



Solvent Assisted Biodiesel Production by Co-processing Beef Tallow and Soybean Oil Over Calcium Catalysts

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Received: 22 July 2019 / Accepted: 25 November 2019 / Published online: 30 November 2019
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Abstract

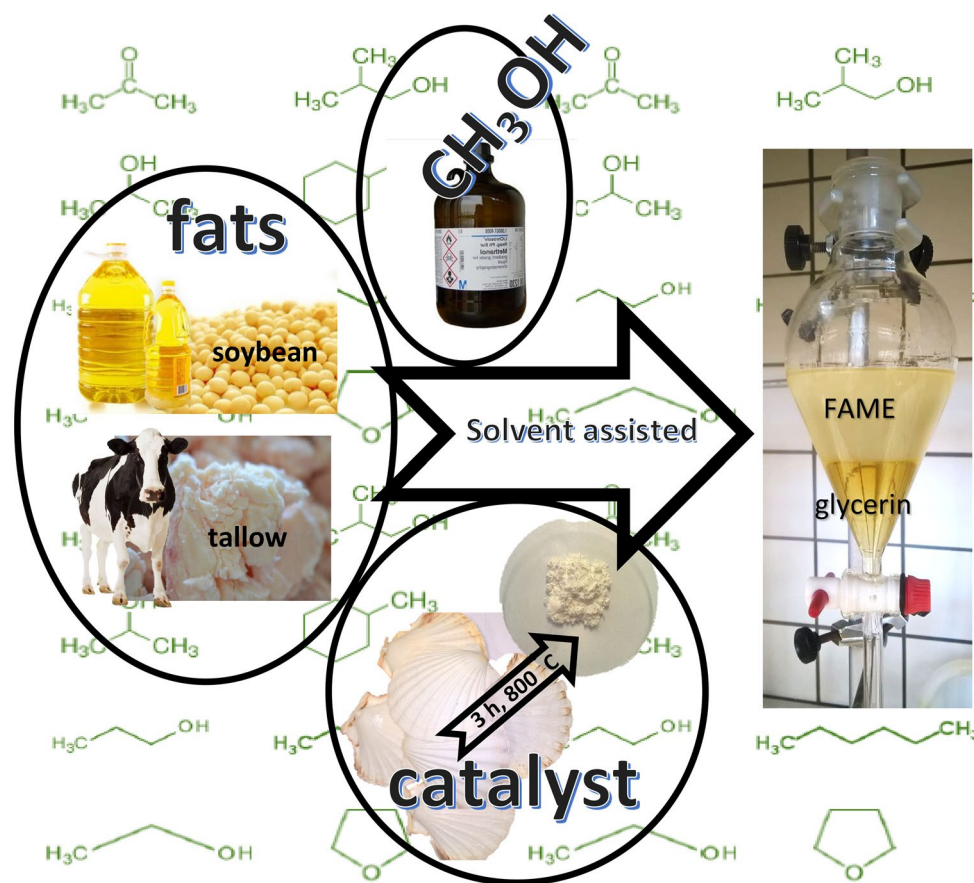
Due to sustainability issues, biodiesel must be produced from low-grade fats and the conventional homogeneously-catalyzed processes must be replaced by more efficient and more profitable production processes such as heterogeneous ones. Biodiesel (fatty acids methyl esters, FAME) was produced from a mixture (50 wt%) of soybean oil and non-edible beef tallow over heterogeneous calcium-based catalysts obtained by calcination of scallop shells. In order to improve the catalytic performances, solvent assisted methanolysis was conducted using alcohols (ethanol, 1-propanol, isopropanol and isobutanol), acetone, methylcyclohexane, and tetrahydrofuran (THF) with $V_{\text{methanol}}/V_{\text{solvent}} = 2.8$. Catalytic data revealed that alcohol solvents adsorb competitively with methanol on the catalyst active sites reducing the FAME yield due to their slower alcoholysis rates. Hexane and methylcyclohexane are inadequate for methanolysis reactions since they are immiscible with methanol. THF and acetone are immiscible with the co-produced glycerin, which favors methyl esters formation by displacing the chemical equilibrium towards reaction products. Acetone performs better than THF (FAME yield gain of 14% against 3%) because of its higher miscibility with methanol. THF was the most effective solvent to avoid fat adsorption on the catalyst surface, a key factor for catalyst stability, and to improve the glycerin purity.

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Graphic Abstract



Keywords Biodiesel · Sustainability · Low grade fats · Calcium catalyst · Solvents · Glycerin purity

Statement of Novelty

Low grade fats can be processed/co-processed with vegetable oils over basic heterogeneous catalysts using solvents. The immiscibility of solvent/glycerin seems to play a chief role.

Introduction

The correlation between economic growth and energy consumption is complex [1] but energy, in parallel with water and food, plays a crucial role in human life [2]. With a fast rising of energy consumption around the world (Fig. 1) and an energy mix dominated by coal and oil it is imperative to find renewable and sustainable sources of energy. In a sustainable development low-carbon scenario, renewable energy sources will double their share in the energy mix, up to 40% until 2040 [3].

Biodiesel, a mixture of alkyl esters of fatty acids, is pointed out as a feasible renewable and low-carbon substitute for fossil diesel in the transport sector [5]. Biodiesel is mainly produced by catalyzed transesterification of fats with short-chain alcohols, such as methanol [6]. The most common feedstocks used in biodiesel production are vegetable oils, which are expensive and raise several ethical issues related with the use of arable lands [7]. The raw material prices represent about 70–95% of the total biodiesel production cost [8]. To improve the biodiesel sustainability and reduce the production costs, biodiesel can be produced from different, non-edible oils and animal fats.

Among the different non-edible animal fats beef tallow, pork lard, chicken fat, and grease can be used to produce biodiesel. These feedstocks are wastes or by-products resulting from animal meat processing and rendering companies with relatively low price [9]. The reuse of these wastes minimizes the environmental impact of its accumulation [10]. Additionally, biodiesel produced from animal fats has a higher cetane number, a better oxidative stability and higher calorific value

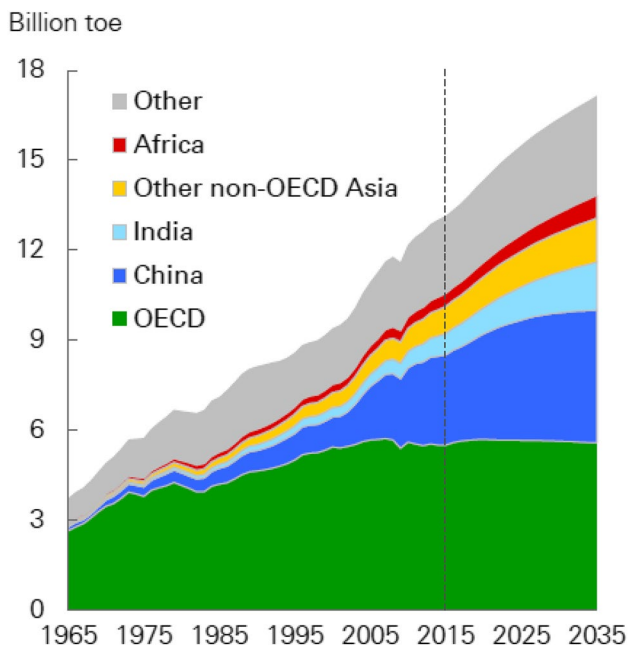


Fig. 1 Energy consumption by region (adapted from [4])

(advantages) when compared with the biodiesel produced from vegetable oils. However, because animal fats have a significant content of saturated fatty acids, the produced biofuel presents a higher cloud point (disadvantage) [11]. Although the most common process for biodiesel production is using homogeneous basic catalysis, there has been a growing interest in the use of heterogeneous basic catalysts since they are easily separated from the reaction mixture, improving the quality and purity of reaction products. They can also be reused, being able to be employed in continuous processes [9]. Calcium oxide is a heterogeneous basic catalyst with good catalytic activity and low solubility in methanol and biodiesel [6]. This catalyst is also low-priced, environmentally friendly and can be prepared from natural sources, such as rocks, bones or calcium-rich food wastes, by calcination [12–14]. Recently Kouzu et al. [15] reported the industrial feasibility of calcium catalyst for biodiesel production.

Feedstocks containing high Free Fatty Acids (FFA) content, such as animal fats, are a challenge for the base-catalyzed transesterification process. FFA react with the base catalyst forming soaps, which leads to loss of catalyst and reduces the Fatty Acid Methyl Ester (FAME) yields which, consequently, increases the production processing costs. To minimize this drawback, two strategies can be implemented separately or together. First, fats can be co-processed with other raw materials improving the biodiesel properties. Taravus et al. [16] studied some physical properties of biodiesel obtained from different mixtures of sunflower oil and beef tallow. They reported that the physical properties of biodiesel obtained using the mixture of 60% sunflower oil met the European and

American standards, EN 14214 and ASTM D6751, respectively. Additionally, the use of beef tallow slightly increased the heating value of the biodiesel. Pereira et al. [17] studied the oxidative degradation of soybean/beef tallow biodiesel 70/30 and 50/50 wt% during long-term storage. The results showed that both biodiesel samples presented higher oxidative stabilities than soybean biodiesel. Furthermore, the blends met the limits proposed by EN 14214 for oxidative stability.

As recognized by the majority of researchers, the immiscibility of alcohol and fat makes the transesterification reaction slow due to mass transfer limitations [18]. This effect is most pronounced when the catalyst is heterogeneous. The immiscibility undesired effect can be minimized if the transesterification reaction is carried out in the presence of a solvent [19]. For homogeneously-catalyzed (KOH) oil methanolysis, Encinar et al. [20] evaluated the use of several ethers and tetrahydrofuran (THF) as solvents. The authors obtained higher biodiesel yields for shorter reaction times when solvents were used. The best results were attained for diethyl ether and THF solvents, but THF was easier to recuperate from the reaction mixture. Duc et al. [21] studied acetone assisted biodiesel production from used cooking oils by KOH catalyzed process. They obtained 98% of FAME using the optimized reaction conditions (acetone/methanol = 1/5). The authors underlined the fact that acetone has many advantages but must be removed from FAME mixture, which may hinder the advantages related to the elimination of the immiscibility of the reaction components. Solvent assisted methanolysis was also used to produce biodiesel from low-grade animal fats. Janchiv et al. [22] reported the use of *n*-hexane solvent during pork lard methanolysis catalyzed by KOH. Other researcher also used *n*-hexane to process waste frying oils. Janchiv et al. [22] reported a high volume of solvent (60%) to process lard, whereas Yusuf and Athar [23] used 25% of the same solvent to process vegetable oil. Roschat et al. [6] also reported a reaction time decrease when THF was used as solvent during oil methanolysis over river snail shells-derived CaO. Analogous effect was observed by Alhassan et al. [24] for cotton oil methanolysis. They reported a drop of 60% in reaction time when solvents such as diethyl ether and acetone were used with the additional advantage of improvement of some biodiesel properties. Tang et al. [25] used glymes as solvent in lime catalyzed methanolysis and attributed the improvement of the reaction rate to the glyme capacity to dissolve the triglycerides. Additionally, a decrease of soap formation when glymes were used was reported, with the additional advantage of avoiding the catalyst pre-treatment since they remove the surface layer of CaCO₃ and Ca(OH)₂. Recently Todorović et al. [26] used biodiesel as solvent in sunflower methanolysis over CaO catalysts. The author reported a relevant solvent effect on the catalytic performances, including catalyst stability, but the use of FAME solvent do not avoided the formation of calcium diglyceride which is usually reported as

responsible by catalyst leaching and glycerin contamination with Ca species [27].

As described above, several solvents can be used to improve the biodiesel production process. In order to contribute to the knowledge in this field, data on solvent assisted biodiesel production by methanolysis of mixtures of beef tallow and soybean oil are presented.

Experimental

Catalyst Preparation and Characterization

Methanolysis tests were carried out over a Ca catalyst prepared by calcination of scallop shells (*Argopecten irradians*, 800 °C for 3 h). The calcination temperature was selected considering the thermal degradation profile of raw shells under air flow [12]. The collected shells were washed, dried and coarsely grounded. After calcination, the chalky white material was reduced to powder in an agate mortar. The fresh and post-reaction catalysts were characterized by X-ray diffraction and infrared spectroscopy.

The XRD diffractograms were recorded with a Rigaku Geigerflex equipment with a Cu K α radiation at 40 kV and 40 mA (2°/min) and, in order to identify the reaction species (hydroxyl, methoxide and others) on the catalysts surface, infrared spectra were collected, for post-reaction catalysts, with a resolution of 4 cm⁻¹, using a FT-MIR Perkin Elmer Spectrum Two IR Spectrometer. A horizontal total

attenuated reflection accessory (ATR), from PIKE Technologies, with a ZnSe crystal, was used.

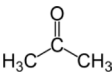
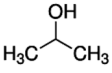
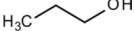
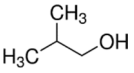
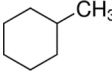
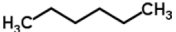
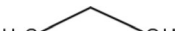

The post-reaction catalysts were also characterized by thermogravimetry, under air flow, to evaluate the reaction species which remain adsorbed and, thus, to infer about their stability [28]. The thermograms were acquired in an alumina crucible using a Netzsch TG–DTA–DSC thermobalance (20 °C/min).

Methanolysis Catalytic Tests

The methanolysis tests were carried out in pirex round flask reactor for 2.5 h, at methanol reflux temperature, using 5 wt% of catalyst (oil basis) and methanol/fat = 12 molar ratio. For each reaction batch, the catalyst was previously contacted with methanol for 1 h (65 °C) and then, the pre-heated mixture tallow + oil (50 g of each fat) and solvent (when used) was added to the reaction flask. After the reaction period, the slurry was filtrated to separate the catalyst. The oily phase, containing biodiesel and unreacted oil, and the glycerin phase were separated by gravitational settling in a funnel. Details on the reaction procedure are given elsewhere [12]. The acidity of fats was evaluated by KOH titration [12, 29] giving 0.6 mg_{KOH}/g for soybean oil and 3.9 mg_{KOH}/g for tallow.

The solvent effect was studied for alcohols and non-alcohols solvents. Isopropanol, 1-propanol, isobutanol, methylcyclohexane, hexane, acetone, ethanol, or tetrahydrofuran, were mixed with methanol using a methanol/solvent volume ratio of 2.8. Physical–chemical properties of the used

Table 1 Solvents physical–chemical properties

Solvent	Structure	Molar mass (g/mol)	Flash Point (°C)	Boiling	Density at 25 °C (g/cm ³)	Miscibility ^a		
						Methanol	Glycerin	Fat
Acetone		58.08	–17	56	0.791	Y	X	Y
Isopropanol		60.10	12	82	0.785	Y	Y	Y
1-Propanol		60.10	22	97	0.804	Y	Y	Y
Isobutanol		74.12	28	108	0.803	Y	Y	Y
Methylcyclohexane		98.19	–4	101	0.770	X	X	Y
Hexane		86.18	–23	68–70	0.672	X	X	Y
Ethanol		46.07	14	78	0.816	Y	Y	Y
Tetrahydrofuran		72.11	–17	65–67	0.889	Y	X	Y

^aY miscible, X immiscible or low miscibility

solvents are in Table 1. Solvents were selected taking into account the capacity to dissolve the triglycerides and the boiling point, which must be similar to the methanol boiling point [30]. All the used solvents were *p.a.* grade.

The solvent and the unreacted methanol remained distributed between both glycerin and oily phases. Solvents distribution in both oily and glycerin phases will be a function of their properties (Table 1).

Oily phases were characterized by FTIR to quantify the formed esters. The quantification was performed considering the reflectance bands in the range 1480–1410 cm^{-1} , being the band at 1436 cm^{-1} attributed to biodiesel (FAME). Details of the computation procedure are given elsewhere [31, 32]. The purity of glycerin co-produced with biodiesel

in transesterification reaction was assessed by ATR-FTIR [12, 29].

The reproducibility of the catalytic tests was evaluated using four replicas of the reference test (soybean oil without solvent).

Results and Discussion

XRD pattern of the fresh catalyst was similar to those published for analogous Ca based catalysts. Due to the used, relatively low, calcination temperature the X-ray diffraction pattern was mainly composed by lines belonging to calcite (JCPDS 01-086-2334). An analogous pattern was

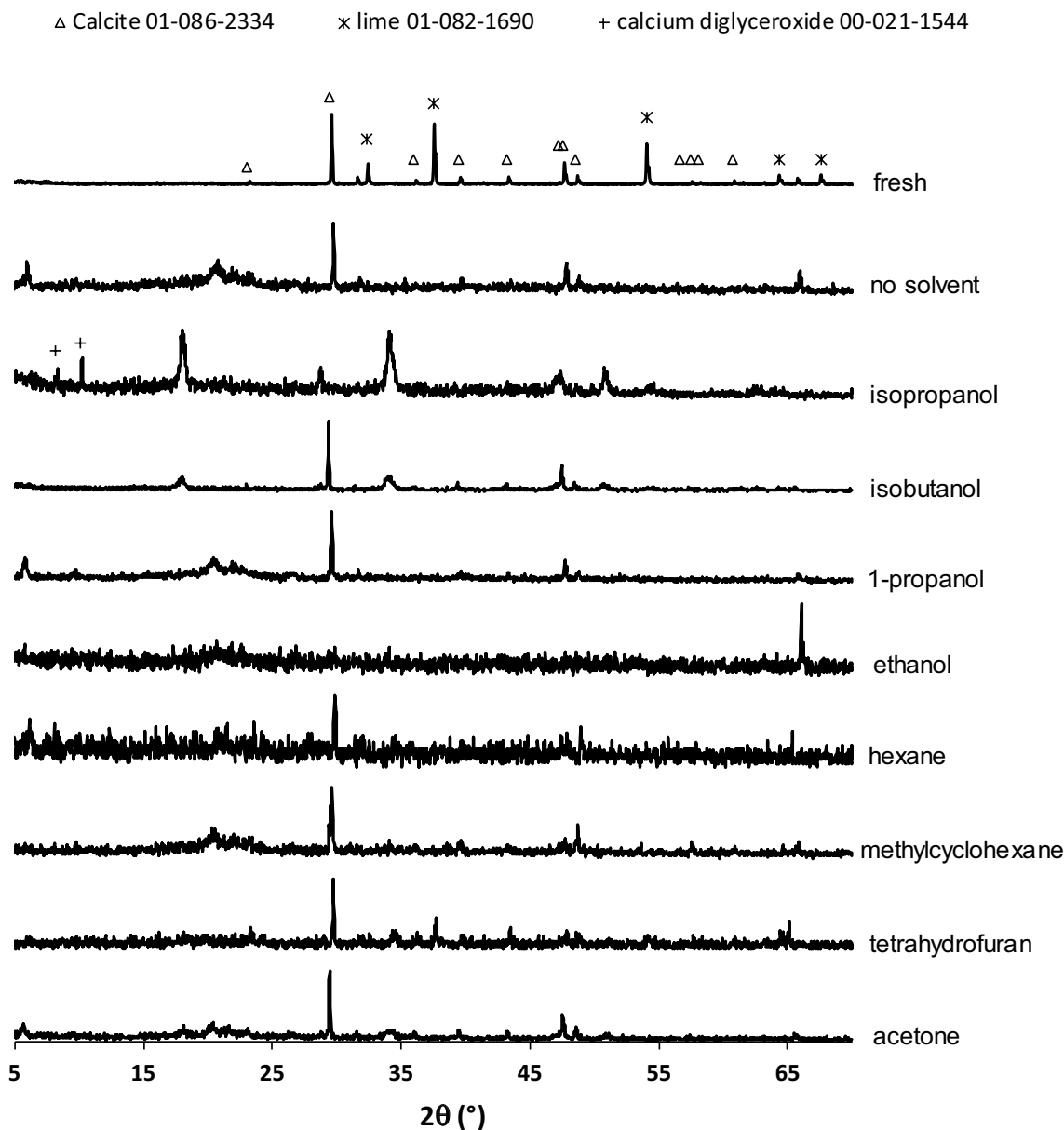


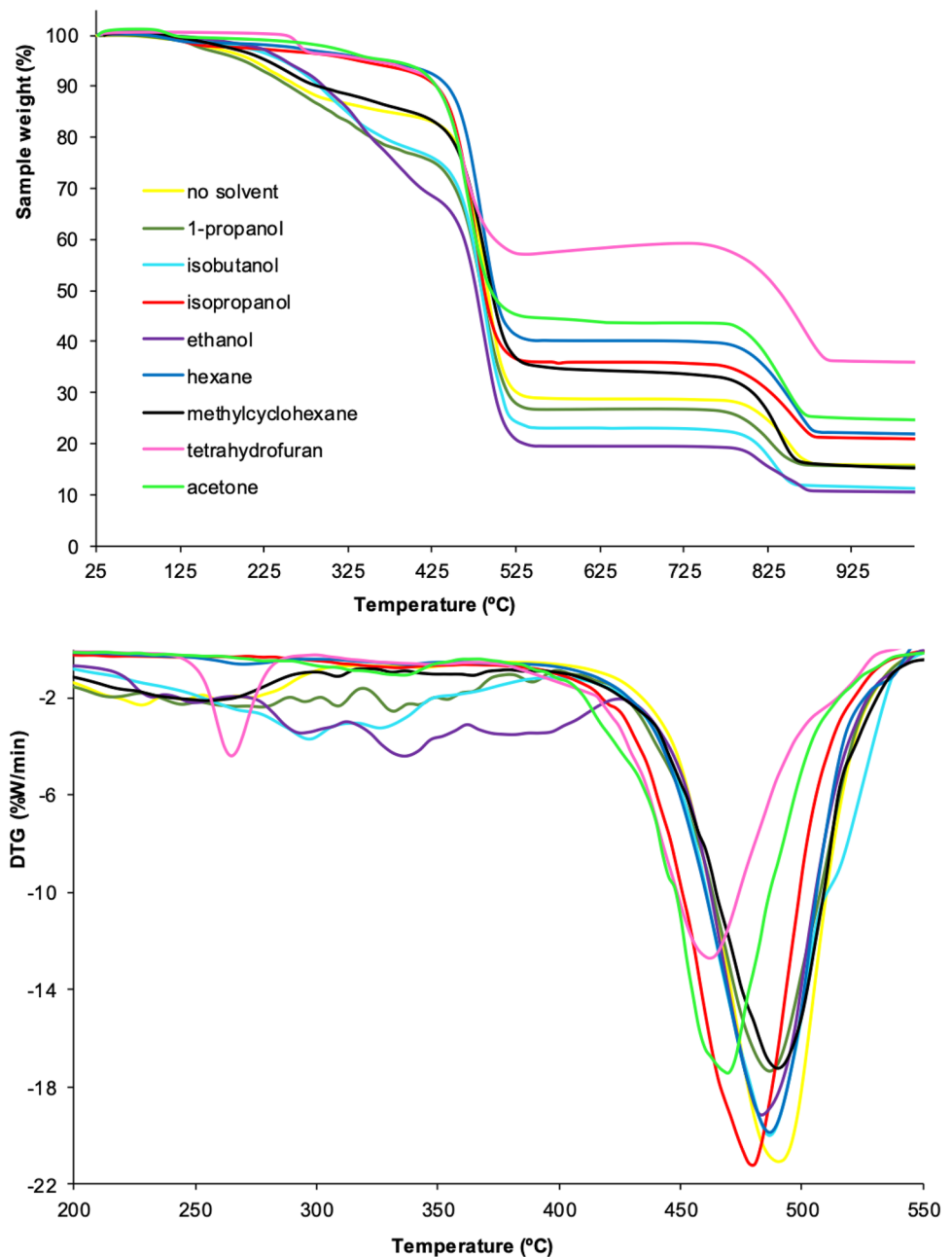
Fig. 2 XRD patterns of fresh and post-reaction catalysts (JCPDS standard files were used to crystalline phases identification)

observed for the powdered raw Scallop shells. Calcination step at 800 °C was unable to totally convert calcite into lime (Fig. 2). Low intensity XRD lines belonging to lime (CaO, JCPDS 01-082-1690) are overlapped with calcite pattern showing that only a small part of calcite was de-carbonated during calcination.

The post-reaction catalysts (Fig. 2) showed significant amorphization, being this occurrence more noticeable for catalysts used with hexane and ethanol solvents. The marked structural changes observed, more remarkable than that previously reported for situations where only vegetable oil is processed [28], is due to the co-processed tallow

acidity and to the fact that the catalyst has been calcined at a relatively low temperature. In fact, several researchers reported an increase of catalyst stability for calcination temperatures above 800 °C [33]. The XRD pattern of catalyst obtained with isopropanol displays X-ray lines belonging to calcium diglyceroxide (JCPDS 00-021-1544) and portlandite (Ca(OH)₂). As previously reported, calcium diglyceroxide promotes fast homogeneous catalyzed reaction but is responsible for catalyst deactivation [34] and contamination of glycerin and oily phases with soluble Ca species. From all the used solvents, acetone seems to prevent drastic structural modifications of catalyst, maybe due

Fig. 3 Thermograms of post reaction catalysts (air flow, 20 °C/min)



to its immiscibility. Acetone seems to prevent diglyceroxide formation, probably because glycerin, once formed, is removed from the catalyst surface.

The post-reaction catalysts were characterized by thermogravimetry (TG) in order to evaluate the amount of reaction species which remained adsorbed. As reported by Dias et al. [28], Ca catalysts stability can be correlated with TG data.

The thermograms obtained under air flow (Fig. 3) showed that all the catalysts lose an appreciable amount of weight in the 375–525 °C temperature range due to fats and biodiesel species adsorbed. The DTG curve (differentiated weight loss curve) can be used to distinguish between fat and biodiesel species thermal degradation [28]. Thus, comparing to the thermal degradation profiles of fat (oil and tallow) and biodiesel, it can be stated that fat adsorbed on catalyst decomposes around 490 °C whereas biodiesel decomposes for lower temperatures showing a maximum rate of degradation at 460 °C. Only acetone and THF prevent the adsorption of fat species. This result can also be attributed to the fact that, both acetone and THF lead to higher levels of fat conversion (Table 2), which means that catalysts remained less time in contact with the fat, thus minimizing its adsorption. The post-reaction catalyst obtained with THF as solvent shows a distinct process around 267 °C corresponding to the thermal degradation of calcium diglyceroxide [28]. This occurrence was prevented by acetone due to glycerin/acetone immiscibility.

Additionally, post-reaction catalysts were characterized by ATR-FTIR spectroscopy (Fig. 4a). The FTIR spectrum of fresh catalyst was used for comparison, showing the analyzed range of wave numbers reflectance bands at 1407, 873 and 712 cm^{-1} belonging to calcite [35]. The main reflectance band of CaCO_3 , around 1407 cm^{-1} was vanished for all the post-reaction catalysts. All the post-reaction samples

presented similar infrared spectra showing features belonging to FAME and fat (Fig. 4b) [28]. The main band of methyl esters centered at 1750 cm^{-1} , the pair of bands around 1580 cm^{-1} and 1436 cm^{-1} plus a complex feature in the range 1400–1300 cm^{-1} belonging to fat [36] confirms catalysts surface contamination with species from the reaction medium. Only THF was effective to minimize the fat adsorption on the catalyst surface.

The FTIR spectra of oily phases containing the methyl esters (Fig. 4b) are in accordance with previously published data [37]. The FAME quantification was accomplished using FTIR features in the wave number range 1480–1410 cm^{-1} were biodiesel and raw fats present significant differences [38].

The catalytic activity of the prepared catalysts was evaluated through the solvent assisted methanolysis reaction of SBO plus tallow mixture (50 wt%). The methanolysis of pure SBO was used as reference. The reproducibility of this catalytic test, using four replicas, showed a variance of 0.1%. As reported before [12], Ca catalyst derived from mollusk shells, not only scallop shells, presents excellent catalytic performances for soybean oil methanolysis, allowing to obtain a FAME yield higher than 98% in tested conditions. The high content of CaCO_3 of the catalyst had no detrimental effect on the catalyst activity, even if the majority of researchers report a beneficial effect of rising the calcination temperature on the catalytic performances of powders obtained from Ca-rich biogenesis materials [39]. Rising the calcination temperature will prompt the decarbonation of CaCO_3 into CaO , which is believed to improve the catalyst activity. Temperatures above 1000 °C will promote unwanted sintering of powders. As expected, tallow promoted an activity decay since its acidity partially neutralized the basic active sites on the catalyst surface [28, 40] leading to undesired soap formation.

The use of alcohol solvents had a negative effect on the FAME yield because alcohols can adsorb competitively with methanol on the catalyst active sites being the alcoholysis rate slower for higher molar mass alcohols [41]. Hexane and methylcyclohexane also depreciate the FAME yields, which can be related with their immiscibility with methanol. Some researchers [42] reported a positive effect of hexane during the direct transesterification of oils from microalgae since hexane extract oils from algae biomass making them more available in the reaction mixture. Acetone and THF improved the FAME yield, being the acetone the best solvent. Both solvents are immiscible with glycerin which appears to be the key factor for their good performances. Formed glycerin is separated from the reaction mixture, due to its immiscibility with acetone, thus displacing the reaction equilibrium towards methyl esters formation. Acetone performs better than THF because its miscibility with methanol is higher.

Table 2 FAME yields assessed by ATR-FTIR ($V_{\text{solvent}}/V_{\text{methanol}}=0.36$, methanol reflux temperature, 5 wt% catalyst loading (fat basis), methanol/oil = 12 molar ratio, 2.5 h)

	FAME yield (%)
Soybean oil (SBO)	98.0
SBO + tallow (50% w/w)	
Solvents	
None	74.5
Methylcyclohexane	58.5
Isobutanol	59.9
Isopropanol	62.8
1-Propanol	65.1
Ethanol	66.1
Hexane	67.5
Tetrahydrofuran	76.0
Acetone	85.3

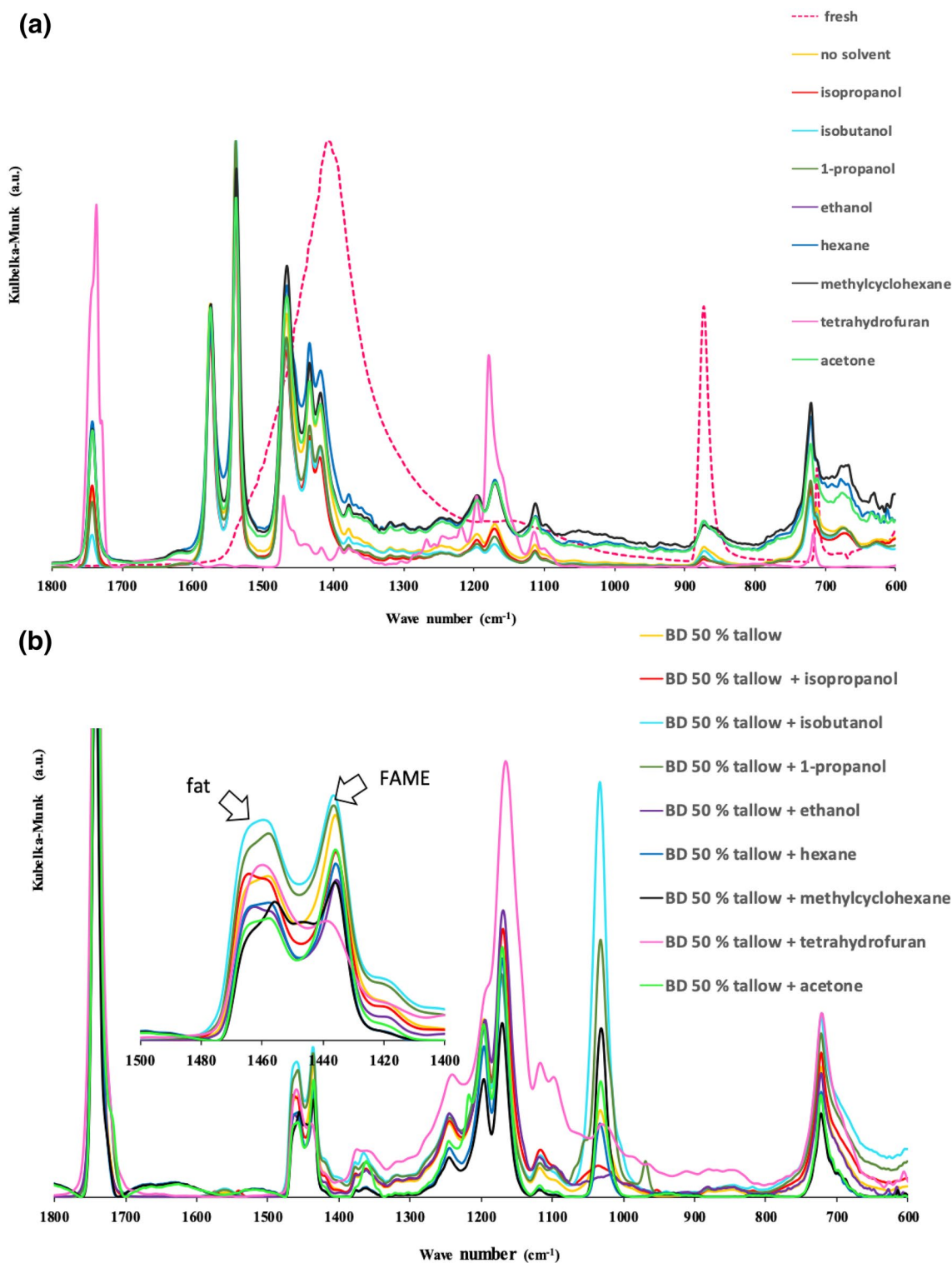
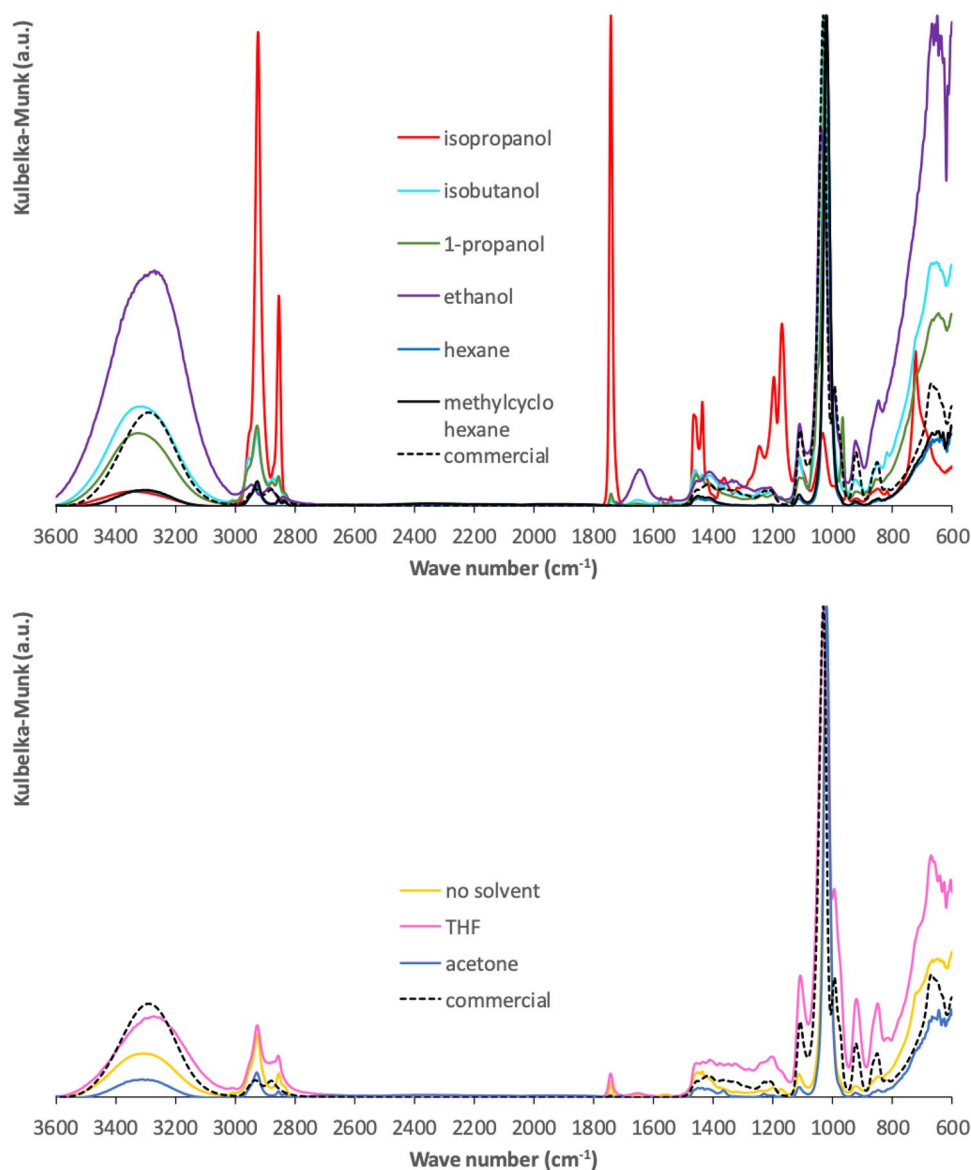


Fig. 4 ATR-FTIR spectra of post reaction catalysts (a) and oily phases [containing FAME (b)]

Since the glycerin purity plays a chief role on the biodiesel production economy [43], the obtained glycerin were characterized by ATR-FTIR to detect possible contamination with MONG (Matter Organic Non-glycerol)

and solvents (Fig. 5). Co-produced glycerin depicted a light yellow shade, thus indicating contamination with MONG (biodiesel, unreacted fat, among others), being the sample obtained with acetone solvent the lighter colored.

Fig. 5 ATR-FTIR spectra of glycerin co-produced with biodiesel



FTIR spectra showed that alcohol solvents lead to glycerin highly contaminated with solvents and species from the reaction medium (FAME and fats), with visible FTIR features from solvents, FAME and fats. The isopropanol solvent led to the worst glycerin, showing the main reflectance bands of FAME. From the glycerin purity point of view, the solvent/glycerin immiscibility is, once more, a key factor to improve the sustainability of biodiesel process since it allows to reduce the MONG content in glycerin.

Conclusions

Solvent assisted biodiesel production was successfully accomplished using a mixture (50 wt%) of soybean oil and low-grade, non-edible beef tallow. The methanolysis of fat

mixture, with a relative high acidity of 2.25 mg_{KOH}/g, was carried out over a basic calcium catalyst obtained by calcination of alimentary waste scallop shells. The methanolysis reaction was solvent assisted using several solvents, some of them selected from the literature. Alcohol solvents had a depreciative effect on the catalytic activity since alcohol molecules adsorb competitively with methanol, the smallest alcohol, on the catalyst active sites. Larger alcohol molecules, such as isobutanol, had a more pronounced effect on the FAME yield decay since the alcoholysis rate decreases as the alcohol molar mass increases. Besides alcohols, solvents protect catalyst against fat adsorption, thus having a beneficial effect on the catalyst stability. Solvents such as hexane and methylcyclohexane, which are immiscible with methanol, are not appropriate for methanolysis reaction. They are able to decrease the fat viscosity but can increase the mass transfer limitations in the reaction medium. On

the other side, acetone, which is immiscible with glycerin, was the best solvents since it helps to displace the reaction equilibrium toward the methyl esters product, by moving away, from the reacting mixture, the formed glycerin. THF is also immiscible with glycerin but acetone seems to be more effective than THF due to its higher miscibility with methanol. Both solvents also contribute to improve the glycerin purity. THF was the best solvent to protect the catalyst against adsorption of species from the reaction medium. Acetone having a lower boiling point than THF will be easier to be separated from the FAME than THF.

Acknowledgements The authors acknowledge FCT (Fundação para a Ciência e Tecnologia, Portugal) for funding Project PTDC/EMS-ENE/4865/2014 and Project UID/EMS/50022/2019 that helped supporting this work through LAETA, IDMEC. The authors also acknowledge Prof. Manuel Freitas (Universidade Atlântica, Oeiras, Portugal) for the permission to use the FTIR spectrometer. This work was also supported through IDMEC, under LAETA, project FCT UID/EMS/50022/2019.

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