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Research paper

Pyrolysis of pellets made with biomass and glycerol: Kinetic analysis and evolved gas analysis

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A B S T R A C T

Glycerol is a co-product compound of biodiesel production with an interesting heating value. In this work pyrolysis kinetic parameters for a pellet made with a mass fraction of 90% sawdust and a mass fraction of 10% glycerol are derived through thermogravimetric analysis. A new parallel reaction scheme with four components (cellulose, hemicellulose, lignin and glycerol) is adopted and the kinetic triplet for each component is derived using a model fitting approach applied to this particular kind of pellet. The isoconversional method Kissinger-Akahira-Sunose is employed both to provide initial values for model fitting simulations and to check final results. Results show that activation energies and pre-exponential factors are respectively: 149.7 kJ mol^{-1} and $1.98*10^{11}$ s^{-1} for hemicellulose, 230.1 kJ mol^{-1} and $1.84*10^{17}$ s^{-1} for cellulose, 154.3 kJ mol^{-1} and $5.14*10^{9}$ s^{-1} for lignin, 74.5 kJ mol^{-1} and $2.17*10^{5}$ s^{-1} for glycerol with a first reaction order for all components, except for lignin ($n = 2.6$). Through evolved gas analysis it was demonstrated that the thermal degradation of glycerol contained in the pellet can increase hydrogen content in pyrolysis gases.

1. Introduction

Glycerol is the main co-product of the first generation biodiesel industry with potential energetic applications. It has been demonstrated that [1] using glycerol in a CHP unit could supply the entire electricity consumption of a biodiesel plant and 50% of the heat. Raw glycerol cannot be fed easily into a reactor, such as the rotatory kiln IPRP (Integrated Pyrolysis Regenerated Plant), designed and realized at the University of Perugia, see Refs. [2,3]. This is due to the fact that raw glycerol, obtained from transesterification plants, is fluid. For this reason, a promising alternative is to mix biomass and glycerol. In this way glycerol can act as an additive for biomass, improving its characteristics, and providing a biofuel that can compete with other fossil fuels, such as coal.

In literature, there are few works on the co-pyrolysis of glycerol with biomass, but with promising results. In [4] a mixture with a mass fraction of 25% crude glycerol and a mass fraction of 75% olive kernels was pyrolysed at two different temperatures (720 and 520 °C) to verify which pyrolysis gas contained more H_2. From a comparison of the two experiments, it has been noted that a higher pyrolysis temperature leads to an increase of hydrogen volume fraction in the gas of 11.6%. Another work which described co-pyrolysis of coal with glycerol in a laboratory scale reactor is the one of [5]. In this work, fast pyrolysis has been conducted with mixtures with a mass fraction of 15 and 20% of glycerol and a mass fraction of 85% and 80% of lignite coal at different temperatures (650, 750 and 850 °C). The results show that using a mixture with a mass fraction of 20% of glycerol at 850 °C resulted in high hydrogen yield (65.44% in volume fraction, normalized). The slow pyrolysis of crude glycerol with corn straw has been described in Ref. [6]. It has been noted that the blend in proportion [1:1] had a good heating value and produces a gas which is rich in hydrogen. Other works present glycerol combustion with low rank coal and developments in biomass kinetics (see Refs. [7–10]).

The authors of this work have already pyrolysed pure glycerol in the project TERVEG, funded by the Italian Ministry of Agriculture, Food and Forestry with National funding call “bando bioenergetico

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Symbols

α	Mass loss fraction	–
A	Pre-exponential factor	s^{-1}
C	Carbon	–
c	Contribution to weight loss	–
E	Activation energy	kJ mol^{-1}
H	Hydrogen	–
KAS	Kissinger-Akahira-Sunose method	
m	Mass	g
N	Nitrogen	–
n	Order of reaction	–
R	Gas constant	J K^{-1} mol^{-1}
R^2	Correlation coefficient	–
S	Mean squared difference	–
t	Time	s
T	Temperature	°C

Subscripts

0	Initial	–
i	Biomass component	–
f	Final	–
t	Temporary	–

DM 246/2007, GU No. 94 del 27/11/2007, see Ref. [7]. In this new work, it is proposed to mix wood pellets with glycerol. This has not been done so far for energy purposes. The idea to produce pellets using glycerol as an additive is original. For this reason, it has been conducted an experimental campaign on glycerol pellets in the framework of the European project BRISK (Biofuels Research Infrastructure for Sharing Knowledge, website: http://briskeu.com/). The experimental campaign was managed by Bioenergy 2020+ (http://www.bioenergy2020.eu/). A first publication on the economic feasibility of the energetic valorisation of glycerol pellet has been already published by the authors in the 23rd European Biomass Conference and Exhibition, see Ref. [11]. The study proposed in this paper aims at the determination of pyrolysis kinetic parameters for pellets made by glycerol and biomass, using TGA analysis. These parameters will permit to simulate the pyrolysis process happening in a rotary kiln working with glycerol pellet, this process can be useful to produce part of the energy required by a biodiesel plant, as shown in Ref. [11]. Being the slow pyrolysis process characterised by low heating rates, to be sure that glycerol actually pyrolyses instead of evaporating during the heating of the pellet, evolved gas analysis was also performed to check pyrolysis gas composition during the whole thermal degradation process.

The novelty of the paper is due to the fact that pellet with glycerol as an additive has never been produced nor tested in pyrolysis experiments. Mass loss in biomass pyrolysis is commonly described with a parallel reaction scheme with 3 components (cellulose, hemicellulose and lignin) (see Ref. [12]). In this work, it will be discussed for the first time how to describe the co-pyrolysis of biomass and glycerol. The calculation of kinetic parameters such as activation energies, pre-exponential factors and order of reaction for all the pseudo-components is of fundamental importance to provide data for developing detailed kinetic schemes such the one of Ranzi and the RAC for biomass (see for example [13,14]).

2. Materials and methods

2.1. Materials

Softwood pellets with a diameter of 6 mm were bought at a commercial retailer in Umbria (Italy), and were produced by HS Holzexport Schuster Gesellschaft m.b.H. from species belonging to the fir genus grown in Austria, Innsbruck. Pure glycerol was bought at a chemicals retailer in Umbria, Italy.

Different pellets produced from glycerol were tested at the Biomass Research Centre laboratories and durability was measured with a New Holmen TekPro machine. Preliminary tests have shown that pellet obtained by mixing glycerol with sawdust in a mass ratio higher than 15% has a durability which is not satisfactory at the moment. For this reason, it has been decided to produce pellets with a mass fraction of glycerol of 10% and a mass fraction of sawdust of 90% and to perform pyrolysis tests in a reactor and in a thermogravimetric balance. It has to be taken into consideration that [15] tested similar concentration of glycerol to produce pelletized pig feed and they report that the durability of the pellets could increase by 9% just by adding glycerol, so the effect of this additive is also dependent on the nature of the material with which it is mixed.

The mixture of wood pellets with pure glycerol was prepared in a 1 L volume glass jar mixing 500 g of wood pellets and 55 g of glycerol (see Fig. 1). At first, the material was mixed for 20 min, then, when no drops of glycerol were visible inside the jar, the raw

Fig. 1. Raw material used, A-pure glycerol, B- wood pellets, C- glycerol-wood pellets.