



## Research article

# Pyrolytic oil production by catalytic pyrolysis of refuse-derived fuels: Investigation of low cost catalysts



Henrietta Essie Whyte, Khaled Loubar\*, Sary Awad, Mohand Tazerout

GEPEA, UMR 6144, Department of Energetic Systems and Environment, Ecole des Mines de Nantes, La Chantrerie, 4 rue Alfred Kastler B.P. 20722, F-44307 Nantes Cedex 3, France

## ARTICLE INFO

## Article history:

Received 1 April 2015

Received in revised form 5 August 2015

Accepted 19 August 2015

Available online 31 August 2015

## Keywords:

Catalytic pyrolysis

Refuse derived fuel

ZSM-5

Char

Oyster shell

## ABSTRACT

Low cost catalytic pyrolysis options were studied by using spent and regenerated ZSM-5, RDF char and oyster shell in the pyrolysis of RDF. The pyrolysis was performed at a temperature of 500 °C, sweeping gas flow rate of 20 ml/min and heating rate of 10 °C/min. The catalysts were effective in reducing tar yield and oxygen content and increasing the organic fraction. ZSM-5 lost some activity after one use but regeneration helped to increase its effectiveness. The catalytic bio-oil had density, heating value and viscosity comparable to the conventional diesel fuel. Gases from catalytic pyrolysis have significant heating values ranging from 17.1 to 21.9 MJ/m<sup>3</sup> but the use of the catalyst led to an increasing production of CO<sub>2</sub>. Catalyst use did not alter significantly the characteristics of the solid residue.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Municipal Solid Waste (MSW) management and energy security are currently two of the most challenging global problems and one way to solve these two problems at once is by the use of Waste to Energy (WtE) Technologies. The benefits of energy recovery from MSW are largely unquestionable, both for the energy benefit itself and for the positive environmental implications [1]. Advanced thermochemical technologies like gasification, pyrolysis and liquefaction are promising options for the treatment of MSW. The heterogeneity of MSW however, makes it difficult to be used as feedstock as it leads to variable (and even unstable) operating conditions which result in product quality fluctuations [2]. Refuse derived fuel (RDF), made from the combustible fraction of MSW constitutes a good material and presents several advantages over MSW, including its relatively constant density and size, uniform composition, higher heating value, and easy transport [3,4].

Pyrolysis is the thermal degradation of organic matter in an inert atmosphere and has the potential to enhance the energy and economic value of the derived pyrolytic products (gas, oil, and char). However, during the pyrolysis of RDF, the heavy molecular tar fraction condenses and solidifies along the wall of the condenser forming wax-like substances which consequently lead to blockages. Also, the bio-oil produced has undesirable characteristics such as high oxygen content, low heating value, high viscosity, corrosiveness and thermal instability which limit its direct application as a fuel.

Catalytic pyrolysis is a promising technique which exists for tar reforming/wax elimination and bio-oil upgrading. It consists of the addition of catalysts to the pyrolysis process. The use of catalysts confers an additional value since an adequate catalyst can improve the products' quality and lead towards the selectivity of more valuable products [5]. The catalysts used are expected to enhance the cracking reactions of the tar molecules in pyrolysis products resulting in the production of lighter and less complex tar molecules. They also reduce the formation of carboxylic acids making bio-oils less corrosive and induce the reactions that involve the removal of the reactive oxygenated species, especially carbonyl compounds, leading to the production of bio-oil of higher heating values and better stability [6]. Han et al. [7] have investigated the catalytic upgrading of coal pyrolysis tar in a dual-stage reactor over char and metal impregnated char. They reported that the catalytic upgrading caused the lower total tar yield and the higher non-condensable gas yield but the fraction of light tar increased.

The catalyst cost is an important factor in the comparison between thermal and catalytic pyrolysis as the use of expensive catalyst may economically cripple the process, due to the high amounts of catalyst which would be necessary in an operating plant. Therefore, exploring low cost options is vital to the economic sustainability of the pyrolysis process.

CaO has been reviewed as one of the most effective and widely used alkaline earth metal oxides as a catalyst for bio oil upgrading. Recently, research interest has been growing in the utilization of natural calcium sources from waste materials as catalysts [8]. Some researchers have found that the derived CaO catalysts from waste shells, such as oyster, not only exhibit a high potential use as biodiesel synthesis catalysts but also add value to the green biodiesel process due to their eco-friendly characteristics and cheap cost [9]. There have been several

\* Corresponding author.

E-mail address: [khaled.loubar@mines-nantes.fr](mailto:khaled.loubar@mines-nantes.fr) (K. Loubar).

reports in the literature of the use of shells for transesterification. Nakatani et al. [10] reported a high biodiesel yield of 73.8% when they examined the transesterification of soybean oil catalyzed by combusted oyster shell. Wei et al. [11] and Boey et al. [12] respectively investigated the viability of chicken eggshells and crab shell as solid catalyst for transesterification and found that they were active for biodiesel production. Boro et al. [13] investigated the performance of *Turbonilla striatula* shells as catalyst in the transesterification of mustard oil and found it active for biodiesel production. All these works revealed that the waste shell-derived catalyst showed high potential to be used as a low-cost biodiesel production catalyst. However, to the best of our knowledge no work has been conducted on the use of shells as a catalyst in the pyrolysis process for tar reforming and bio oil upgrading.

Char is often considered to be a by-product of pyrolysis process and could be used as an energy source. However, several studies have proven that char is a valuable product that has the potential to be used in catalytic applications. Shen et al. [14] investigated the catalytic conversion and upgrading of tar using Rice husk char and recorded a tar removal efficiency of 42%. Min et al. [15] reported the catalytic effects of char-supported iron/nickel catalysts on the steam reforming of biomass tar and claimed that char could disperse the catalysts and interact with the catalysts to enhance their activity for the steam reforming of biomass tar. Wang et al. [16] studied the catalytic performance of char on the reduction of brown coal tar in an entrained flow reactor under a wide range of experimental conditions. It was found that the char showed encouraging results for the reforming of tar derived from the pyrolysis and gasification of Shengli brown coal. Char is a low cost material, and as indicated it has quite high catalytic activity because it contains metals and minerals (ash) which are catalytically active and are well dispersed on the char surface [17]. RDF contains quite high ash content which remains in the char thus making the char interesting as a catalyst [18,19].

Apart from examining the use of these novel catalysts, it is also necessary to look at the regeneration and reusability of some of the conventional catalysts. Among the wide variety of conventional catalysts used in tar reforming and bio oil upgrading, ZSM-5 exhibits the best performance in terms of the production of aromatic hydrocarbons, deoxygenation and resistance to coke deposition [20]. This performance is due to its strong acidity and shape selectivity, the latter depending on the particular textural properties (structure and pore size) of each zeolite [21]. Despite the advantages, one of the main challenges observed is the deactivation of the catalysts. The catalyst deactivation of different type of catalysts is reported in the literature [22–26]. Two different deactivation mechanisms were observed by Serrano et al. [26] a reversible deactivation by coke deposition and an irreversible or permanent deactivation by other factors. It is very important that the regeneration and also the re-usability of spent catalyst are studied. There are a few references in the literature concerning ZSM-5 regeneration [26,27] and fewer on reuse of ZSM-5 [21] and most of them have been carried out in pyrolysis of plastics and none so far on mixed feedstock like RDF.

The objective of this work is to study the use of oyster shells and RDF char in the pyrolysis of RDF and also to evaluate the ability to use ZSM-5 more than once. With this objective, a characterization of the products

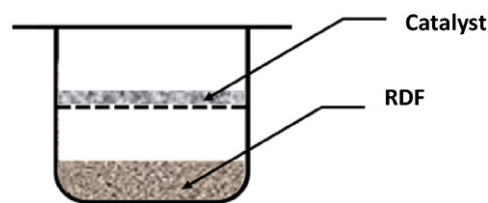
**Table 1**  
Composition of RDF.

Proximate analysis (wt.%)		Ultimate analysis <sup>a</sup> (wt.%)	
Moisture	3.7	C	37.4
Volatile matter	68.3	H	4.8
Fixed carbon	6.0	N	1.0
Ash	22.1	O <sup>b</sup>	34.6
HHV (MJ/kg)	17.2	S	n.d.

n.d.: not detectable—<0.2%.

<sup>a</sup> Dry matter.

<sup>b</sup> By difference.



**Fig. 1.** Catalyst bed configuration.

obtained in pyrolysis with fresh, regenerated and spent ZSM-5, oyster shells and RDF char is presented in this paper. The catalysts are evaluated on their ability to reduce tar (wax) yield and also to improve physical properties of the bio oil while producing acceptable levels of the organic (oil) fraction yield.

## 2. Materials and methods

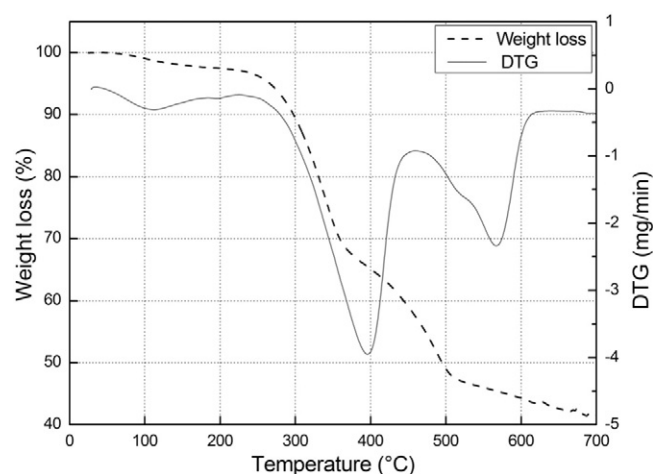
### 2.1. Materials

The RDF samples used were obtained from a French RDF manufacturing company. The RDF was produced after some process phases (dehydrating, separating of recyclables and shredding). RDF used in the pyrolysis experiments was in the fluff form. The characteristics of the sample are presented in Table 1. A commercial ZSM-5 provided by Acros Organics was used for the catalytic experiments. The catalyst has a 400 nominal mol SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio and was used as received, without any activation process. RDF char used for the experiments was obtained after pyrolysis of RDF at 10 °C/min to 500 °C and held there for 30 min. The oyster shell was ground to 1 mm particle size. Both catalysts were used without activation.

### 2.2. Experimental method

A fixed bed laboratory scale reactor was used to pyrolyze the samples. The cylindrical reactor was made of stainless steel with an inner diameter of 9.5 cm, a thickness of 0.5 cm and a height of 9 cm. The reactor was heated by electrical resistance with temperature controlled by a PID (Proportional, Integral, and Derivative). A K thermocouple is placed at the wall and the center of the reactor to measure the temperature evolution.

35 g of the sample was placed in the reactor and the catalyst was placed on a catalyst bed and put in the reactor (Fig. 1) at a ratio of 10%. The sample was heated to 500 °C at 10 °C/min followed by an isothermal step of 30 min. The vapors leaving the reactor were swept away by a 20 ml/min nitrogen flow.



**Fig. 2.** TG and DTG curves of RDF.

Download English Version:

<https://daneshyari.com/en/article/209296>

Download Persian Version:

<https://daneshyari.com/article/209296>

[Daneshyari.com](https://daneshyari.com)