



Microwave-assisted and carbonaceous catalytic pyrolysis of crude glycerol from biodiesel waste for energy production



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ABSTRACT

Biodiesel proliferation as a sustainable fuel has led to a glut of crude glycerol as co-product. This scenario made a previously lucrative co-product in the food and pharmaceutical sectors into a bioresource waste. The present study investigates the utilisation of a microwave-assisted pyrolysis technique to convert crude glycerol from biodiesel waste into usable bioenergy source. Operating conditions ranged from a temperature of 300–800 °C at carrier gas flow rates of 100–2000 mL/min, with the effects of carbonaceous catalyst on the selectivity of reaction pathway being investigated. Within the aforementioned conditions, the proportion of products phases is mainly dependent on the residence time inside the quartz reactor, followed by the reaction temperature. This is due to the combined factors of the reaction sequence and provision of activation energy to change product phases. The third factor of carbonaceous catalyst shows a predisposition towards hydrogen gas selectivity, leading to a lower overall gaseous product mass when factoring in products from all phases. An analysis of the energy content revealed that overall energy profit increases with decreasing temperature and increasing residence time. This concurs with solid energy content increasing in the same conditions, while it increases for liquid and gaseous products with decreasing temperature and flow rate, respectively. The conversion of waste into portable and energy profit positive products through pyrolysis makes crude glycerol a potential candidate for bioenergy production of bio-oil and syngas.

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1. Introduction

The increasing demand for energy stems from the needs of growing energy consumption, energy security and cleaner environment, has provided the impetus to search for clean and renewable source of alternative fuels. In recent years, biodiesel has gained much attention as potential alternative to fossil fuels. Biodiesel is produced from bio-resources such as vegetable oils and animal fats through transesterification process, in which the triglycerides from vegetable oils react with methanol to form methyl esters and by-product glycerol [1]. The growing importance of biodiesel is evident with the increasing annual production and blending mandates implemented in various countries [2]. The global production of biodiesel was 2.3 billion litres in 2004, increasing

by fifteen-fold to 30.1 billion litres in 2014 [2,3], while the global crude glycerol production was estimated to increase from 0.2 million tonnes in 2003 to more than 2 million tonnes in 2012 [4]. Although crude glycerol is widely used in pharmaceutical, cosmetic and food industry by further processing into secondary products [5], the supply of glycerol will eventually exceed the industrial demand based on the projected trend of growing biodiesel production [4]. One potential way to reduce the supply glut is to convert crude glycerol into bio-oil or bio-gas as renewable energy source.

Various methods and processes have been used to convert glycerol into useful products, including acetylation of glycerol to produce acetins [6], esterification to convert glycerol into different types of ester [7], ammoxidation of glycerol to produce acrylonitrile [8], gasification [9] and steam reforming [10–12] of glycerol to produce synthesis gas. Pyrolysis is another promising thermochemical conversion method [13,14], operating at elevated temperature in the absence of oxygen that enables the production of organic liquids, gases and char from glycerol by varying the

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residence time. In general, pyrolysis can be classified into fast, moderate and slow pyrolysis [15]. Fast pyrolysis requires rapid heating rates and short residence time to gain maximum yield of liquid product. Moderate pyrolysis operates at the residence time of 1–5 s, targeting gaseous product while slow pyrolysis targets solid product, i.e. char [16]. The heat source for pyrolysis can be from furnace or microwave irradiation [17]. The latter was shown to be more advantageous by providing rapid, energy-efficient heating and can selectively promote reactant heating [18].

Previous investigations of glycerol pyrolysis have mostly focused on the production of synthesis gas (syngas), which consists primarily of H₂ and CO [19–21]. Valliyappan et al. [20] reported that 72 mol% of gaseous yield converted from glycerol at 800 °C contained 93.5 mol% of syngas with the H₂/CO ratio of 1.05. The heat source was provided from conventional furnace heating. By varying the carrier gas flow rate and temperature, different gas yields and compositions can be achieved. Gas production was favoured at lower particle size of the packing materials. Conversion of glycerol into syngas occurs via dehydration [22] and decarbonylation [23] during glycerol pyrolysis. Stein et al. [21] investigated glycerol pyrolysis in the gas phase. Light hydrocarbons of carbon monoxide, ethylene, methane and hydrogen were produced from initial pyrolysed compounds such as acetaldehyde and acrolein as pyrolysis temperature increased. Fernandez et al. [24] pyrolysed glycerol to produce syngas by using microwave-induced pyrolysis technique and reported high gas yield of 81 vol.%, consisting of 34.6 vol.% of H₂ and 45.9 vol.% of CO. The study did not report the effect of carrier gas flow rate on product yield. Microwave processing technique was reported to promote higher conversion rate of glycerol into gaseous products compared to conventional heating processes in all cases, but the effects on solid and liquid products were not known nor characterised [25]. In another related work by the same group, glycerol was shown to produce more syngas than other feedstock such as sewage sludges and coffee hull [26]. The hot spot generated by microwave pyrolysis in the reactor enabled higher gas yield compared to conventional pyrolysis.

To enable predictive capability of glycerol oxidation via CFD simulation for practical application and plant optimisation, Fantozzi et al. [27] developed a reduced skeletal kinetic scheme of glycerol which contains 44 species and 452 reactions based on the detailed mechanism proposed by Anca-Couce [28]. The reduced kinetic model was validated against experimental data obtained from a batch pyrolysis reactor, showing good agreement with experimental result with increasing pyrolysis temperature. At high pyrolysis temperature of 750–800 °C, gas yield of 70 wt% can be achieved, of which 44–48 vol.% consist of hydrogen.

In view of the potential of glycerol to produce syngas, some researchers have attempted to pyrolyse biomass blended with glycerol. Manara et al. [29] showed that by fast pyrolysing blends of glycerol with lignite in a non-continuous, wire mesh reactor, a maximum conversion rate of 71 wt% was observed at pyrolysis temperature of 850 °C for the blend of 20 wt% glycerol with lignite, of which the hydrogen yield was 65.44 v/v%. The total volatiles released was higher compared to the case of pyrolysing only pure lignite. Bartocci et al. [30] investigated the pyrolysis kinetic parameters of a pellet made of 90% saw dust and 10% glycerol by mass fraction via a thermogravimetric analysis. The reaction rate of glycerol decomposition was determined by using a first order reaction. It was reported that thermal degradation of glycerol contained in the pellet can increase hydrogen content in pyrolysis gases.

Xiu et al. [31] hydrothermally pyrolysed swine manure mixed with crude glycerol at various ratios to produce bio-oil. A maximum yield of 68% of oil was obtained at the ratio of swine manure to glycerol of 1:3 (by weight) at 340 °C and 15 min. The free fatty acid in the glycerol increased the oil yield from 23.9% to 70.9%. Delgado et al. [32] pyrolysed crude glycerol blended with corn straw

in a slow co-pyrolysis reaction. Pyrolysis of crude glycerol was shown to produce a low yield of gas of 23 wt% with a lower heating value of 46 MJ/m³, whereas pyrolysing crude glycerol mixed with corn straw at the ratio of 1:1 increased the gas yield to 39 wt%. Skoulou et al. [33] showed that by pyrolysing a mixture of crude glycerol (25 wt%) with olive kernel at 720 °C, an increase of H₂ concentration by 11.6 v/v% was achieved compared to pyrolysis at 520 °C. The increase in gas yield was attributed to the moisture available in crude glycerol that promotes steam reforming reactions.

Most glycerol-for-energy product processing techniques focused on optimising operating conditions to obtain synthesis gases without emphasising on the solid and liquid products [24], while others focused only on the effect of catalyst to produce gaseous products [20]. In the present experiment, the effects of carrier gas flow rate, operating temperature and carbonaceous catalyst on the end products of crude glycerol pyrolysis are investigated by using a microwave-assisted pyrolysis rig. The crude glycerol obtained directly from biodiesel plant is used as target feedstock for pyrolysis process, with the aim to convert low value by-product into useful bioenergy source. All pyrolysed products, including biochar, bio-oil and biogas are characterised and the basic mechanism route for feedstock-product conversion is determined. Coupled with product energy balance analysis, the outcome of this study will also provide guidelines to produce pyrolysis products that have positive energy profits. This allows bio-energy to be produced from glycerol via an energy-efficient method in order to further lower the cost of biodiesel production by recovering more energy.

2. Experimental

2.1. Test apparatus and operating conditions

Pyrolysis of glycerol was carried out by using a single mode microwave oven (Samsung ME711k) capable of supplying a maximum power output of 800 W. A quartz reactor with a diameter of 100 mm and height of 180 mm was used to contain the feedstock and catalyst. The quartz reactor is connected to a nitrogen line supply while the reactor outlet is connected to a condenser. A thermocouple is placed inside the reactor to measure the temperature of feedstock and to provide a feedback signal for heating control. Nitrogen was supplied to the reactor to purge the oxygen-containing air out of the reactor for 5 min prior to experiment. During pyrolysis, the inert nitrogen gas flow was supplied at a constant flow rate, while the reactor was heated to elevated temperature via microwave irradiation. Pyrolysed gases flown out of the outlet were passed through a condenser that is cooled by tap water of 25 °C. The condensed liquid product was collected in a flask. The remaining non-condensable pyro-gases flow through a bed of silica gel used as moisture absorbent before being collected at the outlet using a gas sampling bag. The solid biochar produced that remains in the quartz reactor is mechanically harvested. The yield of the products is determined gravimetrically.

Investigation of the effect of pyrolysis temperature was conducted at the range of 300–800 °C at an interval of 100 °C, while the inert carrier gas flow rate was varied at 100, 1000 and 2000 mL/min to study the effect on the product yield and quality. The ratio of catalyst to glycerol was fixed at 1:1 for all test cases. The mass of crude glycerol used as feedstock for all cases was 50 g. The carbonaceous catalyst is required to raise reaction temperature to above 400 °C. This meant that a total of 24 flow rate-temperature-catalyst combinations were investigated. The duration of each batch of pyrolysis process is 45 min. The heat supplied from microwave irradiation provides the enthalpy of vaporisation

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