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Effect of microwave pretreatment on pyrolysis of crude glycerol–olive kernel alternative fuels

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ABSTRACT

Pyrolysis is considered to be a sustainable energy technology and is practiced widely in waste management. In this study, three issues were explored: (a) the implication of crude glycerol addition to lignocellulosic biomass in pyrolysis, (b) the effect of microwave pretreatment on the pyrolysis product yields and (c) study of pyrolysis parameters and assessment of products quality. Characterization of the above glycerol–biomass mixtures along with pyrolysis products was performed by ICP–OES, SEM, EDX and GC techniques. It was resulted that higher liquid yield (max 59.53% v/v) obtained by pyrolysis of pretreated mixtures at 500 °C, compared to pyrolysis yields of non-pretreated mixtures, due to the prevalence of recombination reactions in pyrolysis of the microwave-pretreated mixtures. The gas produced from the microwave pretreated feedstock-based pyrolysis showed an enriched syngas (H_2 + CO) concentration (84.9% v/v), compared to the non-microwave pretreated samples (79.1% v/v), at 720 °C. No significant effect, either on the char yields or on the char structural characteristics were observed. Consequently, microwave pretreatment before pyrolysis, can serve as a potential pretreatment for enhanced production of fuels via post-pyrolysis.

1. Introduction

The increase in the production of biodiesel by process plants fueled with vegetable oils, waste oils and fats, has inevitably led to a parallel rise in low grade crude glycerol ($C_3H_8O_3$) [1]. Refining the produced crude glycerol depends on the availability of a highly efficient purification facility in the biodiesel plant which significantly affects the cost of production. While, large scale producers worldwide refine and sell it to other industries, small and medium scale biodiesel process plants (most common in south east Europe) cannot generally afford the extra cost of crude glycerol distillation and purification, and hence face significant problems concerning their stocked crude glycerol [2]. More often, the stock is usually burnt in furnaces for heat production, resulting in the release of increased particulate emissions (due to residual catalysts content) in to the atmosphere [3]. As a result, a proper design for efficient combustion of glycerol is essential for small and medium scale process plants, for direct valorization/co-valorization of glycerol with residual biomass.

A wide variety of conventional and non-conventional technologies have been developed throughout these years for agro-biomass residue management. Amongst direct combustion, pyrolysis, gasification and liquefaction; pyrolysis has been a subject of interest for investigators due to its feasibility, high safety and low cost [4]. In addition to its flexibility in production, marketing, handling, transportation and storage, it also yields char, bio-oil and gaseous products [5,6]. It should be noted that pyrolysis yields are subjected to biomass characteristics, heat and mass transfer limitations in the reactor, catalytic effect of alkali and alkaline earth metals and pretreatment. A more recent approach to biomass pretreatment is the microwave irradiation that has been encouraged over conventional process [7–9].

Pretreatment of any carbonaceous material is carried out with the intention of increasing its surface area. Pretreatment using conventional heating processes decrease the drying rate continuously and reduces the moisture content, resulting in a slower moisture migration (from the interior to surface of the sample) and evaporation rate (from surface to air causing lower heat transfer). Since microwave is electromagnetic (frequency of 2.45 GHz) it propagates through the material, and the accompanying transport processes results in dissipation of electric energy into heat (internal and volumetric) [10–12]. However, the amount of microwave energy absorbed by the sample depends on its dielectric properties. As the dielectric constant and dielectric loss factors are greater at higher crude glycerol content of the material, the sample

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absorbs more microwave power and the heating is quicker, resulting in an immediate and a complete drying [13–15]. Earlier investigations performed on cellulosic compounds, ceramics, food materials have shown that microwave heating has assisted the convective drying by drastically reducing the associated drying times [14,15]. Furthermore, investigation by one of our authors on microwave drying of plaster of paris reported: reduction in the drying time from 900 min (convective heating) to 10 min (microwave drying) [13].

In general, most of the attempts correspond to the restricted experimental output of the individual investigators using their own materials; leaving room for improvement in the field of agro-based waste management. Researchers showed that microwave preheating of biomass resulted in an increase of bio-oil and char, simultaneously decreasing the gas yield [16,17].

In these study mixtures of crude glycerol and olive kernels were subjected to pyrolysis before and after microwave pretreatment. The specific interest in this work focused on investigating the impact of introducing an effective pretreatment method, the microwave pretreatment, to advance the structural characteristics of the waste biomass fuel used as feedstock in pyrolysis. The present study is part of a on-going research project "the GlyCo Biodiesel Project" partially funded by EU and the Greek state. The project aims to explore new possibilities for crude glycerol valorization and to offer a solution to small and medium scale biodiesel producers facing the problem of crude glycerol management. Thus, the researchers' specific interest focused on utilizing crude glycerol, as received, without refining and upgrading i.e. without any physical/chemical pretreatment.

2. Methods and materials

2.1. Fuels preparation and pretreatment

The olive kernels used were collected from Northern Greece. They were cleaned to remove impurities and subsequently size reduced (using a mill), to obtain a particle size of dp < 1 mm. The crude glycerol used in the research was procured from a local biodiesel industry, located near Thessaloniki, Greece. The crude glycerol contained traces of potassium (47680.3 ppm) and sodium (173.5 ppm) salts. It is worth noting that the elemental analysis was determined for the crude glycerol without any physical/chemical pretreatment.

Mixture of crude glycerol–olive kernel (25:75) was prepared, using a rotary mixer and stocked in air-tight bottles for a few days to achieve homogeneous adsorption of glycerol onto the olive kernels. Microwave pretreatment was performed in a domestic Samsung microwave oven (Model No. MW711W, Samsung electronics (UK) Limited, Hampshire, United Kingdom). The prepared mixture was spread uniformly on a watch glass placed at the center of the turntable and then microwave irradiated.

2.2. Fuels pyrolysis experimental setup and procedure

Fast pyrolysis experiments were conducted in a laboratory scale, wire mesh type reactor as shown in Fig. 1. The experimental setup comprised a pair of electrodes, an electrical circuit, water cooling coil system, moisture trapping mechanism, two filters (to trap the produced liquid hydrocarbons), a temperature controller and a gas sampling collection unit. The carrier gas used in the experiment was Helium (99.99%). The solid sample (~0.5 g) was encapsulated in a stainless steel sieve (100 mesh) and placed between the electrodes. A type-K Chromel–Alumel thermocouple (temperature accuracy of ±0.5 °C) was inserted through the mesh into the sample to analyze the drift in temperature prevailing within. The thermocouple data acquisition was connected to a work station to continuously monitor and record the data acquired using Advantech GeniDAQ software version 4.25.

All experiments were carried out in a temperature range of 450–750 °C, with a heating rate of approximately 50 °C s^{-1}, in an inert environment at atmospheric pressure. It was ensured that the experiments were stopped, when the gas evolution was not

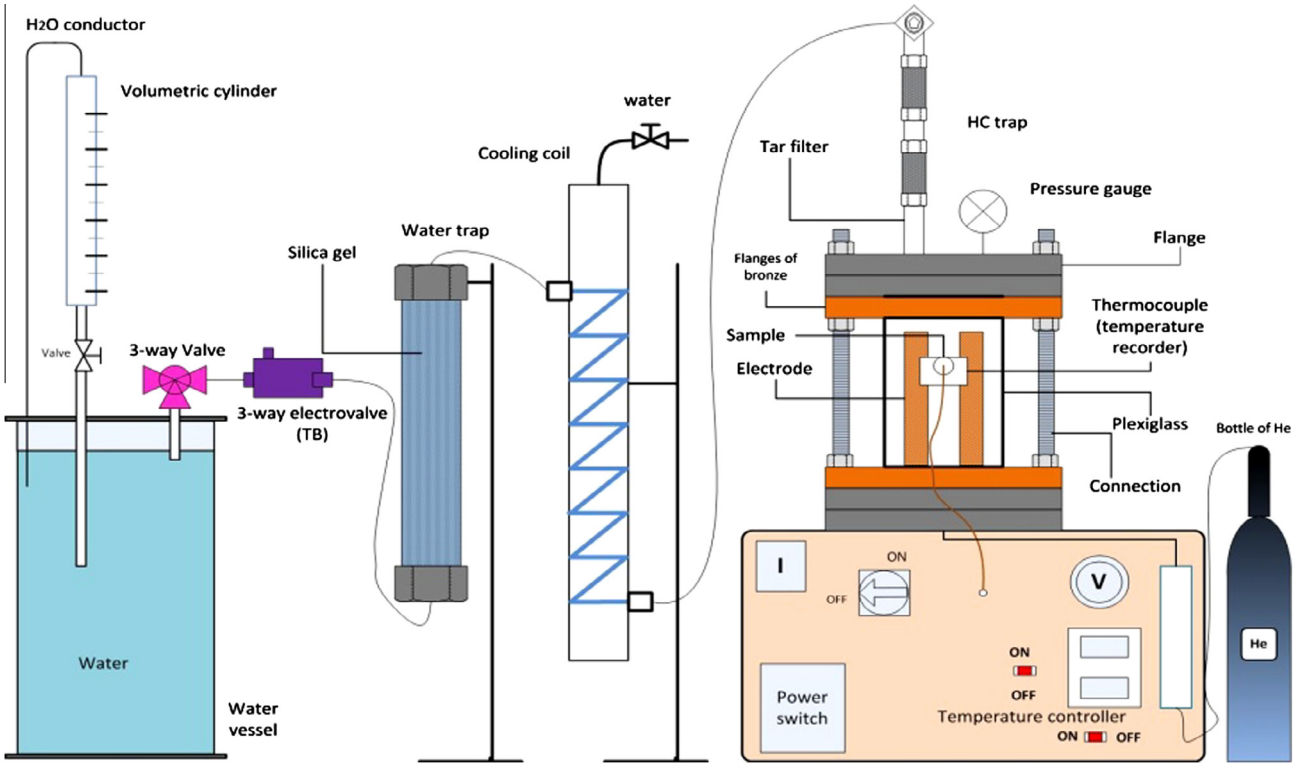

Fig. 1. Schematic representation of the fast pyrolysis experimental setup.