from glycerol in a microactivity test reactor at $700\ ^\circ\text{C}$, $30\ \text{h}^{-1}$ and 30 s on stream [10]. However, dealumination of the zeolite can occur at these conditions [18,19] requiring frequent catalyst replacement. As a baseline, we show in Fig. 2 the results of glycerol dehydration over HZSM-5 at $500\ ^\circ\text{C}$. The acrolein and acetaldehyde yields reached a steady state of approximately 68% and 30%, respectively, by 100 min on stream. Complete glycerol conversion was observed for the entirety of the experiment and is outlined stoichiometrically in Eq. (1).

It is unlikely, however, that steady-state yields of acrolein and acetaldehyde are possible due to the likely creation of a staged bed at 100% conversion. A 20% yield of C_{2-4} olefins was obtained at 20 min on stream but the yield decreased to 5% by 60 min and became negligible for the remainder of the experiment. At $500\ ^\circ\text{C}$ and 20 min on stream, 30% aromatics were formed from glycerol dehydration. The aromatics yield became negligible by 40 min on stream with only acrolein and acetaldehyde remaining suggesting that acrolein and acetaldehyde can undergo further cyclization and dehydrogenation to form aromatics. Hoang et al. obtained an initial 40% aromatics yield and 17% light olefin yield over HZSM-5 at $400\ ^\circ\text{C}$ and $0.1\ \text{h}^{-1}$ [7]. They observed that both aromatics and olefin yields became negligible over time while acrolein and acetaldehyde yields increased to steady state values of $\sim 80\%$ and 20%, respectively.

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