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# REACTIVE EVAPORATION OF CRUDE GLYCEROL IN A FLUIDIZED BED REACTOR

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**Abstract:** Crude glycerol is a co-product of the trans-esterification of vegetable oils to biodiesel that usually contains as much as 5% salt. Processing the glycerol to value added products may require an expensive distillation step. In this work, we propose a new process in which crude liquid glycerol is fed directly to a fluidized bed in which it vaporizes then reacts to form acrolein over a tungsten doped zirconia catalyst. The salt in the crude glycerol crystallizes and accumulates in the fluid bed and may attrit with time to be collected overhead with cyclones and filters. The focus of this work has been to evaluate the effect of salt on catalyst activity as well as its attrition resistance, which is a critical operating parameter for a commercial reactor. There was little evidence to suggest that the salt crystallizes in the interior of the catalyst particles – after one day of continuous operation, catalyst activity remained stable. Tests on a standard air jet mill suggest that the mechanical stresses typical in a fluidized bed will be sufficient to attrit the salt and thus minimize its accumulation in the reactor with time.

**Keywords:** Reactive vaporization, Fluidized bed, Crude glycerol, Acrolein, Attrition, Tungsten doped zirconia

## 1. INTRODUCTION

Renewable feedstocks have taken centre stage as a compliment to traditional fossil energy sources. Bio-diesel is an interesting alternative energy vector but glycerol and salt are major co-products in the standard trans-esterification of vegetable oil. The production of bio-diesel is growing as is the glycerol consequently the price for glycerol has dropped considerably due to an oversupply. Many new processes that use glycerol as a primary feedstock are still in the development stages and a couple have proceeded to commercialization. Although crude glycerol is inexpensive, the processing costs to separate the salt and water from the glycerol through distillation are considerable since the boiling point of glycerol is 290°C. New processes based on glycerol appear very attractive due to its low cost but may be unattractive due to the high cost of separation.

Recent developments using glycerol as a primary feedstock include the selective oxidation to glyceric acid (Garcia et al., 1995; Dimitratos et al., 2006) tartronic acid (Gallezot, 1995), dihydroxyacetone (Ciriminna et al., 2006) and ketomalonic acid (Ciriminna and Pagliaro, 2003). Oxygenates are valuable fuel additives since glycerol is non volatile and thus may not be added directly to fuel (Liotta et al., 1994). The conversion of crude glycerol into propylene glycol based on hydrogenolysis is also an interesting opportunity (Dasari et al., 2005) and ADM is pursuing the commercialization of this process. In the reforming process, glycerol, in the aqueous phase, is converted into hydrogen and carbon monoxide (syngas). Syngas is a primary feedstock for of fuels and chemicals via Fischer-Tropsch or, alternatively, for methanol synthesis (Soares et al., 2006). Glycerol can be used as a feedstock for fermentation of one of the primary components of Sonora and Corterra polyester fibers (Lin, et al, 2005). Glycerol carbonate can serve as a source of new polymeric materials such as glycidol, component in the production of a number of polymers (Rokicki et al., 2005). Epichlorohydrin can be synthesized from glycerol by a catalytic reaction with HCl followed by dehydrochloranition with NaOH. A commercial plant is to be built by

Solvay to produce epichlorohydrin with  $\text{Ca}(\text{OH})_2$ . A recent study reported a route to produce the bioplastic PHB by fermentation from crude glycerol (Mothes et al., 2007). Another investigation proposed crude glycerol for atmospheric autocatalytic organosolv pretreatment (AAOP) to enhance enzymatic hydrolysis (Sun and Chen, 2008). Other likely chemicals for development include tetrahydrofuran, acrolein (Holderlich and Dubois, 2008) and acrylic acid (Dubois and Patience, 2008).

Some laboratory-scale experiments of acrolein production from glycerol have been recently published in the literature (Chai et al., 2007; Corma et al., 2008; Ning et al., 2008; Ott et al., 2005; Pagliaro et al., 2007; Tsukuda et al., 2007; Watanabe et al., 2007). In these studies, good selectivity of acrolein has been reached for different catalysts and operating conditions. For example Ott et al. (2005) reached a yield of 40% with zinc sulfate in SCW. However, the tests were performed using purified glycerol as the reactant while crude glycerol produced by the biodiesel industry is generally contaminated by salt and water.

Studies in the open literature on the influence of salt impurities on the catalyst structure, which makes it difficult to develop process using crude glycerol as a feedstock, have yet to be reported. Different hypothesis can be formulated on the influence of salt impurities on the catalyst structure and performance. On the one hand, the salt impurity in crude glycerol can migrate into the catalyst pores and destroy the catalyst structure, which decreases the catalyst activity and reaction selectivity. On the other hand, the salt may deposit on the catalyst surface while the glycerol goes into the catalyst pores to react. Also, due to the high mechanical stresses in fluidized bed, the salt is expected to attrite and to be captured in filter downstream.

The understanding of the influence of salt impurities is necessary to develop processes for the acrolein production using crude glycerol as feedstock. For that purpose, the objective of this work is to characterize the influence of salt on the catalyst structure for the acrolein production. More specifically, it consists of determining if the salt crystallizes on the catalyst surface and can then be removed by attrition or if the salt migrates into the catalyst pores in a reactive vaporization of crude glycerol process.

## 2. EXPERIMENTAL

### 2.1 Glycerol dehydration

To study the vaporization of crude glycerol, three types of experiments were conducted. All catalytic testing was carried out in a Hastelloy C-276 vessel 41 mm in diameter and 790 mm tall. The reactor was immersed in an electrically heated sand bath (30 A) to maintain near isothermal conditions. The axial temperature gradient was monitored with a 10-point thermocouple positioned equidistant along the height. The temperature was constant along the bed height but dropped substantially in the freeboard section, indicating that gas-phase product decomposition was minimal.

Crude glycerol was introduced to the reactor through a tube from the top of the fluid bed or together with a diluents gas at the bottom. The gases that enter from the reactor at the bottom passed through a line that was coiled around the circumference of the reactor in the sand bath to preheat the gas. It then entered the bottom of the reactor into a plenum and then through a sintered metal frit that distributed it evenly across the diameter. We tested various superficial gas velocities, but most experiments were conducted in the bubbling fluidized-bed regime with a solids bed height between 100 and 500 mm. A flanged upper section minimized solids entrainment to the top of the reactor, and a sintered metal filter retained all catalyst in the reactor.

Different feed configurations and compositions were explored. Salt would crystallize and block the inlet feed line when crude glycerol was fed together with nitrogen into the fluid bed below the grid. Blocking was also problematic when glycerol was fed through the top of the bed into the freeboard. For each experimental condition, a solution of glycerol in water was fed to the reactor at a specified gas velocity. The crude glycerol used in this work contained 4.8 wt % NaCl, 10% water and impurities including free fatty acids and sulfur and about 10% water.

A mixture of air and argon was preheated in the sand bath and introduced to the bottom of the reactor to fluidize the bed. Their flow rates were controlled with Tylan FC-2900V-4S flow controllers. The effluents rose through the bed

and passed a filter installed in the transport disengagement section. The effluents were subsequently condensed in distilled water and the salt concentration was measured using an electrical conductivity meter with 4 cell probe. The accumulated organics in the quench/absorber were sampled frequently and analyzed offline by high performance liquid chromatography (HPLC; Hewlett- Packard 1050) equipped with a variable-wavelength UV detector.

In the first experiments, the reactor was charged with spherical glass beads to investigate the salt deposition in the fluidized bed. A mass balance was carried out to confirm that the salt crystallizes in the reactor and remains with the solids. The second series of experiments involved VPO catalyst (vanadyl pyrophosphate  $(\text{VO})_2\text{P}_2\text{O}_7$ ) to determine if the salt remaining in the reactor deposits on the exterior surface of the catalyst and if it could easily be removed by mechanical attrition. The third series was conducted with a tungsten doped zirconia catalyst  $(\text{WO}_3)_{0.056}(\text{ZrO}_2)_{0.944}$  with DIKK trade name Z-1044). This was carried out to verify if the salt remaining in the reactor altered the structural properties of the catalyst particles, which would affect the reactivity or selectivity, or if the salt would remain on the exterior surface of the catalyst. Furthermore, the acrolein yield achieved with this catalyst was estimated.

In addition, after the second and third experiments the VPO and Z-1044 catalysts were characterized using SEM (Scanning Electron Microscopy) and EDS (Energy Dispersive Spectroscopy) techniques, allowing us to examine the catalyst surface and to determine its composition.

## 2.2 Attrition testing

An air jet attrition mill was designed to simulate the mechanical stresses inherent in a commercial fluid bed to examine whether or not the salt could be separated passively from the catalyst during normal operating conditions. The jet mill consists of an orifice 0.41 mm in diameter through which air is introduced at velocities of 230 m/s. The ensuing jet impinges on the particles causing the particles to collide at a high frequency causing attrition. As the particles attrit, the fines that are created are carried upward through a tube to an overhead filter. The attrited particles and the bed were analyzed by SEM and EDS.

In this work, the mill was loaded with 11 g of VPO sample which were on stream for 15 hours in the fluidized bed reactor. The jet impinged the particles for a period of 18 hours after which the mass of attrited particles in the thimble filter and particles in the jet cup was measured. Essentially, the vast majority of particles collected in the filters were salt crystals.

# 3. RESULTS AND DISCUSSION

## 3.1 Evaporation over glass beads

This experiment was conducted to confirm that the salt impurity in crude glycerol will remain in the bed while the glycerol is evaporated. The reactor was loaded with 150 g of glass beads. A solution of 5% (w/w) salt, and 45% glycerol in water at 0.5 ml/min with argon at 500 ml/min was fed to the reactor operating at 300°C for 2 hours. The off gases were condensed in water and electrical conductivity was measured. Based on conductivity measurements and a mass balance it was found that 99.8% of salt remained in the reactor – essentially all of the salt.

## 3.2 Evaporation over VPO catalyst

The fluidized bed was charged with 150 g of VPO catalyst. A solution of 20% crude glycerol in water was fed at a rate of 3 ml/min from the of the reactor into the bed of catalyst operating at 350°C. A 50/50 mixture of air and argon entered below the frit at the bottom of the reactor at a rate of 220 ml/min. The experiment was run for 15 hours and four catalyst samples were collected after 4, 8, 12, and 15 hours. For each catalyst sample, SEM photos were taken to visualize its surface and EDS was employed to determine the composition of the catalyst surface.

Initially, the VPO particles appear almost perfectly spherical. After four hours, the bridges form between particles and smaller particles are evident around these bridges at 8 hours. After 12 hours, large salt crystals – the size of the VPO catalyst are observable. Figure 2 shows the results of SEM pictures of the VPO before use and after 12 hours.

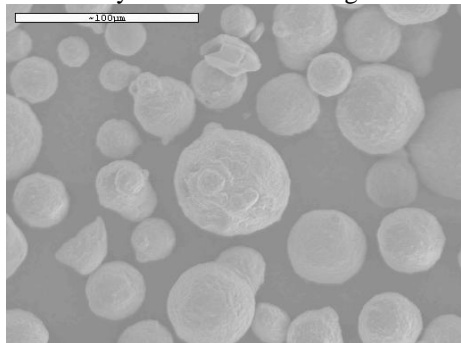


Fig. 1. VPO catalyst before use.

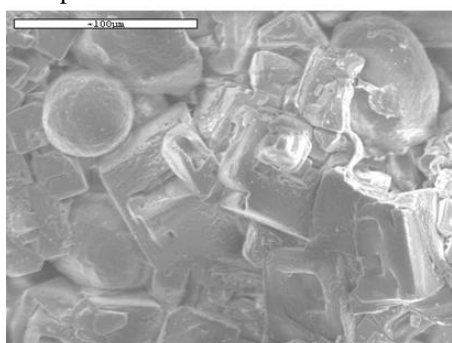


Fig. 2. Solids removed from fluid bed after 12 h.

The results of EDS measurements indicated that the concentration of the salt increased with increasing time in the fluid bed.

After 15 hours, the total salt introduced to the bed with the glycerol was approximately 27 g. A sample of 11 g of the VPO-NaCl mixture was loaded into the attrition mill. Fig. 3 illustrates the unattrited particles that remain in the mill after the 18 hour test with a scale of 200 μm. The attrited particles collected in the filter are shown in Fig. 4 with a four times higher magnification. Based on EDS measurements, there is a significantly higher concentration of Na and Cl in the thimble filter compared to the jet cup, which indicates that the salt is preferentially attriting. Furthermore, this result would indicate that the mechanical stresses typical of a fluid bed would be sufficient to separate the salt from the catalyst

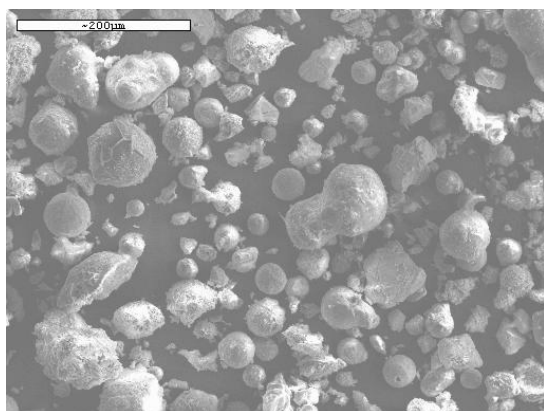


Fig. 3. Solids collected in the attrition mill after 18 h.

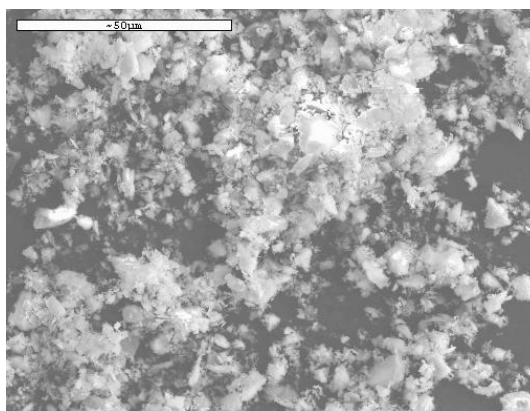


Fig. 4. Solids collected in the filter of the attrition mill.

### 3.3 Reactive evaporation over Z-1044 catalyst bed

In this experiment, the reactor was loaded with 150 g of Z-1044 catalyst. The experiment was conducted at an operating temperature 350°C during 24 hours. A solution of 20% crude glycerol in water (3 ml/min) was fed from the top to the bottom of the reactor and air (220 ml/min) and argon (220 ml/min) were preheated in the sand bath and entered the bottom of the reactor to fluidize the bed. Crude glycerol was evaporated reactively over Z-1044 catalyst and the acrolein yield was estimated. The outlet of the reactor was condensed in water and analyzed by Varian HPLC. The Chrompack column was maintained at 28°C and water was used as mobile phase for analysis.

The acrolein yield was calculated 25% at 350°C. It was constant throughout the course of the 24 hours. Samples were taken on an hourly basis and yield remained unchanged.

The catalyst particles were characterized by using FIB (Focus Ion Beam), EDS, and SEM techniques. In order to analyze inside the catalyst particles, the particles were cut with FIB and EDS was employed to measure the composition inside the particle. The concentration of Na and Cl were very low in the central part of the catalyst and it was much higher on the exterior surface indicating that migration of salt towards the centre was negligible.

#### 4. CONCLUSIONS

Evaporation of glycerol over an inert bed was experimentally investigated in this work. It was demonstrated that crude glycerol will evaporate in a fluidized bed reactor leaving behind salt crystals. This experiment demonstrates the potential to eliminate the salt content in crude glycerol from the products. The salt either will form a discontinuous layer on the surface of the catalyst particles or form crystals independent of the catalyst. Based on attrition testing in a jet mill, we showed that the salt was only loosely bound to the surface and detached from the catalyst with mechanical agitation typical of commercial fluid bed reactors.

Based on an extended experiment with a Z-1044 catalyst, glycerol appears to react with the catalyst unimpeded by the salt – that is, salt does not appear to block the pores of the catalyst or migrate to the interior to any great extent.

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