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An experimental and kinetic modeling study of glycerol pyrolysis

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HIGHLIGHTS

- Glycerol pyrolysis can produce about 44–48%v hydrogen at 750–800 °C.
- A simplified 452 reactions kinetic model of glycerol pyrolysis has been developed.
- The model has good agreement with experimental data.
- Non condensable gas yields can reach 70%.

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ABSTRACT

Pyrolysis of glycerol, a by-product of the biodiesel industry, is an important potential source of hydrogen. The obtained high calorific value gas can be used either as a fuel for combined heat and power (CHP) generation or as a transportation fuel (for example hydrogen to be used in fuel cells). Optimal process conditions can improve glycerol pyrolysis by increasing gas yield and hydrogen concentration. A detailed kinetic mechanism of glycerol pyrolysis, which involves 137 species and more than 4500 reactions, was drastically simplified and reduced to a new skeletal kinetic scheme of 44 species, involved in 452 reactions. An experimental campaign with a batch pyrolysis reactor was properly designed to further validate the original and the skeletal mechanisms. The comparisons between model predictions and experimental data strongly suggest the presence of a catalytic process promoting steam reforming of methane. High pyrolysis temperatures (750–800 °C) improve process performances and non-condensable gas yields of 70%w can be achieved. Hydrogen mole fraction in pyrolysis gas is about 44–48%v. The skeletal mechanism developed can be easily used in Computational Fluid Dynamic software, reducing the simulation time.

1. Introduction

EU goals for biofuels, as set out in the RED 2009/28/EC (see mandatory goals) [1], have promoted the use and production of biodiesel. The EU Energy and Climate Change Package (CCP) became operative on April 6, 2009. The Renewable Energy Directive (RED), which is part of this package, came into effect on June 25, 2009. The CCP includes the "20/20/20" goals for 2020: a reduction of 20% in greenhouse gas (GHG) emissions compared to 1990; an improvement of 20% in energy efficiency (compared to forecasts for 2020) and a 20% share of renewable energy in the total European energy mix. Part of this last 20% share is represented by a 10% minimum target for biofuels in the transport sector to be achieved by all Member States. This percentage was slightly modified by a proposal of Indirect Land Use Change (ILUC). Given this framework, the current biofuels scenario will bring to a stable production of first generation biofuels, that will hardly increase, and a slight increase in second generation biofuels (second generation bioethanol mainly). New European targets should be still fixed.

The 2014 USDA Foreign Agriculture Service statistics [2], show that a production of biodiesel equal to 10,890 Ml was reached in Europe in 2014, this means a production of 916,000 t per year of glycerol. This product has an interesting energy content and can be used to provide heat and electricity to the same transesterification plant, as it is reported in D'Alessandro et al. [3]. The analyses proposed by Fantozzi et al. [4], Manos et al. [5] and Manos et al. [6] describe how integrating CHP technologies inside a biofuel plant is part of the "agroenergy district" promotion strategy. Authayanun et al. [7] have performed experiments feeding directly glycerol in

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a high-temperature polymer electrolyte membrane fuel cell (HT-PEMFC). Beatrice et al. [8] have tested in a compression engine a bio-derivable glycerol-based ethers mixture (GEM). Besides Beatrice et al. [9] have also synthesized an oxygenated fuel additive (glycerol alkyl-ether) suitable for blending with diesel and biodiesel. Martín and Grossmann [10] have performed fermentation tests on glycerol. Nanda et al. [11] have designed and tested a continuous-flow reactor for the conversion of glycerol to solketal, through ketalization with acetone. Pedersen et al. [12] have performed hydrothermal co-liquefaction of aspen wood and glycerol with water phase recirculation.

Pyrolysis of glycerol and reforming are interesting techniques that can be used to produce hydrogen for transportation, see Wulf and Kaltschmitt [13].

Several works in literature take into account pyrolysis or gasification of glycerol. Experimental works can be classified based on reactor typology and process parameters.

Encinar et al. [14] used a cylindrical tube of stainless steel 316, set in vertical position. In the upper part of the reactor a thermocouple was used to control the temperature. A second reactor was placed under the first one, aiming at increasing the residence time of the material at a fixed reaction temperature. A solution of water and glycerol is inserted inside the reactor with the help of a pump.

In the work of Fernandez et al. [15] pyrolysis of glycerol was performed in an electrically heated furnace and in a microwave reactor. Glycerol was supplied to the upper part of the reactor through an injector, and activated charcoal was used as a catalyst for the reaction.

Peres et al. [16] have performed continuous pyrolysis tests in a steel reactor that was filled with alumina oxide. A pump used for liquid gas chromatography was employed to supply glycerol in the reactor. The reactor was heated using an electrical furnace. The produced gas was sampled in tedlar bags. Vallyiappan [17] and Vallyiappan et al. [18] used a packed fixed bed reactor full of quartz and silicon carbide, to simulate a plug flow reactor. Packing material was contained inside a plug of quartz wool, which was inserted on a supporting mesh at the center of reactor. Vallyiappan obtained interesting yields of hydrogen (about 50% in volume), performing pyrolysis at 800 °C. Baker-Hemings et al. used these sets of experimental data [19] to develop and validate a detailed kinetic model of glycerol pyrolysis.

A detailed CFD model of the above hinted reactors has never been reported in literature, for this reason this work has two main goals. One is to provide new experimental data, aimed at further validating a detailed kinetic mechanism for glycerol pyrolysis. The second goal is to develop a simplified skeletal kinetic mechanism, suitable for CFD simulations. This new and simplified skeletal mechanism, which represents a novelty in the state of the art of glycerol pyrolysis simulation, is the added value of this work and it is available in the supplementary material. The new tool can be used for reactor design and optimization.

The paper presents the analysis and optimization of an energy process (pyrolysis of glycerol), to compare its performance with other alternative processes (such as steam reforming or steam gasification), this indicates that the results presented are interesting for the scientific and technical community involved in the development of processes to produce hydrogen from glycerol and to use it in different cogeneration devices (among them fuel cells).

The originality of the work is based on a new skeletal model. This has the advantages to be enough simplified to be used in CFD modeling for reactor optimization. It is the first step in the development of a new process in which a unique reactor can reform glycerol using biochar as a catalyst and achieve an increase of biochar porosity (so partially activating it).

2. Materials and methods

All the analyses of the samples were performed at the Biomass Research Centre of the University of Perugia, see the analysis protocols described in Bidini et al. [20]. The proximate analysis of the raw materials and of the char and tar were determined using the thermogravimetric analyzer Leco TGA-701 according to the CEN/TS 14774-14775 [21,22]. The amounts of chemical elements like nitrogen, hydrogen and carbon were characterized by the Leco TruSpec CHN analyzer, according to the UNI EN 15104:2011 [23]. The calorific value of the sample and products was determined with an LECO AC-350 analyzer, according to the UNI EN 14918:2009 [24].

Pyrolysis gas composition was determined by Micro-GC 490, Varian, using a Thermal Conductivity Detector (TCD). The Micro GC includes a heated injector, backflush and Genie membrane filter to remove particles and liquids from analyzed gas samples. The Micro-GC contains two analytical modules: Molecular Sieve capillary column with Argon as carrier gas used for the analysis of CH_4, CO, H_2, O_2, N_2 and Pora Plot Q capillary column with Helium for the analysis of CO_2, C_1-C_3 gaseous species.

A batch reactor used in the laboratory of CRB was employed to perform pyrolysis (see Fig. 1). This was already described in Bartocci et al. [25], Paethanom et al. [26] and Bidini et al. [20]. It is a plant in which it was possible to perform pyrolysis of solid/liquid samples and to characterize the products from different experiments. The experimental setup used in the laboratory during this study is shown in previous works, see Bidini et al. [20]. Pyrolysis tests were carried out in a reactor with a height of 30 cm and the inner diameter of 15 cm. At the top of the reactor there is a nitrogen inlet pipe (N_2), a valve to feed the glycerol, one thermocouple connected to the P.I.D device to maintain the programmed temperature inside the reactor (T1), one thermocouple to measure the temperature inside the reactor (T2), a pressure sensor (p). The heating system is made of two semi-spherical electric heaters, each with a power of 4.8 kW.

Before the experimental test, nitrogen was fed into the reactor to remove air and create inert atmosphere conditions for the pyrolysis process. The reactor was heated from ambient temperature to 600 °C at a heating rate of about 20 °C/min. When the reactor reached the desired temperature, the sample (of a total mass of 100 g) was gradually inserted into the reactor, with an average mass flow of 3 g/min. Volatiles exited from a pipe and passed through the tar sampling line. The gas sampling line cooled the volatiles, which reached ambient temperature values. The portion

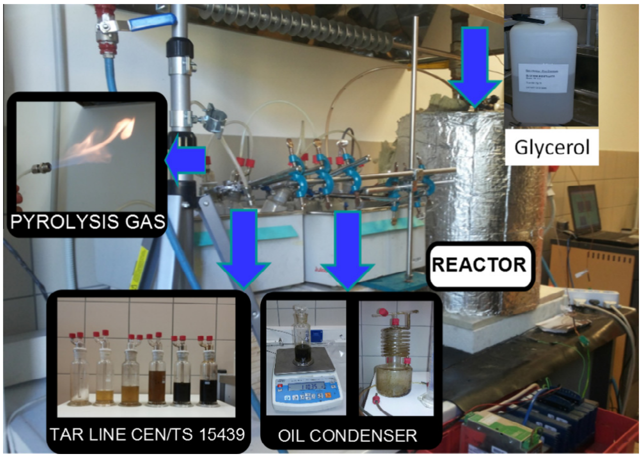

Fig. 1. Batch reactor description and tar sampling methodology.