Bioresource Technology 100 (2009) 2613–2620

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Thermogravimetric kinetics of crude glycerol

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ARTICLE INFO

Article history:
Received 22 July 2008
Received in revised form 14 November 2008
Accepted 18 November 2008
Available online 22 January 2009

Keywords:
Glycerol
Pyrolysis
TGA
FTIR
Kinetics

ABSTRACT

The pyrolysis of the crude glycerol from a biodiesel production plant was investigated by thermogravimetry coupled with Fourier transform infrared spectroscopy. The main gaseous products are discussed, and the thermogravimetric kinetics derived. There were four distinct phases in the pyrolysis process of the crude glycerol. The presence of water and methanol in the crude glycerol and responsible for the first decomposition phase, were shown to catalyse glycerol decomposition (second phase). Unlike the pure compound, crude glycerol decomposition below 500 K leaves behind a large mass fraction of pyrolysis residues (ca. 15%), which eventually partially eliminate in two phases upon reaching significantly higher temperatures (700 and 970 K, respectively). An improved iterative Coats–Redfern method was used to evaluate non-isothermal kinetic parameters in each phase. The latter were then utilised to model the decomposition behaviour in non-isothermal conditions. The power law model (first order) predicted accurately the main (second) and third phases in the pyrolysis of the crude glycerol. Differences of 10–30 kJ/mol in activation energies between crude and pure glycerol in their main decomposition phase corroborated the catalytic effect of water and methanol in the crude pyrolysis. The 3-D diffusion model more accurately reproduced the fourth (last) phase, whereas the short initial decomposition phase was poorly simulated despite correlation coefficients ca. 0.95–0.96. The kinetics of the 3rd and 4th decomposition phases, attributed to fatty acid methyl esters cracking and pyrolysis tarry residues, were sensitive to the heating rate.

1. Introduction

Biodiesel has become more attractive recently as alternative diesel fuel to reduce dependency on fossil fuel imports. It is biodegradable, non-toxic, near CO_2-neutral and environmentally beneficial (Ma and Hanna, 1999). The transesterification of renewable biological sources such as vegetable oils and animal fat oils with an alcohol using alkaline or acid catalysts is the most common process for biodiesel production (Ma and Hanna, 1999; Tapanes et al., 2008), yielding 1 mol of glycerol for every three of fatty acid methyl esters (FAME). With a production of biodiesel on the increase through the building of new bio-refineries worldwide, the crude glycerol by-product becomes a waste problem, and pure glycerol is in surplus (Adhikari et al., 2007).

Crude glycerol from the biodiesel process often contains many impurities and is a very poor fuel, which is not used in either petrol or diesel engines (Slinn et al., 2008). It can be purified by distillation to use in both food and pharmaceuticals or can be sent to water treatment for digestion. However, these processes are very expensive and exhibit a low yield (Slinn et al., 2008). Several alternatives are being explored to utilise crude glycerol, and some commercial plants have been established to produce 1,3-propanediol, polyglycerols and polyurethanes from glycerol (Valliyappan et al., 2008; Adhikari et al., 2008). One mole of glycerol ($C_3H_5(OH)_3$) can theoretically produce up to 4 mol of hydrogen gas, and in addition, it is possible to get CO as one of the gaseous products due to the high oxygen content. Glycerol as a potential feedstock via pyrolysis, gasification or steam reforming to produce H_2, CO or other fuel gases has received considerable research attention (Valliyappan et al., 2008; Stein et al., 1983; Zhang et al., 2007; Dauenhauer et al., 2006; Czernik et al., 2002; Buhler et al., 2002; Douette et al., 2007; Sun and Li, 2008; Ranjbar and Pusch, 1991). In a previous study on hydrogen production from unmixed steam reforming of sunflower oil fuels, the thermal decomposition of the fuel was found to play a significant role in the H_2 production and coke formation (Dupont et al., 2007). There are also many opportunities for liquid biofuels to pyrolyse upstream of a steam reforming catalyst during the consecutive stages of the process, from the fuel injection, evaporation, to the mixing and reacting of the vapourised fuel with the steam in the reformer. Understanding the pyrolysis of crude glycerol is therefore important to design steam reforming processes that avoid tar and coke formation.

The pyrolysis of glycerol without catalyst is a very simple and a cheap method for energy conversion. Stein et al. (1983) studied the pyrolysis of glycerol in steam in a laminar flow reactor. The initial products of decomposition were CO, acetaldehyde and acrolein, and then acetaldehyde and acrolein further decomposed to

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doi:10.1016/j.biortech.2008.11.037

produce primarily CO, CH_4 and H_2. Valliyappan et al. (2008) reported the hydrogen or syngas production from glycerol by pyrolysis at temperatures higher than 600 °C and the products were mainly gases consisting of CO, H_2, CO_2, CH_4 and C_2H_4. The thermal decomposition of glycerol in near-critical and supercritical water was also carried out by Buhler et al. (2002) in a tubular reactor and a conversion between 0.4% and 31% was observed. They reported the main products of the glycerol degradation included methanol, acetaldehyde, ethanol, CO, CO_2 and H_2. The decomposition is highly endothermic for glycerol

$$C_3H_8O_3 \rightarrow 3CO + 4H_2 + 245\,\text{kJ/mol}.$$

Due to high oxygen content, complex intermediates and high impurity levels, it is also very difficult to understand the characteristics of pyrolysis of the crude glycerol from the biodiesel production process. In this paper, following characterisation by GC–MS and CHNS analysis of crude glycerol from a biodiesel refinery, its pyrolysis was carried out in dry N_2 was studied by thermogravimetry coupled with Fourier transform infrared spectroscopy (TGA–FTIR). Other feedstocks such as pure glycerol, water/glycerol and methanol/glycerol mixtures were also analysed in TGA experiments to obtain a better understanding of the crude glycerol decomposition behaviour.

The thermogravimetric experimental data were interpreted by an improved iterative Coats–Redfern method, which allows the kinetic parameters to be estimated iteratively by linear regression and thus enhances the accuracy (Coats and Redfern, 1964; Urbanovici et al., 1999). A number of forms of the mechanism integral function $g(\alpha)$ were tested with the experimental data, including:

(i) the power law model, $g(\alpha) = \alpha^{1/m}$, m = 1, 2, 3, 4
(ii) the reaction order model $g(\alpha) = (1-(1-\alpha)^{1-n})/(1-n)$ with n the order of reaction ($g(\alpha) = \ln(1-\alpha)$ when $n = 1$)
(iii) 1D, 2D and 3D-diffusion models (e.g. 3D: $g(\alpha) = (1-(1-\alpha)^{1/3})^2$).

The kinetics parameters were evaluated by minimizing the equation for the sum of the squares of residual errors (S_{res}) (Urbanovici et al., 1999), and the best model identified by its correlation coefficient's closeness to 1.

2. Experimental

2.1. Materials

The crude glycerol was obtained from D1-Oils Ltd., Middlesborough, UK. It mainly consisted of 70–90 wt% glycerol compound based on the data sheet from Directive 2001/58/EC provided by the manufacturer. Other compounds listed by the manufacturer were methanol (<15%), water (<15%), inorganic salts (<5%) and polyglycerol (<5%). In order to reduce its viscosity and allow the crude glycerol to be pumped, the manufacturers usually dilute the crude phase with ca. 10% water, the mixture can then be used as oil-fired in power plants. The sample investigated here had undergone such a procedure. The CHNS elemental composition of the crude glycerol was determined for three samples using a CE Instrument Flash EA 1112 Series. The resulting average elemental molar formula was $C_{3\pm0.2}H_{8.9\pm0.4}O_{3.4\pm0.2}N_{(5\pm2)\times10^{-3}}$, with the O content derived by difference from one of the sum of the measured C, H, N mass fractions. This indicates higher H/C and O/C ratio compared to pure glycerol ($C_3H_8O_3$). This would have been partly contributed by the presence of the H_2O and methanol (CH_3OH) content in the crude, unlike the fatty acid methyl esters impurities H/C and O/C ratios are lower than those of glycerol. Simple, non quantitative characterisation by GC–MS was carried out in this study using a Trace GC 2000 TOP (Thermo electron), with a splitless injector and a mass spectrometer Fisons MD800. The column used for GC is the 25 m × 0.25 mm RESTEK RT and the helium of 1 ml/min was used as the carrier gas. The GC–MS analysis was performed with an oven temperature program from 333 to 583 K at 5 K/min and the solvent used to dissolve the crude glycerol was selected as methanol. The composition of crude glycerol varies depending on the plant oils or animal oils employed as primary source. The GC–MS spectrum obtained for the sample indicated the presence of glycerol $C_3H_5(OH)_3$, and of significant methyl esters products of the biodiesel process, among them, linoleic ($C_{19}H_{34}O_2$), palmitic ($C_{17}H_{34}O_2$), oleic ($C_{19}H_{36}O_2$), and stearic ($C_{19}H_{38}O_2$) acid methyl esters. With the aim of discussing some of the crude glycerol components contributions to its thermal degradation behaviour, pure glycerol and mixtures of 10% distilled water in glycerol and 10% methanol (99.5% purity) in glycerol, were subjected to similar thermal gravimetric experiments as the crude. The glycerol (99.1% purity) and the methanol (99.5% purity) were purchased from Sigma–Aldrich.

2.2. TGA–FTIR studies

Thermogravimetry coupled with Fourier transform infrared spectroscopy (TGA–FTIR) experiments were carried out to study the pyrolysis of the crude glycerol. Thermogravimetric data were collected from 300 to 1123 K at the heating rates of 5, 10, 15, and 20 K/min, under dry nitrogen atmosphere by using a Stanton Redcroft TGA apparatus. For comparison, pure glycerol samples were also analysed at the same heating rates, while the 10% water–glycerol as well as 10% methanol–glycerol were analysed at the heating rate of 5 K/min in the TGA. Sample masses of about 20 mg were used. The pyrolysis products were carried through a stainless steel line into the gas cell for IR absorption detection. Both the transfer line and the gas cell were kept at 150 °C to prevent gas condensation although the less volatile gases such as vapours of some compounds with high boiling point were expected to condense partially in this line. IR spectra were obtained using a magna system 560 spectrometer with a resolution of 4 cm^{-1} averaging 100 scans in the wavenumber range of 4000–500 cm^{-1} and the detector is the DTGS KBr. Total data collection time was 70.25 min.

3. Results and discussion

3.1. Analysis of thermogravimetry

Fig. 1 shows the TG mass loss curve of the pure glycerol with a 15 K/min heating rate and those of crude glycerol at various heating rates (5, 10, 15 and 20 K/min) in order to study the effect of heating rate on non-isothermal kinetics. As can be seen, the pyrolysis pattern of the crude glycerol at the different heating rates for each sample was similar, indicating four phases in the pyrolysis process. The mass loss, initial mass loss temperature, maximum mass loss temperature and final mass loss temperature for each phase in the pyrolysis of crude glycerol are shown in Table 1 for the four heating rates 5, 10, 15 and 20 K/min. Table 2 lists the same parameters for the pyrolysis of pure glycerol. The TG mass loss curve of the pure glycerol was simple and only presented one phase, covering 95% of its mass loss, spanning from (423–453) K to (503–556) K depending on the heating rate. The decomposition of the pure glycerol was almost complete, leaving only 2% mass residue upon further heating. For the crude glycerol, the mass loss values during the first phase (PH1) were about 10–15% and spanned from (322–343) K to (426–440) K depending on the heating rate. The removal of water and some low temperature volatiles such as methanol, the co-reactant in the transesterification of veg-