



## Catalytic pyrolysis of sugarcane bagasse and pinewood in a pilot scale unit



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### ARTICLE INFO

#### Article history:

Received 18 March 2016

Received in revised form 29 July 2016

Accepted 4 August 2016

Available online 10 September 2016

#### Keywords:

Biofuels

Bio-oil

ZSM-5

Pyrolysis

Sugarcane

Bagasse

### ABSTRACT

Recently, many studies have been published on the catalytic pyrolysis of biomass, to improve the quality of the liquid product from fast pyrolysis, especially with ZSM-5 catalysts. However, only a few studies in the literature were not limited to the use of woody biomass as feed.

This paper describes a catalytic pyrolysis study with two different biomass types (sugarcane bagasse and pinewood) using a commercial ZSM-5 catalyst and silica as a reference in a pilot-scale circulating fluidized bed unit. The chemical characterization of the liquid products was performed by comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC × GC-TOFMS).

The gas yields increased with temperature and the presence of ZSM-5 contributed to greater quantities of gaseous deoxygenation products. The coke yields decreased with reaction temperature, but were not influenced by the bed reactor material. Bagasse produced more gas and less coke than pinewood. The liquid yields passed through a maximum at 500 °C.

The catalytic pyrolysis with ZSM-5 generated a significantly greater amount of valuable aromatic compounds, such as toluene and C2-benzene isomers (xylenes and ethyl-benzene), which are petrochemical intermediates with high added values. The source of biomass proved to be relevant to define bio-oil chemical composition. Hydrocarbon and ketone yields were higher for pyrolysis of pinewood, while carboxylic acids, cycloketones, and O-heterocyclic compounds increased when bagasse was pyrolyzed.

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### 1. Introduction

The purpose of second-generation biofuel processes is to add value to materials that would otherwise be considered agricultural wastes, such as sugar cane bagasse, straw, or other solid residues of similar composition. These materials are rich in lignocellulosic organic matter and are therefore potential carbon sources for the production of renewable fuels and products. Different biochemical and thermochemical routes for the conversion of biomass have been studied. However, unlike the first-generation processes, which use consolidated technologies, technical and economic challenges to the implementation of a second-generation biofuel plant on a commercial scale still exist [1].

One of the most promising routes for converting biomass into valuable products is fast pyrolysis, a thermochemical process char-

acterized by the ability to obtain high liquid yields (up to 75 wt.%) from the conversion of biomass in a one-step process in the absence of oxygen [2–6]. This liquid fraction, known as bio-oil, contains a large amount of oxygenated compounds. The product distribution and quality of bio-oil are affected by reaction temperature, residence time and heating rate. According to Bridgwater [2], the char and the gas generated during pyrolysis typically contain 25% and 5% of the energy present in the feedstock, respectively. The energy necessary for the pyrolysis reactions represents approximately 15% of the feedstock energy content; thus, char may be used to supply heat to the process. The use of a circulating fluidized bed reactor (CFB) with the continuous combustion of coke and char in a regenerator offers gains in energy efficiency because the reactions occurring during pyrolysis are highly endothermic and require a continuous supply of energy.

However, despite the advances in research on applications for bio-oil, obstacles still exist to the direct use of bio-oil as a transportation fuel, mainly due to its high content of oxygen, water and suspended solids [7]. Oxygenated compounds are responsible for

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the high acidity, high viscosity, and chemical instability of the liquid product as well as a significant reduction in its heating value. Because bio-oil is formed by fast heating of the biomass followed by fast cooling of the pyrolysis vapors, the resulting oxygenated molecules are not in equilibrium, promoting secondary reactions during storage and transportation of bio-oil [2,8]. These reactions are often catalyzed by alkali metals present in the bio-oil [8–11]. The presence of these metals in the bio-oil is related to the ash content in the lignocellulosic material (which depends on the source and pre-treatment of the biomass) [10,11], and the efficiency of the solid-vapor separation after the pyrolysis reaction. In addition to causing chemical instability, alkaline metals are known to catalyze pyrolysis reactions that yield additional water and gas and thus decrease the yield of organic liquid from agricultural residues [12,13].

Different upgrading routes aimed at reducing these undesirable characteristics have been proposed, such as hydrogenation and catalytic cracking. Catalytic pyrolysis is a process that uses catalysts instead of silica sand to promote deoxygenating reactions. The *in situ* catalytic pyrolysis process simultaneously pyrolyzes the biomass and upgrades the organic vapors in the same reactor, while *ex situ* pyrolysis separates the process into two compartmentalized steps. Studies in the literature have shown various types of zeolites tested as catalysts [14–28], thereby obtaining a more stable bio-oil as the final product. According to G ng r et al. [25], catalytic pyrolysis with zeolites reduces the bio-oil oxygen content and acidity thus promoting an improvement in quality by partially converting oxygenated compounds into carbon monoxide, carbon dioxide, and water.

The aromatic content in bio-oils may be enhanced by zeolitic catalysts [16–30], producing renewable high-value streams for second-generation petrochemical processes or as octane-number boosters. Among the different zeolite structures, ZSM-5 stands out as the best candidate for increasing the yield of aromatics [17–27]. Some of its properties can be optimized to enhance the selectivity for monoaromatics [21–23].

Recently, many studies on the catalytic pyrolysis of biomass were published. However, most of the studies in the literature were restricted to the use of woody biomass as the feedstock [31], despite the fact that the type of biomass is an important parameter in the pyrolysis process, because it directly affects product distribution and the quality of the bio-oil [12,32,33]. Among the types of woody biomass reported in the literature studies of pyrolysis, pinewood is considered a “clean” biomass because it has low ash content.

In the Brazilian energy scenario, the mass of sugarcane bagasse generated from the production of ethanol has been estimated to be 170 million tons/year [34]. Planted sugarcane has increased 84% in acreage over the past decade [35], which makes it a feedstock with great potential for use in the biomass pyrolysis process. Moreover, a new strain of sugar cane was recently developed for which one of the objectives was to increase the per-acre yield of bagasse [36]. The literature lacks studies that evaluate the combined effects among biomass types, the materials used in the bed reactor, and the reaction temperature on the yield and quality of bio-oil, including consideration of the differences in ash and extractive contents.

This paper describes a catalytic pyrolysis study, using a commercial ZSM-5 catalyst and silica as a reference material, in a pilot-scale circulating fluidized bed unit with a biomass flow rate of 1 kg h<sup>-1</sup>. The effects of ZSM-5 at different reaction temperatures on the yield and chemical composition of bio-oil were investigated, using two biomass types (sugarcane bagasse and pinewood). The chemical characterization of the liquid products was performed by comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC × GC-TOFMS).

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Biomasses

Two types of biomass were used: sugarcane bagasse, supplied by Usina S o Martinho (S o Paulo, Brazil), and Lignocel BK40-90, a commercial pinewood biomass supplied by J. Rettenmaier & S hne GMBH + CO KG (Rosenberg, Germany). The moisture content in these biomasses is approximately 8 wt.%. Elemental and chemical analyses were performed to characterize both biomasses. The elemental composition (carbon, hydrogen, and nitrogen) was determined using a ThermoFinnigan FLASH EA 1112 analyzer, according to the method used for petroleum products ASTM D5291. The experimental procedure used to determine their composition was based on the Laboratory Analytical Procedures developed by the National Renewable Energy Laboratory (NREL) [37]. Some minor differences between the NREL method and procedure used in this study should be highlighted: the fiber size of biomass after grinding and sieving (20 to 80 mesh), the wave length used to quantify the acid soluble lignin (240 nm), the application of two acid hydrolysis steps, and the temperature during burning of the sample to determine ash (575 °C) were modified. The results are presented in Table 1.

#### 2.1.2. Heat carrier materials – acidic zeolite and silica

The acidic zeolite catalyst used in the experiments was a commercial sample based on ZSM-5 and supplied by FCC S.A. (Rio de Janeiro, Brazil), while an inert material composed of silica and clay was used as a reference. A hydrothermal deactivation procedure was carried out on the fresh materials at 805 °C for five hours under 100% steam atmosphere in a fluidized bed unit, commonly used for evaluation tests of catalytic cracking catalysts. Table 2 shows the properties of the ZSM-5 and silica after deactivation.

### 2.2. Setup and procedure

All runs were carried out in a pilot-scale biomass pyrolysis unit as shown in Fig. 1. The pilot plant, made of stainless steel (AISI 310), was fully automated to allow unattended operation.

The unit consisted of a fluidized bed pyrolysis reactor with three sections of 128.5, 62.7 and 21 mm ID, a lift line of 17.8 mm ID and a fluidized bed regenerator vessel with two sections of 102.3 and 26.6 mm ID. An integrated loading system was designed for introducing the biomass into the unit, comprising a hopper (11 L) with

**Table 1**  
Biomass characterization by elemental analysis and Klason method.

Composition, wt.%	Bagasse	Wood
Carbon	42.3	46.1
Hydrogen	6.3	6.3
Nitrogen	<0.3	<0.3
Oxygen (by difference)	44.6	46.7
Ash	6.5	0.6
Cellulose	36.3	39.0
Hemicellulose	20.7	27.5
Lignin	22.9	26.9
Extractives	10.8	3.7
Acetate	2.7	2.3

**Table 2**  
Properties of the ZSM-5 and the silica.

Catalyst	BET Surface Area m <sup>2</sup> /g	Micropore volume cm <sup>3</sup> /g
ZSM-5	127	0.037
Silica	13	0

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