



Esterification of rapeseed oil fatty acids using a carbon-based heterogeneous acid catalyst derived from cellulose

Kristaps Malins*, Janis Brinks, Valdis Kampars, Ilze Malina

Institute of Applied Chemistry, Paula Valdena Str. 3, Riga LV-1048, Latvia

ARTICLE INFO

Article history:

Received 15 February 2016

Received in revised form 17 March 2016

Accepted 18 March 2016

Available online 22 March 2016

Keywords:

Cellulose

Carbon-based solid acid catalyst

Sulfonation

Esterification

Amberlyst-15

Biodiesel

ABSTRACT

The present work demonstrates a single-step preparation of sulfo carbon-based solid acid catalyst (CSO₃H) obtained from cellulose by direct carbonization–sulfonation with conc. H₂SO₄. The variation of reaction conditions, such as, reaction temperature (50–180 °C), weight ratio of H₂SO₄ to cellulose (5/1–30/1) and reaction time (1–10 h) provided CSO₃H with relatively abundant density of acid sites attached on catalyst surface. The CSO₃H with the highest density of SO₃H groups (0.81 mmol H⁺/g) was obtained at 100 °C using weight ratio of H₂SO₄ to cellulose (20/1) after 3 h of reaction. The catalyst was characterized by means of N₂ sorption analysis (average pore diameter 12.8 nm, specific surface area 1.38 m²/g, pore volume 0.004 cm³/g), FT-IR, TG, XRD, FE-SEM and S elemental analysis. The conversion of rapeseed oil fatty acids (RFA) in esterification reactions with CSO₃H as catalyst was quite similar to the commercial Amberlyst-15 and the biodiesel with ester content of ≥96.5% was successfully obtained under optimized reaction conditions.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Biodiesel is renewable, clean biofuel and it can be manufactured from vegetable oils, animal fats and micro-algal oil [1] in transesterification reaction with lower alcohols-methanol, ethanol etc. [2]. Typically the feedstock of commercial biodiesel is a food grade vegetable oil such as soya bean, palm and rapeseed oil (RO) [3]. Furthermore, the biodiesel also can be produced from any kind of raw material containing fatty acids or their glycerides. The properties of biodiesel are close to fossil diesel fuel; thus it becomes a promising alternative fuel for the employment in common diesel engines [4]. NaOH, KOH, NaOCH₃ are the commonly used homogeneous alkaline catalysts for biodiesel production from glycerides with low content of water and free fatty acids (FFA) [5]. Alkaline catalysts have a high catalytic activity in transesterification reactions, but even low amounts of the water (≥0.1 wt.%) and FFA in reaction mixture can significantly affect the biodiesel yield [1]. The alkaline catalysts react with FFA and also glycerides in presence of water forming soaps. This leads to irreversible reduction of catalyst concentration in reaction mixture. The susceptibility of acid catalysts to these contaminants is significantly lower [6]. Strong mineral acids as H₂SO₄ can be successfully used as catalyst for

transesterification [4] and esterification [7,8] reactions of glycerides and FFA, respectively. However the homogeneous catalysts are difficult to reuse, due to its separation from reaction mixture which commonly are technologically complicated and energy consuming processes [9]. The preparation of biodiesel using reusable heterogenous acid catalysts is one of the solutions for development of low-waste technologies and cost minimization of biodiesel production process. High strong acid density and suitable textural properties of carbon-based solid acid catalysts (C_{sac}) usually provides promising catalytic activity in esterification reactions of FFA [10–12]. Furthermore, the carbon materials or their precursors are low cost feedstock for C_{sac} preparation even more increasing its potential for practical application in biodiesel production processes [9]. There are two general groups of C_{sac} described in literature – supported [13] and functionalized catalysts. Functionalized C_{sac} can be synthesized in two main ways – direct sulfonation and sulfonation by alkylation or arylation [10,14,15]. Direct sulfonation of carbon material is the most extensively studied C_{sac} preparation method. C_{sac} have been prepared from different carbon sources such as microalgae residue [16], vegetable oil asphalt [17], lignin [18], glucose [19], glucose/starch mixture [20], cellulose [21] etc. Typically these precursors of carbon material were partially carbonized in N₂ or Ar atmosphere at 400–700 °C and then sulfonated with conc. H₂SO₄ at ~150–210 °C or fuming H₂SO₄ [22]. In the report [21] sulfonation of carbon material was conducted at lower temperature (~80 °C) using H₂SO₄/SO₃ (15 wt.%). Moreover,

* Corresponding author.

E-mail address: mkrist@inbox.lv (K. Malins).

in the paper [23] the preparation of C_{sac} was performed by partial carbonization–sulfonation of glycerol in single-step at 220 °C. In similar manner a C_{sac} was prepared from residual lignin (derived from *Xanthoceras sorbifolia* Bunge hulls) [18] and oilseed cake [24] at 150 and 120 °C, respectively.

Textural properties and overall acid densities of C_{sac} depend on utilized raw materials and reaction conditions [25,26]. The impact of textural properties such as average pore diameter, specific surface area and pore volume on catalytic activity in biodiesel production processes is directly related to the diffusion ability of methanol, FFA and glycerides through catalyst framework and interaction with strong acid sites during the reaction [10,15]. Thereby C_{sac} with mesoporous or larger pore size framework is more suitable for biodiesel production processes. There are two types of acidic surface functional groups of C_{sac} : weak – phenolic hydroxyl (OH), carboxyl (COOH) and strong-sulfo (SO_3H) acid sites. These oxygen containing acidic sites were formed in partial carbonization of feedstock and sulfonation of obtained carbon material [27]. The influence of SO_3H groups on catalytic activity of C_{sac} in esterification reactions is significantly higher in comparison to weak acid sites [10]. Hence, SO_3H density is one of the key factors which determine the catalytic activity of C_{sac} in esterification reactions of FFA. The total and strong acid densities of synthesized C_{sac} varied in wide range [9]. However, the C_{sac} with higher SO_3H densities than ≥ 2 mmol H^+ /g were obtained only in limited number of scientific reports [17]. Furthermore, most of the studies in literature are focused on the C_{sac} preparation using two-step carbonization–sulfonation method without investigation the impact of reaction conditions on SO_3H density of catalysts. The present study is conducted to investigate the effect of different experimental conditions such as weight ratio of H_2SO_4 to cellulose (5/1–30/1), reaction temperature (50–180 °C) and reaction time (1–10 h) on SO_3H density of sulfo carbon-based solid acid catalyst (CSO_3H) prepared in single-step synthesis by direct carbonization–sulfonation of cellulose with conc. H_2SO_4 .

In many scientific reports pure oleic [10,18,20], palmitic [13,28,29] and stearic acid [13] were used as the main reactants in catalytic tests of C_{sac} . The use of FFA consisting of various long chain fatty acids or its mixture with glycerides is more applicable model providing reaction environment closer to industrial biodiesel production processes when FFA content in vegetable oil is elevated. In the present study the effects such as stirring rate (120–1200 rpm), reaction time (20–360 min), reaction temperature (50–65 °C), molar ratio of rapeseed oil fatty acids (RFA) to methanol (1/1–1/40), catalyst amount (1–40 wt.%) on esterification reactions of RFA over synthesized CSO_3H were investigated. The industrial Amberlyst-15, utilized as reference, was also tested under similar experimental conditions. The reusability tests of CSO_3H were conducted using pure RFA and RFA (10 wt.%) / RO mixture.

2. Materials and methods

2.1. Materials

Methanol, ethanol, ethyl acetate, cyclohexane, $NaHCO_3$, $NaCl$, $NaOH$ (purity ≥ 98 wt.%), conc. mineral acids HCl (35.8 wt.%), H_2SO_4 (96.3 wt.%) and Amberlyst-15 hydrogen form-dry were supplied from Sigma–Aldrich. The concentrations of mineral acids were determined using volumetric acid–base titration. Medical cotton wool “Premium” (moisture content 8.4 wt.%) was used as cellulose material and purchased from Mediteks Ltd. C, H and ash content of cellulose was 43.09, 6.21 and 0.06 wt.% (on a dry basis), respectively. N and S content was lower than method detection limit (≤ 0.3 wt.%). RFA was derived from RO by hydrolysis reaction with water in the

Table 1

The main characteristics of rapeseed oil fatty acids (RFA) and rapeseed oil (RO).

Property	Value	
	RFA	RO
Monoglycerides, wt.%	0.8	0.3
Diglycerides, wt.%	0.9	0.7
Triglycerides, wt.%	0.0	97.9
Saponification value, mg KOH/g	N.A. ^a	191.71
Acid value, mg KOH/g	199.91	0.01
Fatty acid composition of RO, wt.%		
Palmitic acid (C16:0)	4.1	
Stearic acid (C18:0)	1.4	
Oleic acid (C18:1)	62.5	
Linoleic acid (C18:2)	21.7	
α -Linolenic acid (C18:3)	8.7	
Arachidic acid (C20:0)	0.4	
Other fatty acids	1.2	

^a Not analyzed.

presence of H_2SO_4 . The main characteristics of RFA and RO are given in Table 1.

2.2. Preparation and treatment of catalysts

Before the carbonization–sulfonation cellulose was dried at 110 °C for 4 h. Effect of different weight ratios of conc. H_2SO_4 to cellulose (5/1, 10/1, 15/1, 20/1, 30/1) and reaction time (1, 2, 3, 6, and 10 h) on S content was investigated. The cellulose (10 g) was gradually immersed in single-neck round-bottom 500 ml flask filled with heated conc. H_2SO_4 (50, 100, 150, 180 °C) for ~5–10 min (depends on the pre-determined temperature, to avoid spontaneous rise of reaction temperature) and stirred (magnetic stirrer, 500 rpm). From this point of reference the reaction time of the carbonization–sulfonation of cellulose was measured. After the reaction, mixture was diluted with warm deionized water to reduce concentration of H_2SO_4 and then filtered. Obtained CSO_3H was washed several times with deionized water to pH ~7 and then with methanol. Washed catalyst was refluxed with water/ethanol/ethyl acetate solution (volume ratio 0.1/1.0/1.0) in Soxhlet extractor for 3 h. After separation and treatment CSO_3H was dried at 65 °C for 6 h in vacuum oven (0.9 kPa) and then grinded and sieved to mesh 200.

The Amberlyst-15 was submerged in methanol for 12 h at room temperature before catalytic tests.

Every experiment was repeated twice and S content, acid densities (SO_3H , COOH and phenolic OH) of CSO_3H , conversion of cellulose to COS_3H and conversion of RFA to rapeseed oil methyl esters (RME) were determined as average arithmetic from two independently repeated experiments. A third independent experiment was performed in cases when previous two experimental values differed more than 5 wt.%, then the average result of experiment was determined using two closest experimental values. In the similar manner results of all quantitative analysis data were obtained and the maximum deviation more than 3.0% was not allowed.

2.3. Characterization of catalyst

Ash content of cellulose and CSO_3H was determined according to ASTM E1755–01 (2007) standard method.

Thermogravimetric (TG) analysis of CSO_3H and cellulose was carried out by Simultaneous Thermal Analyzer (STA) 6000 (PerkinElmer). Experiments were conducted using N_2 flow rate 10 ml/min, heating rate 10 °C/min at maximum temperature 900 °C.

Download English Version:

<https://daneshyari.com/en/article/38902>

Download Persian Version:

<https://daneshyari.com/article/38902>

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