



Direct conversion of glycerol into bio-oil via hydrotreatment using supported metal catalysts



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HIGHLIGHTS

- Glycerol was converted to bio-oil via hydrotreatment over supported metal catalyst.
- High yields of bio-oils up to 40 wt.% were achieved with of MoCoP/zeolite catalyst.
- The obtained bio-oil has a HHV up to 33 MJ/kg.
- The obtained bio-oil consists of mainly substituted phenols and ketones.
- Acidic materials are more effective catalysts than basic or neutral materials.

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ABSTRACT

Hydrotreatment of glycerol (a byproduct of bio-diesel production) was conducted in the presence of a number of different supported metal catalysts at a temperature of 300 °C under 5 MPa initial pressure of H₂. The bio-oil products were comprehensively characterized to determine their physical/chemical properties. Experiments with supported catalyst metals revealed a positive correlation between support acidity and bio-oil yield. It was determined that MoCoP is the most effective combination of catalyst metals, and the bio-oil yield from hydro-treatment of glycerol with the MoCoP catalysts is strongly dependent on the support materials, following the trend of MgO < AC < Al₂O₃ < zeolite. With the MoCoP/zeolite catalyst, a maximum yield of ~40 wt.% bio-oil, and >90% glycerol conversion was achieved for 60 min reaction. The volatile components of the bio-oil were found to consist mostly of substituted phenols and ketones in the C₆–C₉ range. The bio-oils obtained had a maximum HHV of 33 MJ/kg and the majority (~95%) of the compounds present was found to have boiling points lower than 165 °C, making these bio-oils potential oxygenated fuel additives.

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1. Introduction

Over the past century a majority of the world's energy demands was met by fossil fuels, comprising: 30% petroleum, 23% natural gas, 22% coal, 6% nuclear, and 19% renewable [1]. Chemical industry and energy production based on fossil fuel resources are expected to gradually phase out over the course of the 21st century due to the depletion of the fossil resources that these industries rely on [2]. Due to the continuing decline in fossil fuel resources and increasing concerns over greenhouse gas emissions and energy security, there has been a resurgence of interest in renewable bio-energy.

The Earth natural biomass of 150 billion metric tonnes of dry biomass replacement represents an energy supply of around 3000 EJ (3×10^{21} J) per year, or about 6 times the world's total en-

ergy consumption. Although these resources are renewable, carbon-neutral, and remarkably abundant, they are also very bulky and difficult to transport, handle, and store. In order to make use of these resources it is, therefore, necessary to develop cost-effective technologies to convert them into liquid bio-fuels of a higher energy density and other valuable chemicals [3]. Bioenergy and bio-fuels, particularly bio-ethanol, have been promoted worldwide in recent years. For example, the Canadian federal government has enacted a target of 5% ethanol in gasoline by 2010, which will require the production of more than 300 million liters of cellulosic ethanol per year. The European Union has set an objective to substitute conventional fuels with biomass-derived fuels (bio-fuels) in the transport sector with a market share of 5.75% by the end of 2010 (EU Directive 2003/30/EC). The US Renewable Fuels Standard (RFS) calls for at least 36 billion gallons of ethanol and other bio-fuels to be used nationwide by 2022, including a minimum of 9 billion gallons in 2008, and 20.5 billion gallons by 2015 or about 15% replacement of the USA's gasoline consumption.

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Bio-diesel is an alternative to petroleum fuels and other bio-fuels that is rapidly increasing in popularity. Many countries have legislation set in place to promote the use of bio-diesel as a substitute for the petroleum-derived diesel fuel. For example, the production of 500 million liters of biodiesel is planned in Canada [4], and the provinces of Manitoba and British Columbia have already mandated blending of percentages of biodiesel in their provincial diesel supplies, 2% and 5% respectively. The province of Alberta plans to follow this trend with its own mandate of 2% of biodiesel being blended in its diesel supply by the summer of 2010 [5].

Most bio-diesel is produced by trans-esterification of seed oils with methanol. The process produces methyl esters of long chain hydrocarbons and glycerol as a by-product. Approximately 1 kg of glycerol is produced for every 9 kg of bio-diesel formed [6]. Increased production of bio-diesel has led to a dramatic increase in the availability of glycerol, 100,000 tonnes annually in the USA alone. As a result the cost of glycerol decreased from \$2.50/lb. in 2004 to ~30¢/lb. in 2006 [7,8]. As a result of its growing availability and decreased cost, there is increasing interest in the use of glycerol as an economical feedstock for various chemicals and bio-fuels. Much of the research involving glycerol has focussed on converting glycerol into hydrogen gas [9,10], syngas for subsequent Fisher-Tropsch synthesis, or other value-added products such as propylene glycol, acrolein, oxygenates (esters and ethers) for use as fuel additives [11], and various alcohols [8]. Glycerol as an oxygenated organic compound can be a promising feedstock for the production of liquid transportation fuels by de-oxygenation and oligomerization. However, there is no research available in the published literature on this topic.

The primary objective of this work was thus to investigate the direct conversion of glycerol in the presence of catalysts into high energy, low oxygen bio-crude under moderate conditions via oligomerization and de-oxygenation.

2. Experimental

2.1. Materials

The feedstock used in this study was glycerol obtained from Canadawide Scientific (99% purity). The supported metal catalysts including mono metal catalysts of 10 wt.% Co, Ni, Ru, or Mo, or mixed metal catalysts of 10 wt.%–Mo/3 wt.% Co and 10 wt.% Mo–3 wt.%Co–2 wt.%P (MoCo and MoCoP for simplicity) were prepared by successive incipient wetness impregnation. The catalyst support materials tested in this research included MgO, γ -Al₂O₃, activated carbon (AC), X-type zeolite and an acidified X-zeolite using HCl acidification (denoted as H-zeolite). Metal salts including ammonium molybdate tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O, ruthenium (III) nitrosyl nitrate (RuNO(NO₃)₃), cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O) and magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O), as well as the phosphorous promoter (86 wt.% phosphoric acid) were all A.C.S. reagent grade reagents obtained from Sigma–Aldrich and used as received. The solvents for product recovery were distilled water and A.C.S. reagent grade ethyl acetate from Canadawide Scientific.

2.2. Catalyst preparation

Various supported metal (oxide) catalysts were prepared in-house in this study using the wetness impregnation method (or successive incipient wetness impregnation for mixed metal catalysts).

The MgO, AC and alumina supports were dried at 105 °C overnight prior to metal impregnation. Due to zeolite's ability to retain

water, it was dried at 120 °C. All supports were cooled in a desiccator before storage. For the acidified zeolite, approximately 50 g of dried zeolite was suspended in ~500 mL of 1 M HCl. The suspension was stirred vigorously for approximately 2 h and produced a gel. This gel was broken up and suspended in ~1 L of distilled water. The solution was then filtered. This process was repeated until the filtrate reached a pH of ~5.5. The gel was then dried at 120 °C and the dried material was crushed before storage.

Briefly, approximately 20 g of dried support material was weighed into a flask. The required amount of metal compound was weighed into a separate beaker and dissolved in distilled water. The support material and metal solution were combined and the resulting mixture was agitated in a shaker for a minimum of 6 h. After agitation, the water was removed by rotary evaporation at 85 °C. The dewatered material was dried at 105 °C for a minimum 12 h in air (120 °C for zeolite). Where additional catalyst metals were required, the dried catalyst was crushed into a fine powder with a mortar and pestle and the above procedure was repeated for each subsequent metal. After the final drying step, all the impregnated catalysts were calcined at 550 °C for 6 h in air (for the metal oxide-supported catalysts) or in flowing nitrogen gas (for the AC-supported catalysts). The cooled catalysts were crushed to a small (<200 μ m) particle size before storage. The bulk elemental composition (molybdenum, cobalt and phosphorus contents) of fresh catalysts were analyzed by inductively-coupled plasma-atomic emission spectroscopy (ICP-AES). The elemental analysis of these catalysts showed that the metal contents in the catalysts prepared were approximately close to the target metal loadings (except for the Mo content). For instance, the measured metal contents were 6.5 wt.% Mo–2.3 wt.% Co–1.5 wt.% P for Mo-CoP/Zeolite, and 8.1 wt.% Mo–2.6 wt.% Co–1.6 wt.% P for MoCoP/Al₂O₃, as compared the target metal loadings of 10 wt.% Mo–3 wt.% Co–1.5 wt.% P for both catalysts.

2.3. Hydro-treatment of glycerol

Glycerol hydro-treatment experiments were carried out in a micro-reactor made of stainless steel (SS 316L) tubing, sealed with 5/8 in. Swagelok end caps, with an effective volume of 14 mL. In a typical run, 10 g of glycerol was weighed into the reactor, followed by the addition of catalyst at a ratio of 5 wt.% of the glycerol. The reactor was then securely sealed. The air in the reactor was displaced with high purity nitrogen by repetitive evacuation and N₂ purging. Finally, the reactor was pressurized to 5.0 MPa using high purity hydrogen. Supported in a mechanical shaker set at 100 rpm, the reactor was then rapidly heated in a fluidized sand bath to the reaction temperature of 300 °C. After the standard reaction time of 1 h had elapsed, the reactor was removed from the sand bath and submerged in a cold water bath to terminate the reaction. A minimum of two runs were performed for each condition to ensure the reproducibility of the results, and the maximum relative difference between the liquid yield results from the duplicate runs was verified to be within ± 5 . In this study, the average values of char, gas and bio-oil yields are presented along with the corresponding error bars for the yield of bio-oil.

2.4. Separation of reaction products

Once the reactor had cooled, the gaseous products were collected in a pre-evacuated sample cylinder with a fixed volume of 2.81 L. Cylinder pressure was brought to ambient pressure (required for analysis) by addition of high purity N₂. Gas composition was then analyzed by GC-TCD (Agilent 3000 Micro-GC). The total amount of gaseous product comprising CO, CO₂, and C1–C3 hydrocarbon species, denoted as “gas” hereafter, was quantified.

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