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Characterization and application of dolomite as catalytic precursor for canola and sunflower oils for biodiesel production

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HIGHLIGHTS

- Calcined dolomited was evaluated as catalyst for biodiesel production.
- This catalyst is a double carbonate which is thermally converted into CaO and MgO.
- The calcined material showed catalytic activity to oil due to basic properties.
- Biodiesel conversion was optimized analyzing the effect of reaction conditions.

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ABSTRACT

The catalytic activity of precursor dolomite as a heterogeneous catalyst in biodiesel production has been investigated. The dolomitic material is a double calcium and magnesium carbonate, which when calcinated decomposes into CaO and MgO that are highly basic. The materials were characterized by XRD, TG–DTG, CO_2-TPD, FTIR, XPS, SEM, and N_2 adsorption/desorption at −196 °C. The raw material was activated and used as a catalyst for the transesterification of canola and sunflower oils with methanol. The conversion of canola and sunflower oils to methyl esters was optimized, under different catalyst amount and oil/methanol ratio, and the maximum conversions were: canola (98.81 ± 0.02 wt.%) and sunflower (96.52 ± 0.43 wt.%).

1. Introduction

Nowadays our planet is suffering from various ecological changes, leading to increased concerns about the welfare of the environment. Governments have become aware to reduce the greenhouse gas emissions which have increased due to the increasing energy demand in the last decades. Due the depletion of fossil fuel reserves, renewable energy sources have been developed [1], such as power generation from nuclear reactors, sunlight, or wind which have become more efficient and affordable in recent years.

To answer the growing demand for new renewable energy sources, biodiesel, which is biodegradable, nontoxic, and has low CO_2 emissions, unburned hydrocarbons, particulate matter and SO_2 emissions, is currently being studied [2,3]. Among several possible sources, vegetable oil derived biodiesel is attracting increased attention as a promising alternative to conventional diesel fuels [4], since there is not necessary changes to the diesel engine.

Biodiesel is a monoalkyl ester of fatty acids obtained through the transesterification of triglycerides in vegetable oils or animal fats with short-chain alcohols, such as methanol or ethanol, in the presence of a catalyst [5]. The formation of alkyl-esters compounds diminishes the viscosity and flash-point values of oils [6,7]. Transesterification of vegetable oils or fats for biodiesel production can be catalyzed by both acid and base catalysts [8–10] or with the use of lipases as biocatalysts [11,12]. Generally, basic catalysis is preferred over acid catalysis because of the lower activity of acid catalysts and their higher corrosive character.

Using homogeneous catalysts in biodiesel production has several disadvantages such as the inability to reuse the catalyst and the high generation of waste and effluents. In order to circumvent

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Nomenclature

BET	Brunauer–Emmett–Teller
FID	flame ionization detector
FTIR	fourier transform infrared spectroscopy
ICDS	inorganic crystal structure database
SEM	scanning electron microscope
TGA	thermogravimetric analysis
XPS	X-ray photoelectron spectroscopy
X_{MR}	canola or sunflower oil/methanol molar ratio
X_C	catalyst concentration
XRD	X-ray diffraction
Y_{FAME}	fatty acids methyl esters

these problems, the utilization of a successful heterogeneous catalyst will cope with most of the economic and environmental drawbacks of a homogeneous process. Some solid catalysts, basic or acid, have been tested in the transesterification reaction of triglycerides with methanol. Similarly to homogeneous catalysis, basic catalysts showed higher reaction rate than acid solids and they have been preferably studied.

Thus, a large number of different heterogeneous basic catalysts have been tested for biodiesel production such as Calcium supported tin oxides [13], Ca natural [14], Ca/Zn [15], $Ca_xMg_{2-x}O_2$ [16], waste crab shell [17,18], eggshell [18,19], KI-oyster shell [20], solid waste coral fragment [21], $Ca(OH)_2$ [22], TiO_2/MgO [23], crab and cockle shells [24], $CaMg(CO_3)_2$ [25–30], Shell–core $Ca(C_3H_7O_3)_2/CaCO_3$ [31], Chrysolite with K-doped/MgO [32], Nanocrystalline MgO [33], Mg–Al mixed [34], Ca, Mg and Zn mixed oxides [35], calcium/chitosan spheres [36].

These materials have good catalytic activity in transesterification, when thermally modified to form the metallic oxide. However, few previously published studies have demonstrated a detailed characterization of these materials and the correlation between their properties and the activity in the transesterification reaction for biodiesel production.

Dolomite is a carbonate basic mineral mainly composed of calcium magnesium carbonate $CaMg(CO_3)_2$. Dolomite is a common mineral in both continental and marine sedimentary rocks and metamorphic rocks. This mineral is formed by a substitution by ion exchange of calcium by magnesium in the limestone ($CaCO_3$) and is very abundant in nature so dolomite has low cost and non-toxicity.

Thermal activation dolomite has been studied as a heterogeneous catalyst for producing biodiesel using canola oil [27] and palm kernel oil [25]. There are not studies which have been evaluated under weak reaction conditions (catalyst amount, oil/alcohol molar ratio, temperature). Besides that, the mechanism of thermal modification is not well described and the effects of weak reaction conditions on transesterification have not been evaluated as well.

The oxides formed after the thermal modification exhibit catalytic activity in the transesterification reaction due to the high basic characteristics of these calcium–magnesium oxides. In this sense, few research studies have been published that demonstrate the characterization of dolomite after the thermal process and its application as a catalyst for the transesterification reaction of vegetable oils.

The objective of this paper was establish the relation of thermal modification and catalyst activity, using weak reaction conditions, such as, low molar ration of oil/alcohol and catalyst amount. The calcium and magnesium oxides from natural dolomite sources were obtained and evaluated its catalytic activity in the transesterification of canola and sunflower oils with methanol. The catalysts were characterized using several analytic techniques, so to evaluate whether the calcium and magnesium carbonates were converted into calcium and magnesium oxides as well as to verify its catalytic activity.

2. Experimental

2.1. Materials and reagents

Commercially edible grade canola and sunflower oils were obtained from a supermarket (Liza, Brazil). The physical–chemical properties and fatty acid composition of canola and sunflower oils are shown in Table 1. Methanol (99.8%) was supplied from Vetec (Rio de Janeiro, Brazil). The gases used in the experiments were He and CO_2 (99.99%; Air Liquide). The dolomite was obtained from Itamil Ltda. (Fortaleza, Brazil); methyl heptadecanoate with (99.99%) purity was obtained from Sigma–Aldrich. The fatty acid composition of sunflower oil was initially determined by promoting the esterification of the sample, followed by quantification of methyl esters using gas chromatography. This reaction was carried out according to the procedure described in the ISO standard 15304:2002 (E) [37].

2.2. Preparation and activation of material

Before using dolomite as a catalyst, it should be thermally activated by a calcination process. The thermal process to activate the material involved calcinating the material in a muffle and warming it to 850 °C for 3 h at a heating rate of 30 °C/min.

Table 1
Canola and sunflower oils used in study properties. Data are presented as mean ± standard deviation, $n = 3$.

Property	Result	
	Canola oil	Sunflower oil
Acid value (mg KOH g^{-1})	0.41 ± 0.01	0.21 ± 0.02
Water content (wt.%)	80 ± 1	90 ± 20
Specific viscosity at 20 °C $(kg/m)^3$	917.20 ± 0.34	918.80 ± 1.30
Kinematic viscosity at 40 °C (mm^2/s)	35.73 ± 0.09	33.53 ± 0.34
Fatty acid (wt.%)		
Caprylic (C8:0)	⩽0.001	⩽0.001
Caproic (C10:0)	⩽0.005	⩽0.005
Lauric (C12:0)	0.08 ± 0.02	0.05 ± 0.01
Myristic (C14:0)	0.15 ± 0.03	0.09 ± 0.01
Palmitic (C16:0)	8.88 ± 0.06	5.28 ± 0.02
Palmitoleic (C16:1)	0.10 ± 0.01	0.26 ± 0.01
Stearic (C18:0)	3.26 ± 0.01	2.37 ± 0.03
Oleic (C18:1)	25.92 ± 0.04	64.06 ± 0.03
Linoleic (C18:2)	59.46 ± 1.03	17.69 ± 0.98
Linolenic (C18:3)	1.05 ± 0.01	9.03 ± 0.05
Arachidic (C20:0)	0.22 ± 0.02	0.73 ± 0.02
Behenic (C22:0)	0.72 ± 0.01	0.37 ± 0.01
Erucic (C22:1)	⩽0.001	0.07 ± 0.01
Lignoceric (C24:0)	0.16 ± 0.01	0.19 ± 0.02
Σ Unsaturated	86.53	91.11
Σ Saturated	13.47	8.89
Mean molecular weight (g mol^{-1})[a]	879.90	883.27

[a] Obtained from the fatty acid composition.