Fuel 109 (2013) 427–431

Contents lists available at SciVerse ScienceDirect

Fuel

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

Biodiesel production by transesterification of sludge in supercritical conditions

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HIGHLIGHTS

- Process to obtain bio-fuel from wastewater treatment plant sludge.
- Transesterification in supercritical conditions of fatty acids present in the sludge.
- Use of cosolvents to improve reaction conditions.

ARTICLE INFO

Article history:
Received 10 April 2012
Received in revised form 24 March 2013
Accepted 25 March 2013
Available online 6 April 2013

Keywords:
Transesterification
Biodiesel
Wastewater treatment plant sludge

ABSTRACT

In this study wastewater treatment plant (WWTP) sludge was subjected to a reactive pyrolysis treatment to produce a high quality pyro-oil. Sludge was treated in supercritical conditions in the presence of methanol using hexane as cosolvent in a high pressure lab-autoclave. The variables affecting the pyro-oil yield and the product quality, such as mass ratio of alcohol to sludge, presence of cosolvent and temperature, were investigated. It was found that the use of a non-polar cosolvent (hexane) presents advantages in the production of high quality pyro-oil from sludge: increase of the non-polar pyro-oil yield and a considerable reduction of the amount of methanol needed to carry out the transesterification of fatty acids present in the sludge.

1. Introduction

Rising petroleum fuel costs, increasing concern for the environmental impact of emissions from the combustion of conventional fossil fuels and strong reliance on foreign oil sources are increasing the interest and demand of biomass as a sustainable feedstock that can replace diminishing fossil fuels for the production of energy, especially for the transportation sector.

We can consider three general classes of feedstocks derived from biomass that are appropriate for the production of renewable fuels [1]: starchy feedstocks (including sugars), triglyceride feedstocks, and lignocellulosic feedstocks.

Lignocellulosic biomass is the most abundant class of biomass. The most frequently considered strategies for lignocellulosic biomass processing involve thermochemical routes. Pyrolysis is one of the three main thermal routes of treatment, along with gasification and combustion, to provide a useful and valuable biofuel. It offers the advantages of a liquid product – bio-oil – that can be readily stored and transported, and used as a fuel.

Furthermore, the pyrolysis process does not require the extensive pre-treatment steps common to hydrolysis/sugar platforms thus the cost of producing a bio-oil is considerably less than the cost of sugar-based products. However, the bio-oil product is not particularly well suited for use as a fuel and must be treated extensively before it can be used in internal combustion engines. The main limitations to direct bio-oil utilization are the high acidity and oxygenate content of the bio-oil, leading to a low energy density liquid and corrosive properties that are detrimental to equipment lifetime when used in existing engines. Bio-oil can be upgraded to high quality hydrocarbon fuels [2] although at a presently unacceptable energetic and financial cost.

The biodiesel production from vegetable oil through transesterification has been extensively studied in recent years [3–5]. Despite its advantages (nontoxic, biodegradable, renewable, low emissions, etc.) biodiesel production costs from vegetable oils are prohibitively high. The cost of feedstock is a major economic factor in the viability of biodiesel production accounting typically for 80% of the total costs of biodiesel production. To decrease these costs and make biodiesel profitable production processes must use inexpensive triglyceride sources. Additionally, it is preferable to utilize nonedible biomass as a feedstock for the production of fuels and chemicals, such that the production of transportation fuels does

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http://dx.doi.org/10.1016/j.fuel.2013.03.064

not interfere with either the food supply or unduly disrupt land use.

To decrease the production cost of bio-fuels in comparison with petro-fuels, low-cost feedstocks and appropriate processes that avoid pre and post-treatments must be considered.

WWTP sludge is a low-cost, widely available biomass. Furthermore, utilizing sludge as biomass for bio-fuel production may be a viable solution to the problems associated with WWTPs: permanent increase in the sludge production, the high cost of the sludge treatment and the risks that the sludge presents for the environment and the human beings.

Other authors have studied the sludge to bio-fuel conversion process. Li et al. [6] reported a process in which sludge was subjected to deoxy-liquefaction in supercritical ethanol using sludge/ethanol ratio of 1:40 (g/mL). Mondala et al. [7] described a process in which sludge was subjected to an acid-catalyzed in situ transesterification. The effectiveness of catalyzed transesterification reaction is reduced by the inability to process high water and free fatty acid content present in the sludge. On the other hand, it has been reported that transesterification in supercritical methanol can handle feed contaminants. Thus it may be an alternative to the conventional catalyzes methods where feedstock purity plays an important role in the effectiveness of the process [8].

The aim of this research is to present an efficient procedure to obtain high quality pyro-oil from waste water treatment plant sludge, using transesterification in supercritical conditions. This procedure combines the results of a pyrolysis process (thermal decomposition of the organic components in an inert atmosphere) and the transesterification reaction of fatty acids with the reactant (methanol) in order to obtain the fatty acid methyl esters (FAMEs). Wastewater treatment plant sludge was treated in a SS-316 high pressure lab-autoclave with methanol. Hexane was added as cosolvent to improve lipid solubility in the reaction mixture thus considerably reducing the amount of required methanol compared to other processes [6]. The effects of operating conditions such as the mass ratio of methanol to sludge, the role of hexane and the temperature on the pyro-oil yield were examined. Gas chromatography–mass spectrometry (GC–MS) analysis of the product was also conducted to determine the effects of the three factors mentioned on the product quality.

2. Experimental

2.1. Materials

Sewage sludge was provided from a municipal wastewater treatment plant employing an activated sludge process located in Sant Adrià del Besos, Barcelona, Spain. The plant provides service to 3 million habitants. The sample was extruded and dried at the plant before transport using a low temperature drying process. The properties of the sludge sample are shown in Table 1. For the reactive pyrolysis experiments methanol (99.9%) and n-hexane (95%) were purchased from Prolabo and used as received.

Table 1
Properties of sludge sample.

Analysis					
Higher heating value (MJ/kg)	17.17				
Extractives in methanol (wt%)	25.7				
Carbon residue (wt%)	29.6				
Elemental composition (wt%)	N	C	H	S	O
	3.90	37.22	5.54	1.06	22.68

2.2. Reactive pyrolysis

Reactive pyrolysis experiments were performed using a 1 L cylindrical high pressure autoclave made of 316 stainless steel (temperature limit: 273–623 K, pressure range 0–150 bar). The connection diagram and the experimental setup of the high pressure autoclave are shown in Figs. 1 and 2, respectively.

In a typical experiment the autoclave was loaded with the reactants (sludge, water, methanol and hexane). 50 g of dried sludge were weighed for each experiment. Water was added in order to imitate typical sludge conditions when the sludge drying step is eliminated, that is, 70% of humidity (117 g of water). The experimental plan involved two levels of methanol to sludge mass ratio: 0.4 and 0.8 and five levels of cosolvent (hexane) to sludge mass ratio: 0, 1, 2, 3 and 6.

The autoclave was supplied with heat from an external electrical heater and heated to 250 °C. This temperature was selected based on the methanol critical temperature (239.6 °C). Liquid methanol is a polar solvent that has hydrogen bonds between molecules to form methanol clusters. In the supercritical state, depending on pressure and temperature, the intermolecular hydrogen bonding would be significantly decreased, thus the polarity of methanol decreases in the supercritical state. This would allow methanol to act as a free monomer and therefore, supercritical methanol has a hydrophobic nature with a lower dielectric constant [9]. As a result, nonpolar triglycerides can be well solvated with supercritical methanol making the transesterification reaction easier. After reaching the set point, temperature was held for 10 min. An experiment was also conducted at 280 °C in order to study the effects of temperature upon the reaction.

After each run the autoclave was allowed to cool to room temperature. Once completing the cooling period, the gas product was vented without being further analyzed as a very small amount of gas product was formed during the reaction. The liquid–solid mixture was poured into a beaker and a complementary amount of hexane was added to reach a hexane to sludge mass ratio of 6. In this form, the variation of the amount of hexane inside the autoclave only has effects upon the reaction, not upon the extraction mechanism. The mixture was stirred for 30 min and then filtered.

The obtained solid fraction was dried in an oven at 110 °C for 24 h and the liquid fraction, composed of two phases, a polar phase and a non-polar phase, was poured into a decanter. After settling for 1 h both phases were separated and drained to flasks.

Both liquid phases were subjected to removal of dissolvent under reduced pressure in a rotary evaporator and kept in an oven at 110 °C until analyzed. The pyro-oils obtained in this way were named polar pyro-oil and non-polar pyro-oil.

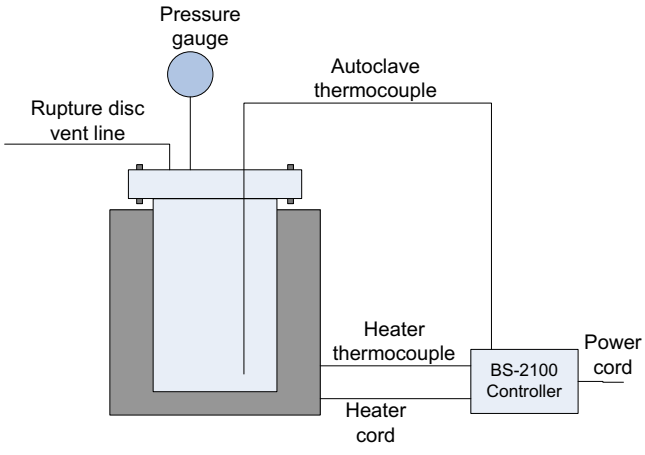

Fig. 1. High pressure autoclave connection diagram.