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Synthesis of char-based acidic catalyst for methanolysis of waste cooking oil: An insight into a possible valorization pathway for the solid by-product of gasification

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ABSTRACT

Gasification-based char from a commercial small-scale gasification plant was converted into an acidic catalyst for methanolysis of waste cooking oil (WCO). The char-based acidic catalyst was synthesized by the sulfonation of gasification char with sulfuric acid. Functional groups, acid density, morphological and surface properties were characterized and measured by using Fourier transform infrared red spectroscopy, ammonia temperature programmed desorption, field emission scanning electron microscope and Brunauer-Emmett-Teller, respectively. Wood char based acid catalyst showed higher surface area of 337 m^2/g and acid density of 2.94 mmol/g. The reaction variables such as methanol/oil molar ratio, catalyst loading, reaction time and temperature, were studied. The optimum reaction conditions, 9:1 methanol/oil ratio, 6 wt% catalyst loadincxg, 130 min reaction time at 65 °C, gave 96% of ester conversion. The recovered catalyst was washed and reused without any activation (calcination), still giving 81% of ester conversion after five reaction cycles. Furthermore, fuel properties of WCO methyl esters were determined as per the ASTM and EN biodiesel standards. The utilization of char from biomass gasification for the synthesis of an acid catalyst for biodiesel production allows achieving a twofold objective. On the one side, the valorization of a material which is presently wasted. On the other side, the production of a catalyst that can effectively convert WCO into biodiesel in a single step process, therefore allowing a simplified procedure and lower operational temperatures. In addition, the obtained catalyst showed an interesting efficiency in decreasing free fatty acid of WCO and a considerable recyclability of the catalyst.

1. Introduction

In the last few decades, energy demand has increased drastically worldwide, with mineral oil being the main source of energy. Depletion of fossil fuel reserves, increase of global warming and fluctuating in mineral fuel prices have gained attention worldwide [1]. Biodiesel has similar properties to fossil fuels and it can be considered as a suitable alternative to complement them [2]. Biodiesel is a mixture of fatty acid methyl esters (FAMEs) that are produced from oil in the presence of catalyst and solvent (alcohol) by the transesterification reaction [3]. Several types of oils have been used for biodiesel production around the world, in particular, the first generation oils termed as edible oils such as palm oil [4] soybean oil [5] and canola oil [6]. Other than the feedstock, process conditions such as oil to alcohol (mostly methanol is used because it is cheaper than other primary alcohols) ratio, reaction temperature and reaction time have a great impact on biodiesel properties and its production cost [7,8]. The range of reaction conditions highly depends on the nature of oil/fat used for biodiesel production. In the case of low-quality feedstocks, higher oil to methanol ratios, longer reaction times and higher amounts of catalyst should be used. Theoretically, for the occurring of the transesterification reaction, three moles of alcohol are required for each mole of oil. Nonetheless, in reality, more than three moles are needed to proceed the reaction in the forward direction.

The extensive utilization of edible oils in the biodiesel industry resulted in a fuel versus food controversy. Second-generation oils (non-edible oils) such as Jatropha [9], neem oil [10], rubber seed oil [11], kapok seed oil [12], palm fatty acid distillate (PFAD) [13] and waste cooking oil [14] have been explored to avoid the controversy. Third generation oil, which is algae oil, has also been tested for biodiesel synthesis [1].

In comparison of fossil fuels, biodiesel is more expensive

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Nomenclature

FAME	fatty acid methyl ester
PFAD	palm fatty acid distillate
H_2SO_4	sulfuric acid
KOH	potassium hydroxide
NaOH	sodium hydroxide
WCO	waste cooking oil
FTIR	Fourier transform infrared
FESEM	field emission scanning electron microscopy
NH_3-TPD	ammonia temperature programmed desorption
BET	Brunauer-Emmett-Teller
XRD	X-ray diffraction
KBr	potassium bromide
ASTM	American society for testing and materials
AOCS	American oil chemist society
EN	European nation's standards

(approximately one and a half time more expensive), because of the feedstock cost, which shares around 70–95% of the total cost of biodiesel [15]. Therefore, it is stated that the use of low-cost feedstock such as waste cooking should reduce the overall production cost. Other than feedstock, a suitable heterogeneous catalyst saves a lot of costs. Acidic catalyst reaction is slow, need longer time than usual and their corrosiveness increase the maintenance cost. Other main costs are catalyst, solvent and waste treatment [16].

Currently, homogeneous (H_2SO_4, KOH/NaOH) catalysts are used in transesterification process [17]. The problems associated with the homogeneous catalysts are: on one side, the need of a high amount of energy for purification, separation of by-products and catalyst from produced esters and on other side, it is impossible to recover and use again [18]. The disposal of acidic wastewater produced during purification and separation process is a serious issue being faced by the industries [19]. Because of these issues, there is a growing trend in the field of heterogeneous catalysts (acidic or basic) for esters production.

Heterogeneous catalysts have several advantages over homogeneous catalysts. They can be reused many times, easily separated from the esters layers and there is no generation of wastewater during the purification stage [20]. Several kinds of heterogeneous catalysts have been reported, such as alkali metal catalysts, alkali and alkaline earth oxide, zeolites based catalysts, zirconia-alumina, amberlyst-15 [21,22]. Unfortunately, high cost, sensitivity to water, rapid deactivation, low acidic site are the major obstacles in the application of these catalysts [18]. In recent years, there is a great interest shown in the generation of carbon-based catalysts. Nonetheless, this type of catalysts is still not fully explored. Carbon-based catalysts have several advantages over other metal-based catalysts; they have higher surface area and they are more stable under acidic and basic conditions. Carbon-based D-glucose solid acid catalyst preparation method was developed by Toda et al. They used this catalyst for biodiesel production from long chain fatty acids [23]. Chen et al. [24] used the glucose-starch mixture and prepared acid catalysts. They claimed that mixture of glucose-starch solid acid catalyst gives 96% conversion on the conditions of oil to methanol ratio 10:1, reaction temperature 80 °C and reaction time 6 h. Li et al. [24] investigated rice husk char based solid acid catalysts for the production of oleic acid for biodiesel production. They claimed that, with this catalyst, the oleic acid conversion was around 98.7%. This catalyst shows very high reusability, after seven cycles the conversion yields decrease from 98.7 to 96%. Hidayat et al. [25] applied the coconut shell char based solid acid catalyst for the esterification of palm fatty acid distillate.

Biomass gasification is a thermochemical process that converts biomass into syngas, liquid tar and solid char. Both tar and char are the unwanted byproducts. Char yield depends on the process conditions and the design of the reactor but, typically, it is around 2–5% of the used feedstock. In South Tyrol (Italy), there are around 40 small-scale biomass gasification plants working. More than 1500 tons of char are produced every year only in this region and industries need to pay the huge amount for its disposal. The char used in this study was collected from a downdraft gasifier during a monitoring campaign which details were published previously [26].

From a general perspective, this work aims at investigating a possible valorization route for char, in particular looking at the possibility of using it for synthesizing an acidic catalyst to convert WCO into biodiesel. The prepared catalyst was characterized by using FTIR, FESEM, NH_3-TPD, and BET by N_2 adsorption-desorption methods. Meanwhile, reaction process variables such as oil to methanol ratio, catalyst loading, reaction temperature, and reaction time for transesterification of WCO were also studied. Reusability study of the catalyst was conducted to analyze the effectiveness of the produced catalyst. Furthermore, important fuel properties have also been investigated.

2. Materials and methods

The WCO was collected from the canteen of the Free University of Bolzano, Italy. WCO free fatty acid value (FFA) was measured by following the AOCS method [27] and resulted to be 6 wt%. Methanol (99.9%), sulfuric acid (98%), n-hexane (99.5%), acetone (99.5%), methyl heptadecanoate internal standard for GC (99%) were purchased from Sigma Aldrich and Merck. Char samples used in this study were collected from a local commercial small-scale gasification plant based on downdraft reactor. The samples were characterized by using elemental compositions and ash content analysis. The results are presented in Table 1.

2.1. Catalyst synthesis

A sulfonated char based acidic catalyst was synthesized by following the methodology reported by Toda et al. [23]. Toda et al. used the natural products such as sugar, starch or cellulose for the production of carbon based catalyst, whereas, in this study a byproduct (char) from commercial scale gasification plant has been used as a support material for the catalyst preparation. Briefly, 20 g of char sample was mixed with 200 ml of sulfuric acid (98%) in a 500 ml round bottom flask. The obtained slurry was then heated and continuously stirred for 12 h at 150 °C. The slurry was cooled down at room temperature and filtered. The char catalyst was washed with 80 °C distilled water until the washing water was neutral. The obtained catalyst was dried at 70 °C in an oven for 1 h before further study. From here onward, the synthesized catalyst is termed as wood-char catalyst

2.2. Catalyst characterization

Wood-char and wood-char catalyst were characterized by infrared spectroscopy to identify the functional groups presents on char surface by using FITR (IR, Perkin Elmer 1725 X). Samples was prepared and analyzed by the KBr method. FTIR spectra were obtained at the average

Table 1
Elemental composition of char.

Ash (%wt_{dry})	C	H	O	N	S
	(%wt_{dry})				
27.84	49.04	0.33	48.18[a]	0.08	2.37

[a] Calculated by difference.