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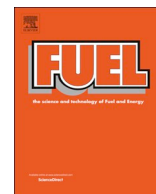
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Full Length Article

Efficient catalytic production of biodiesel using nano-sized sugar beet agro-industrial waste

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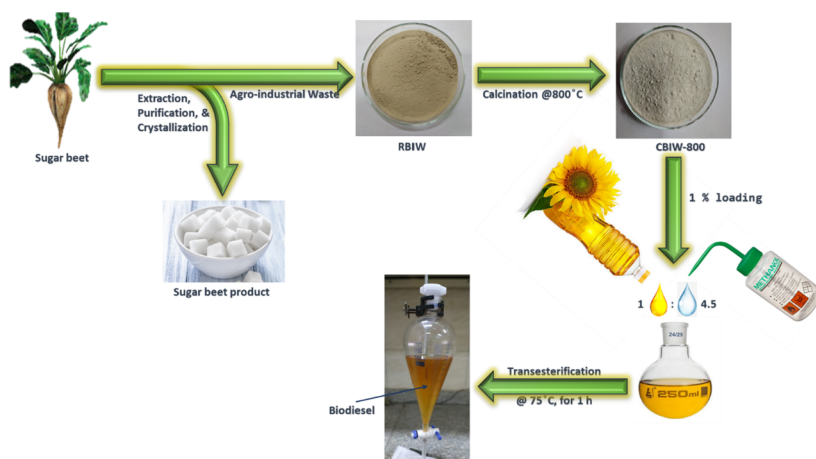
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GRAPHICAL ABSTRACT



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ABSTRACT

This paper addresses the use of agro-industrial residue as a promising heterogeneous catalyst for the efficient production of biodiesel. That is, CaO-rich sugarbeet agro-industrial waste (smashed down to nano-size) shows superb catalytic activity for biodiesel production via transesterification process employing sunflower oil and methanol. Physicochemical properties of the proposed catalyst are probed by TGA-DTG, XRF, XRD, FT-IR, SEM, BET, and CO₂-TPD techniques. Biodiesel conversion (%) of Ca. 93% is achieved under the optimal conditions (catalyst loading of 1 wt%, methanol/oil molar ratio of 4.5:1, refluxed at 75 °C for 60 min). The relatively short reaction time indicates the enhanced kinetics of the process using the proposed agro-industrial residue which imparts its economic feasibility. Also, the proposed CaO-rich residue can be reused twice while retaining its catalytic activity. The thus-produced biodiesel fuel compiles the ASTM D6751 and EN-14214 specifications.

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1. Introduction

Biodiesel is a potential alternative fuel for diesel engines [1,2] in view of its virtues, e.g., biodegradability, non-toxicity together with reduced pollutants emissions [3]. Biodiesel, a fuel that matches the specifications of the European (EN) and American (ASTM) standards [4]. Also, it can be utilized on its own (i.e. in a pure form) or blended in different proportion with petrodiesel in any diesel engine [5].

Biodiesel is basically a mixture of long chain fatty acid alkyl esters which are produced via a catalyzed transesterification process, in which triglycerides (e.g. vegetable oils or animal fats), react with alcohols (commonly methanol) producing fatty acid methyl esters FAME (biodiesel) and glycerol [3,6,7]. Due to the slow kinetics of this transesterification process, several catalysts were proposed to accelerate it. For instance, homogeneous catalysts including alkali hydroxides (e.g. NaOH, KOH, ... etc.), or acid catalysts (e.g. H_2SO_4 , HCl, ...etc.) were suggested where short reaction time and high reaction yield could be achieved [8,9]. However, major drawbacks encounter the use of homogeneous catalysts, e.g., the reactor's corrosion, soap formation, a huge amount of wastewater produced from washing, and separation difficulty leading to increase production cost [10]. Thus, the use of heterogeneous catalysts emerges as a promising alternative particularly alkaline earth metal oxides (like CaO, MgO, etc.). In this context, the use of heterogeneous base catalysts, derived from wastes, has many advantages e.g., environmentally friendly, inexpensive, available, easily recovered from biodiesel product and reusability [11].

Calcium oxide-based wastes and residues derived from several agricultural and industrial activities are largely produced worldwide and are introduced as commercial CaO-based catalysts. Parallel to that, saving the environment from such huge wastes is of prime importance. The incentives behind the use of CaO solid base catalysts are its high basicity, mild reaction conditions, relatively economically [12–14] and environmentally friendly, and with high biodiesel conversion [14,15]. Recently the use of waste materials has been suggested as a source of CaO-based catalyst for transesterification of vegetable oils [4,12,16,17]. This includes the use of lime mud from paper mill industry [18], chicken eggshell [15,19–21], snail shell [22,23], animal bones [24–26], different types of plant ashes [27–29], and hydrocalumite prepared from waste slag [30].

According to The United States Department of Agriculture (USDA), Egypt produces 9.5 million metric ton per year (MMT/year) of beet which is entirely utilized in sugar beet industry [31]. which consumes 2–6% of lime in the purification of sugar beet from non-sugar materials [32]. That means that an average of 0.38 MMT/year of lime is used producing a huge amount of waste lime cake. On the other hand, the annual global production of sugar beet exceeds 301 MMT [33]. Raw Sugar beet agro-industrial waste (RBIW) can be employed as cheap raw materials for preparation high-value catalysts for biodiesel production.

The sugar beet waste, also called lime cake, after drying is

composed mainly of calcium carbonate and magnesium carbonate and traces of other minerals. The objective of this paper is to investigate the catalytic activity of a residue from sugar beet agro-industry as a potential source of CaO-based catalyst. This is derived in view of the huge amounts of this residue. Optimization of the operating parameters is targeted i.e., loading level of catalyst, oil:methanol ratio, reaction time and temperature.

2. Materials and methods

2.1. Materials

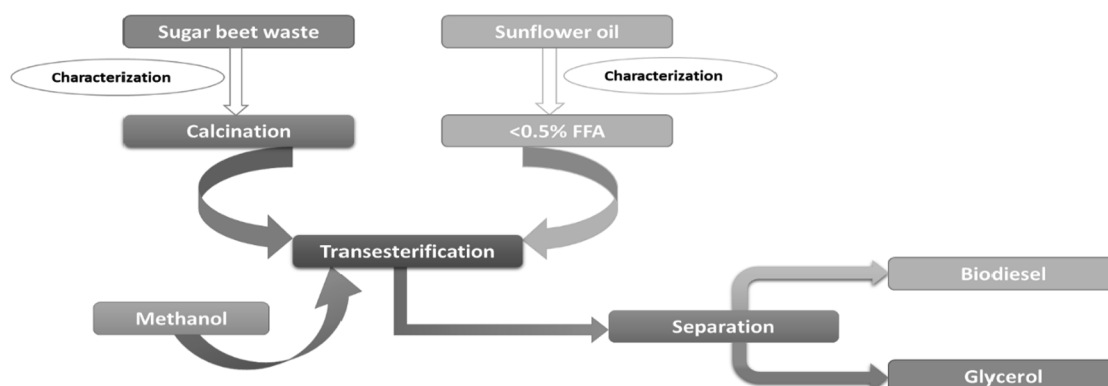
The sunflower oil used in this study with acid value (0.347 mg KOH g^{-1}) was purchased from (Cairo oil and soap Co., Egypt). The fatty acid profile of the oil is shown in the supporting information (see Table S1). Raw Sugar beet agro-industrial waste (RBIW) was supplied by the Egyptian Sugar & Integrated Industries Company (ESIIC). Methanol (99.5%) was purchased from Sigma-Aldrich.

2.2. Catalyst preparation and characterization

RBIW was dried in an oven overnight at 100 °C. then pulverized and calcined at different temperatures (ranging from 600 °C to 1000 °C) with a heating rate of 10 °C min^{-1} for 2 h.

Thermal decomposition of RBIW was examined by a Shimadzu 50H TG/DTA thermal analyzer under nitrogen gas flow with a heating rate of 10 °C/min with varying the temperature from 40 °C to 1000 °C. The elemental composition of RBIW was analyzed by AXS Bruker wavelength dispersive X-ray Fluorescence (XRF) spectrophotometer with an Rh source and tube of 2.2 kW power. The crystal structure of RBIW and the calcined samples was analyzed by the X-ray diffraction (XRD-Bruker D8 Discover Diffractometer) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology of the various materials was disclosed using field emission scanning electron microscopy (FE-SEM-QUANTA FEG 250) attached with EDX Unit (Energy Dispersive X-ray Analyses) and FT-IR spectroscopy using Agilent Technologies Model Cary 630 FTIR spectrometer in the spectral range from 4000 cm^{-1} to 400 cm^{-1} . The surface area was estimated using Brunauer-Emmett-Teller (BET) by a multipoint BET method. Adsorption-desorption isotherm of N_2 was carried out on NOVA Touch 4LX Surface Area Analyzer at -196°C . The degassing process of the samples was conducted at 200 °C for 2 h under high vacuum before measuring the isotherms.

The basicity of the prepared CaO-based catalysts was probed by temperature-programmed desorption (TPD) using (Chemisorb-2705) adsorption unit Micromeritics, employing CO_2 as a probe molecule detected by TCD detector. Briefly, the catalyst samples (500 mg) were preheated under the flux of helium gas at 200 °C for 30 min and then allowed to cool down to 80 °C, at this temperature each sample was exposed to 5% CO_2 in helium with (20 ml min^{-1}) flow rate for 30 min

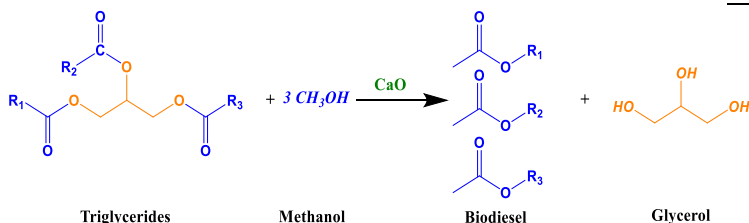


Scheme 1. Schematic diagram of the Biodiesel production process in this study.

and then purged with helium for 1 h at 100 °C to remove the weakly adsorbed CO₂. The CO₂-TPD curves were conducted between 80 °C and 750 °C with a heating rate of 5 °C min⁻¹.

2.3. Transesterification reaction

All transesterification reactions (Eq. (1)) were conducted in a 50 ml round bottom flask attached with a condenser in an oil bath on a hot plate magnetic stirrer with a temperature sensor. The flask (filled with 20 g of sunflower oil) was immersed in the oil bath and heated up to the desired temperature, then a mixture of calcined catalyst and methanol was added to the sunflower oil. The reaction is allowed to proceed for various durations varying from 15 to 360 min at a stirring rate of 800 rpm. After the designed time, the catalyst was separated from the reaction mixture by centrifuge for 10 min at 5000 rpm. Scheme 1 summarizes the sequence of the employed steps.



The excess methanol was evaporated out of the reaction mixture in a dry oven for 2 h at 70 °C. Then the glycerol (lower layer) was separated from the biodiesel (upper layer) by a separatory funnel, after that the biodiesel was washed with hot distilled water to remove any traces of the catalyst particles and glycerol.

2.4. Product characterization

Proton nuclear magnetic resonance (¹H NMR) spectra were recorded for the produced reaction mixture at selected time intervals to probe the conversion percent of oil to biodiesel [34] (see Eq. (2)). This was done using a Varian Mercury VX-300 NMR spectrometer operated at 300 MHz, deuterated chloroform (CDCl₃) was used as the solvent.

$$\%Conversion = \left(\frac{2}{3A_{\alpha} - CH_2} \right) \times 100 \quad (2)$$

where A_{ME} is the value of peak integration of protons of the methyl esters arising at a chemical shift of 3.65 ppm, and $A_{\alpha-CH_2}$ is the peak integration value of α -methylene protons on carbons hereafter the glycerin moiety observed at 2.28 ppm. Moreover, the product (FAME) fuel properties such as kinematic viscosity, density, cetane number, and cold flow properties (pour point, cloud point, and flash point) were determined as well.

3. Results and discussions

3.1. Characterization of the proposed catalyst:

The proposed CaO-rich sugar beet agro-industrial residue (RBIW) is characterized by several techniques including, TGA, XRD, XRF, XRD,

FTIR, SEM, and BET surface area.

3.1.1. TGA analysis

Thermogravimetric analysis (TGA) of RBIW is shown in Fig. 1, to select the appropriate thermal treatment to produce CaO Nano-catalyst from the Agro-industrial waste. Three distinct steps of weight loss were observed (1) at the temperature range of 50 °C to 180 °C (ca. 3.5%) due to loss of water from the waste, (2) at 200 °C to 550 °C (ca. 6.5%) owing to degradation of organic residue present in the waste, and (3) at 580 °C to 810 °C (ca. 39%). Note that above 810 °C, the weight of the sample remains unchanged. Whereas in the derivative thermogram (Dr-TGA) curve three peak maxima were observed at 72, 315, and 720 °C respectively. This result confirmed that the raw material should be

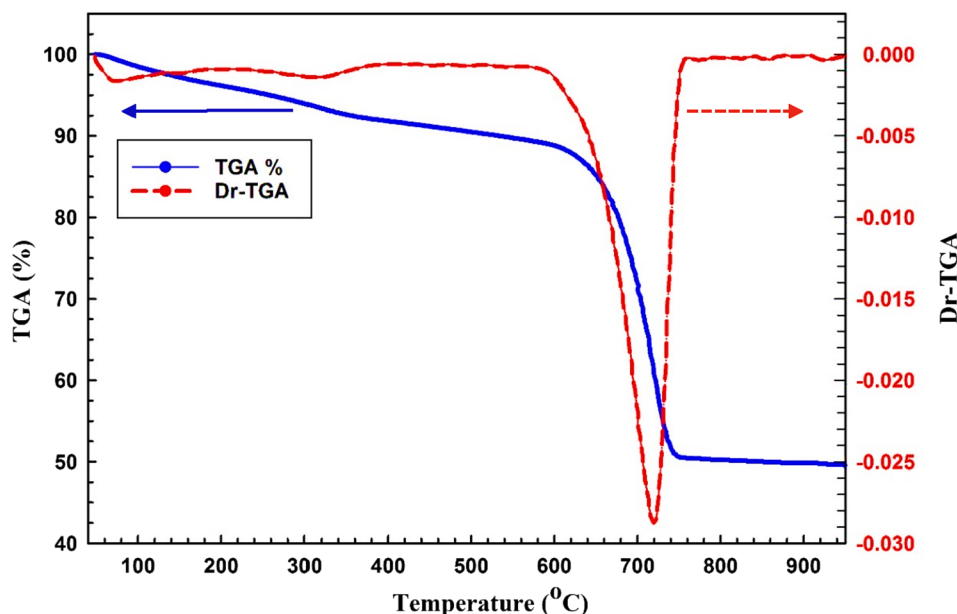


Fig. 1. TGA and Dr-TGA of Dry sugar beet industrial waste (RBIW).

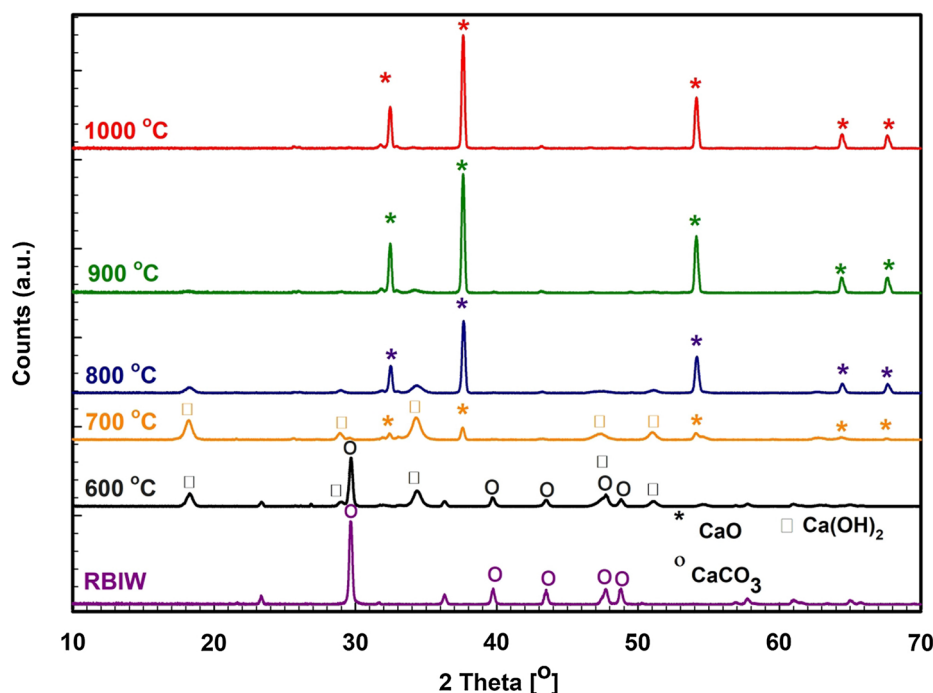


Fig. 2. X-ray diffraction patterns of raw sugarbeet industrial waste (RBIW) and CBIW-samples calcined at 600 °C to 1000 °C.

calcined at a temperature > 700 °C to transform CaCO_3 to CaO according to the following thermal decomposition equation (Eq. (3)).



This is consistent with the findings of Wei et al. [19] and Nakatani et al. [35] who reported that a temperature > 700 °C is required to transform CaCO_3 in waste shells to CaO .

XRF, XRD, FTIR, SEM, N_2 adsorption-desorption, and ^1H NMR analyses were employed to explicate the catalyst features and activity towards biodiesel production after varied calcination conditions.

3.1.2. XRF analysis

The elemental composition of the raw material used for the preparation of the catalyst was examined by XRF, the results (see Table S2) show that RBIW is composed, essentially, of CaO ($> 90\%$), together with traces of metal oxides (MgO , SiO_2 , P_2O_5 , Al_2O_3 , and Fe_2O_3) in small amounts together with Na_2O , K_2O , and MnO . These mixed acidic and basic oxides have been reported to exhibit catalytic activity toward transesterification (basic oxides) of triglycerides and esterification (acidic oxides) of traces of free fatty acids (FFA) [15,36,37].

3.1.3. XRD analysis

The XRD pattern for RBIW and the samples calcined at different temperatures are revealed in Fig. 2. This figure shows that the untreated RBIW and the samples calcined at 600 and 700 °C have diffraction patterns of blended crystalline phases, i.e., CaO , Ca(OH)_2 and CaCO_3 . In contrast, sharp peaks of a crystalline CaO phase were obtained for samples calcined at 800–1000 °C. The XRD patterns for calcined beet waste at 600 and 700 °C show major peaks at $2\theta = 29.4$, 39.4 , 43.2 , 47.2 , 48.5° which is typically CaCO_3 (calcite) with (hkl) indices $(1\ 0\ 4)$, $(1\ 1\ 3)$, $(2\ 0\ 2)$, $(0\ 1\ 8)$, and $(1\ 1\ 6)$ (JCPDS file 01–083-3288) and peaks at $2\theta = 18.0$, 28.7 , 34.1 , 47.1 , 50.8° corresponding to the (hkl) indices $(0\ 0\ 1)$, $(1\ 0\ 0)$, $(1\ 0\ 1)$, $(1\ 0\ 2)$, and $(1\ 1\ 0)$ of Ca(OH)_2 (portlandite) (JCPDS file 00–044-1481) while, for the catalyst calcined at 800–1000 °C peaks at $2\theta \approx 32.2$, 37.4 , 53.9 , 64.2 , 67.4° are ascribed to the (hkl) indices $(1\ 1\ 1)$, $(2\ 0\ 0)$, $(2\ 2\ 0)$, $(3\ 1\ 1)$, and $(2\ 2\ 2)$ the of CaO (lime) (JCPDS file 04-003-7161). In addition, the average crystallite size (D_p) is determined using Debye-Scherrer equation from the

corresponding peaks [38]:

$$D_p = \frac{k\lambda}{\beta \cos \theta} \quad (4)$$

where, k is a crystallite shape factor (0.9), λ is the wavelength of the XRD beam (1.5406 Å for $\text{Cu K}\alpha$), β is the full-width at half-maximum (FWHM) is in radian, and θ is the Bragg's angle or position of the diffraction peak maximum (deg.).

The calculated values of the crystal size are listed in Table 1. This table shows a decrease of particle size from ca. 49 nm for CBIW-600 to 33 nm for CBIW-800 (almost 30% decrease in particle size) causes a three-fold increase (from 33% conversion to 99% conversion) in the efficiency of the transesterification process. In this regard, two parameters play the prominent role, i.e., the particle size and more importantly the composition and crystal phases of the catalyst as mentioned above. Thus, the decrease of particle size with temperature may arise from the thermal decomposition of the large particles from CaCO_3 to CaO . Moreover, at elevated temperature, some organic residues around the particles decomposed into gaseous products leading to a significant lowering in the particle size with increasing the calcination temperature.

Table 1

Physicochemical properties of RBIW and CBIW-samples calcined at various temperatures and the corresponding conversion (%) (Reaction conditions: catalyst loading = 2% methanol/oil ratio 9:1, $T = 75$ °C, reaction time = 6 h, and stirring rate = 800 rpm.)

Sample	S_{BET}^a ($\text{m}^2 \text{g}^{-1}$)	Particle Size ^b (nm)	Ca^c (%)	Conversion ^d (%)
RBIW	17.7	170	48	0
CBIW-600	21.0	49	49	33
CBIW-700	23.3	36	74	91
CBIW-800	27.9	33	74	99
CBIW-900	34.9	33	73	90
CBIW-1000	46.5	25	71	94

^a BET surface area.

^b determined by XRD.

^c Determined by mapping EDX

^d Determined by ^1H NMR.

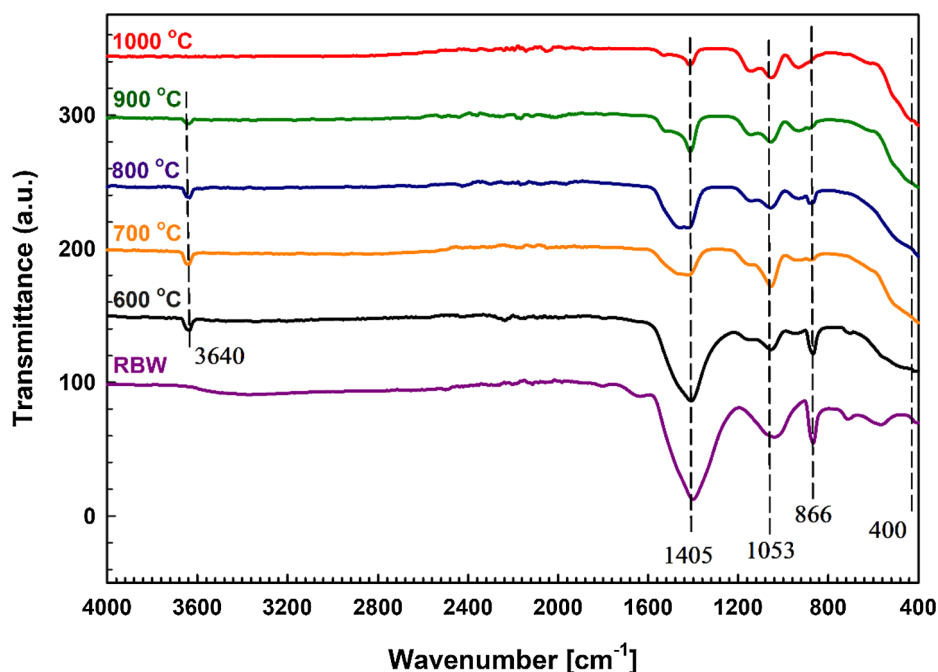


Fig. 3. FT-IR spectra of raw sugarbeet industrial waste (RBIW) and CBIW-samples calcined at 600 °C to 1000 °C.

3.1.4. FT-IR analysis

The FT-IR spectra of RBIW and the calcined samples at 600–1000 °C for 2 h are shown in Fig. 3. It depicts that upon calcination of the raw waste, carbonate bands distinguished at 1405, 1053 and 866 cm^{-1} [14,15,38] is miniaturized corresponding to the transformation of CaCO_3 into CaO that is clarified by the appearance of broad vibrational bands at approximately 400–500 cm^{-1} which were ascribed to Ca-O stretching vibrations [14,15,38]. Also, due to hydroxyl stretching vibration, a less intense band at about 3640 cm^{-1} is detected which is attributed to the adsorption of atmospheric water molecules on the catalyst surface. So, the FT-IR spectra depicted that the calcination process led to the formation of CaO consistently with the XRD and TGA data.

3.1.5. BET analysis

Moreover, based on the N_2 adsorption-desorption isotherm results (see Fig. 4.) which revealed Type (II) adsorption isotherm with type H3 hysteresis loop. The BET specific surface area (S_{BET}) of RBIW and the catalysts samples calcined at different temperatures are listed in Table 1. The specific surface area of the samples increases with calcination temperature from 17.7 m^2g^{-1} for RBIW to 46.8 m^2g^{-1} for a sample calcined at 1000 °C. This finding is consistent with the crystallite size results obtained from XRD analysis.

3.1.6. FE-SEM analysis

To pick up a deeper conception of the surface morphology of the calcined catalysts at different stages of heat treatment, the raw material (RBIW) and the calcined catalysts field emission scanning electron

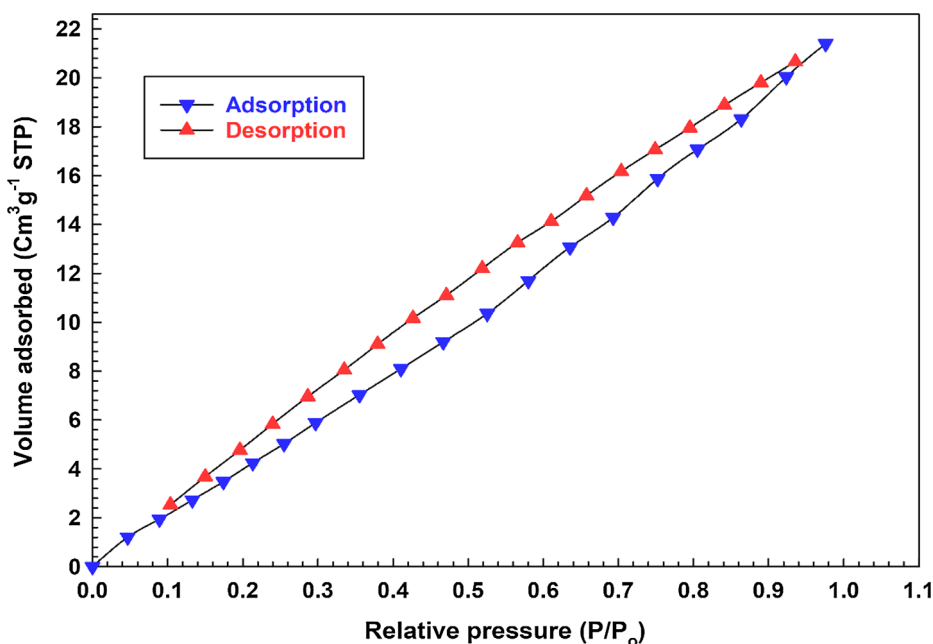


Fig. 4. N_2 adsorption-desorption isotherm of calcined beet industrial waste at 800 °C (CBIW-800).

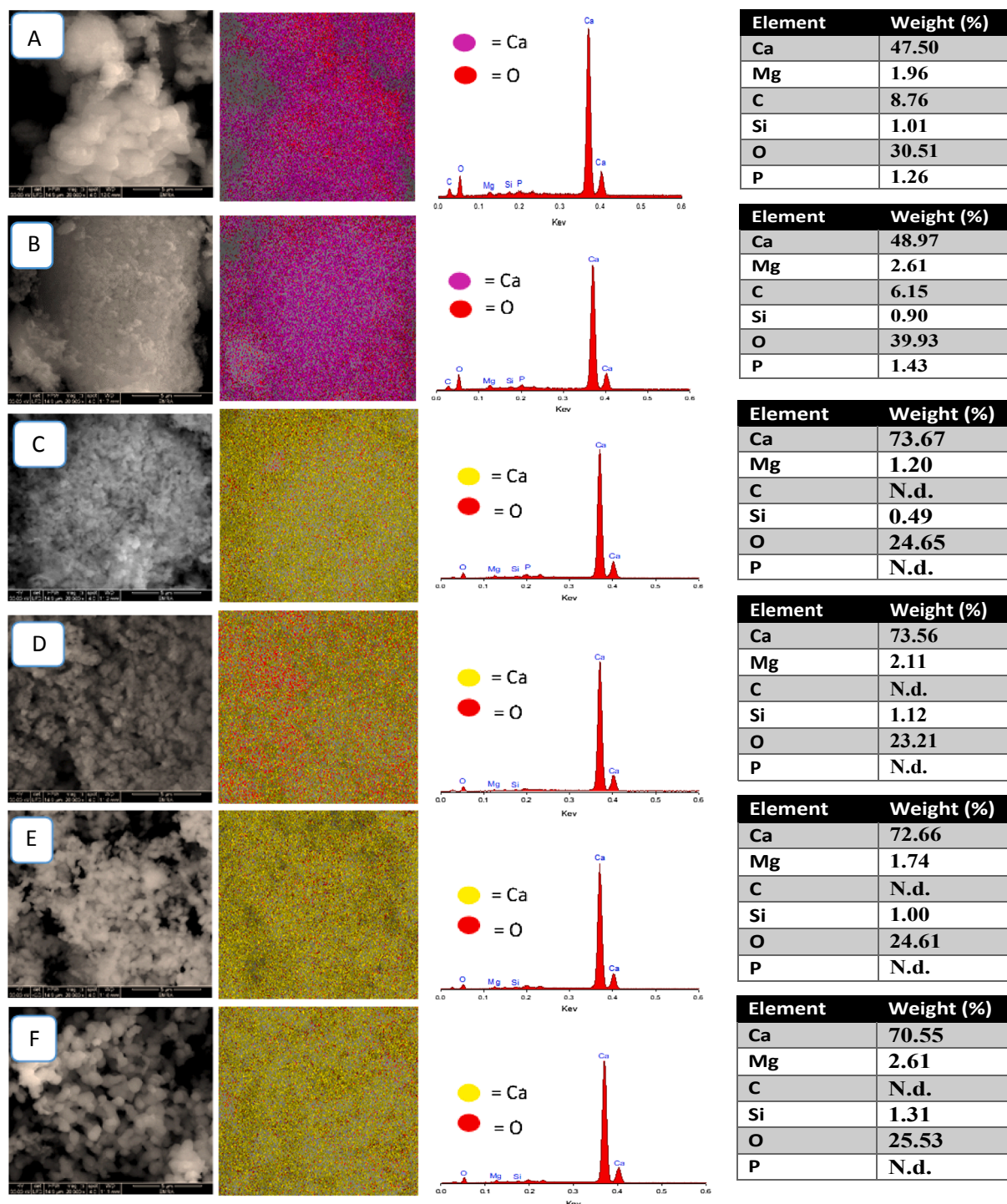


Fig. 5. SEM images, mapping EDX (CaO overlay), and EDX of (A) raw sugarbeet industrial waste (RBIW) and CBIW-samples calcined at (B) 600 °C, (C) 700 °C, (D) 800 °C, (E) 900 °C, and (F) 1000 °C.

microscopy (FE-SEM) and mapping EDX are used and the acquired images are shown in Fig. 5 (A-F), respectively.

It displays the morphology of CaO with infrequent shapes and sizes of particles, such as rod-like, spheres, aggregates which differ from a sample to another. The shape of raw and calcined waste was distinguished by smaller crystals fixed on the large particles, this irregularity can be viewed as a source of high catalytic activity. The surfaces of the calcined catalysts generally encounter the formation of smaller and more homogeneous aggregates of variable morphologies than the raw material possibly due to the decomposition and smashing of the CaCO_3 particles evolving CO_2 gas

causing the fracture of the large particles and forming successfully finer CaO particles (down to the nanometer size). This is also in agreement with the results obtained from the XRD and The BET specific surface area analyses for the raw and calcined samples.

The EDX mapping analysis is shown in Fig. 5. It reflects a homogeneous distribution of CaO species for all samples, the relatively different CaO loading level on the surface of the raw and calcined samples is ascribed to the different heat treatment stages which are confirmed by the corresponding percentage of Calcium and oxygen recorded in the various samples (see Fig. 5).

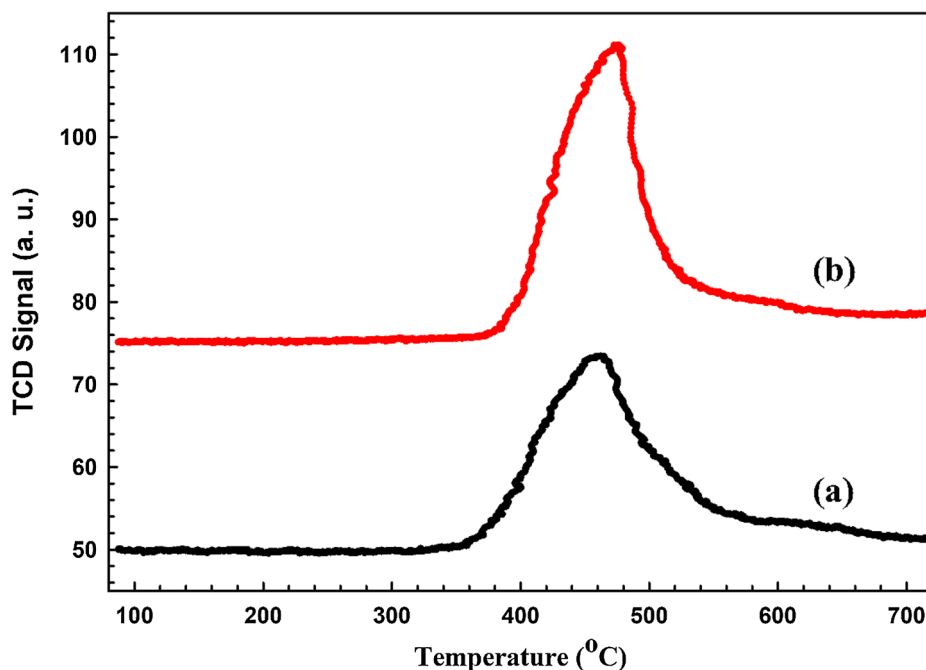


Fig. 6. CO₂-TPD profiles of calcined materials (a) CBIW-800, and (b) CBIW-1000.

3.1.7. CO₂-TPD analysis

CO₂ temperature-programmed desorption (CO₂-TPD) technique is employed, in order to study the basicity of the as-prepared catalysts. The CO₂-TPD profiles of the catalyst calcined at 800 °C and 1000 °C (CBIW-800 and CBIW-1000 respectively) are displayed in Fig. 6. Both catalysts show a well-defined intense peak allocated between 350 and 600 °C which is attributed to desorption of CO₂ from the surface, indicating the generation of strong basic adsorption sites upon calcination of the raw material [12].

3.2. Transesterification reaction

The catalytic activity of the optimum calcined catalyst (CBIW-800) was investigated by monitoring the transesterification reaction of sunflower oil with methanol in accordance with the procedure described in Section 2.4. The optimization of different reaction conditions such as catalysts loading level, reaction temperature, reaction time, and methanol to oil ratio was also studied as shown in Figs. 7–10. All data in these figures are presented as mean \pm standard deviation (SD), with $n = 3$.

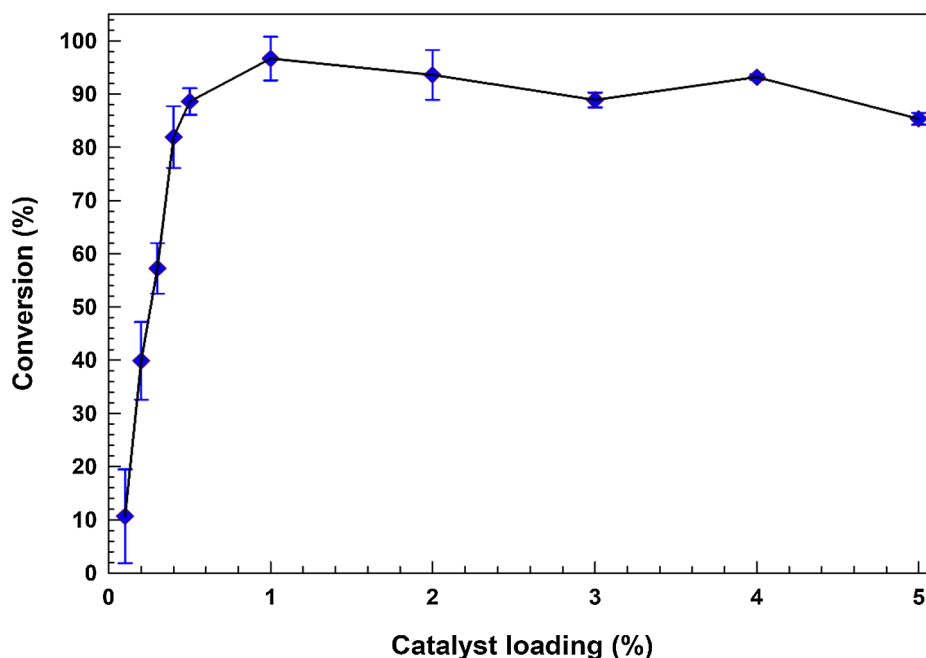


Fig. 7. Effect of catalyst loading on transesterification of sunflower oil using CBIW-800 catalysts at reaction conditions: methanol/oil ratio 9:1, $T = 75$ °C, reaction time = 6 h, and stirring rate = 800 rpm.

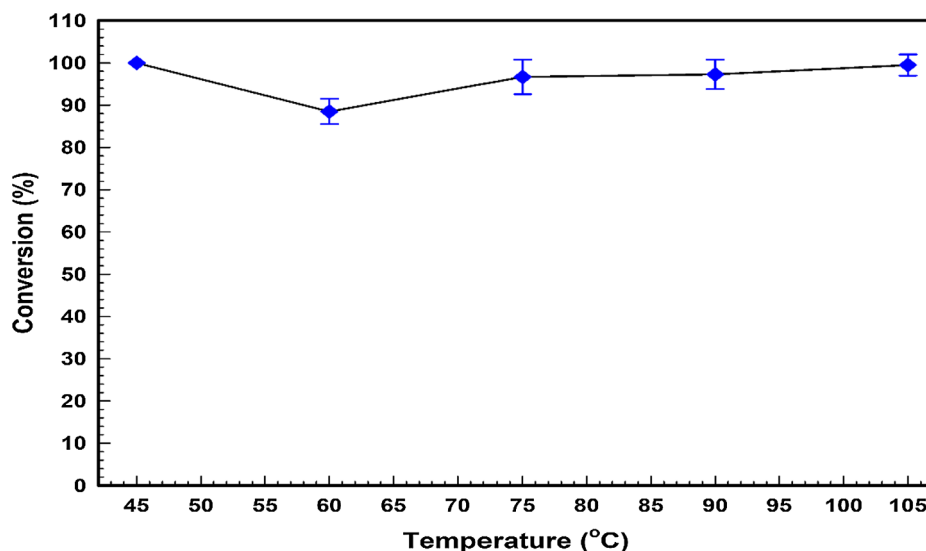


Fig. 8. Effect of reaction temperature on transesterification of sunflower oil using CBIW-800 catalysts at reaction conditions: Catalyst loading = 1%, methanol:oil ratio = 9:1, reaction time = 6 h, and stirring rate = 800 rpm.

Note that, the low conversion % attained using the catalyst calcined at 600 °C (data are shown in Table 1) is ascribed to the incomplete formation of CaO as depicted by XRD and FT-IR results. Also, the lower surface area (S_{BET}) and larger crystallite size of the formed particles compared to the catalyst calcined from 800 to 1000 °C (see Table 1).

Consequently, the temperature of 800 °C was selected as the appropriate calcination temperature. Thus, RBIW is calcined at 800 °C for 2 h in the air. The obtained nano-catalyst (CBIW-800) is used to catalyze the transesterification reaction. The prepared catalyst was characterized by high calcium content (74%), high surface area ($27.9 \text{ m}^2 \text{ g}^{-1}$), small average particle size (33 nm), and relatively large pore diameter (24 Å), that enable the reacting molecules to effectively diffuse into the interior active sites of the catalyst.

3.2.1. Effect of catalyst loading

The influence of CBIW-800 nano-catalyst loading level on the transesterification of sunflower oil was inspected. As shown in Fig. 7, the rate of triglycerides conversion into FAME is noticeably enhanced as the catalyst loading level increases from 0.1 to 5 wt% (with respect to sunflower oil). A larger amount of catalyst molecules increases the exposed surface area and thus the number of active sites accessible for oil and methanol which permits the improvement of conversion percent for the same time interval. The maximum FAME conversion ($97 \pm 3\%$) is obtained using 1 wt% catalyst loading. Though, at loadings > 1 wt%, no significant effect on conversion percent is observed. A similar trend has been reported by Girdhar, et al. [15].

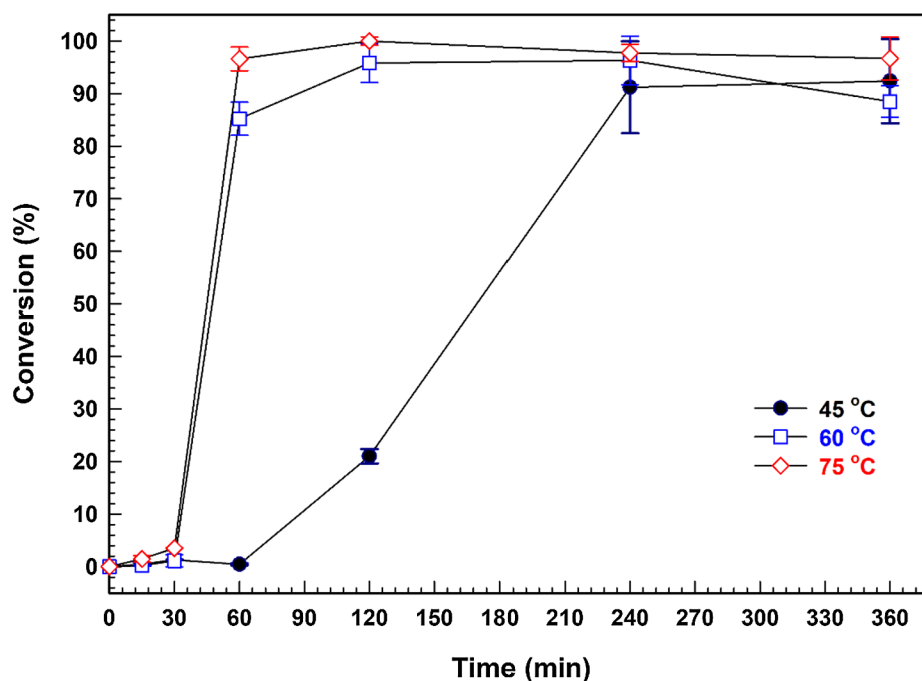


Fig. 9. Effect of reaction time and temperature on transesterification of sunflower oil using CBIW-800 catalysts at reaction conditions: Catalyst loading = 1%, methanol/oil ratio = 9:1, and stirring rate = 800 rpm.

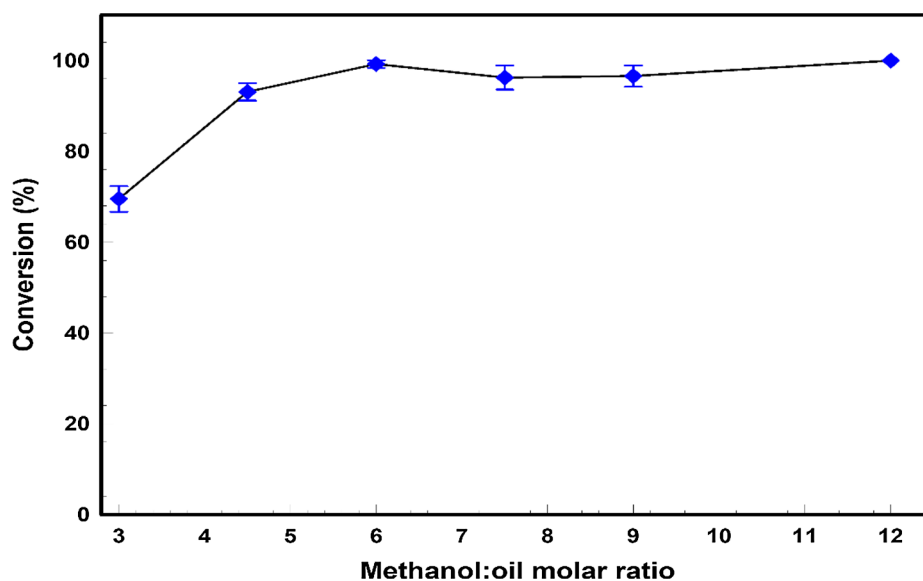


Fig. 10. Effect of methanol to oil ratio on transesterification of sunflower oil using CBIW-800 catalysts at reaction conditions: catalyst loading = 1 wt%, reaction temperature = 75 °C, reaction time = 60 min, and stirring rate = 800 rpm.

3.2.2. Effect of reaction temperature and time

The impact of reaction temperature and time on the conversion of sunflower oil into biodiesel is shown in Figs. 8 and 9. The experiments were conducted at temperatures of 45, 60, 75, 90, and 105 °C (± 1 °C) for 6 continuous hours with a constant stirring rate of 800 rpm. The reaction temperature has no significant effect on the accumulative conversion percent of oil to biodiesel after 6 h. That is a value close to 100% is obtained at low as well as at high reaction temperatures (see Fig. 9). However, it could be noticed from Fig. 9 that there is a sharp increase in conversion (%) of oil to biodiesel at the early stage of the reaction time (t) ca. 30 min. That is, a conversion of 97% was obtained at a temperature of 75 °C after 60 min. While it reached only 85% at 60 °C after 60 min and nearly there was no oil conversion ($< 1\%$) at 45 °C. It is worthy to mention here that a little decrease of the

conversion % (obtained at 60 °C) at prolonged reaction time (ca. 6 h). This may be attributed to the adsorption of the reaction products at the surface of the CaO-based catalyst, and a similar trend was presented by Taufiq-Yap, Y. H., et al. [39]. As a result, reflux at 75 °C for 60 min is selected as the optimum reaction temperature and time for methanolysis of sunflower oil, respectively.

3.2.3. Effect of methanol to oil ratio

The influence of methanol:oil (M:O) molar ratio on sunflower oil conversion into FAME is displayed in Fig. 10. Considering the transesterification reaction stoichiometry shown in Eq. (1), 3 mol of the alcohol reacts with 1 mol of oil, however, owing to the reversible nature of the reaction, excess amount of methanol is essentially required to favor the biodiesel formation. So, alcohol to oil molar ratio of 3:1, 4.5:1,

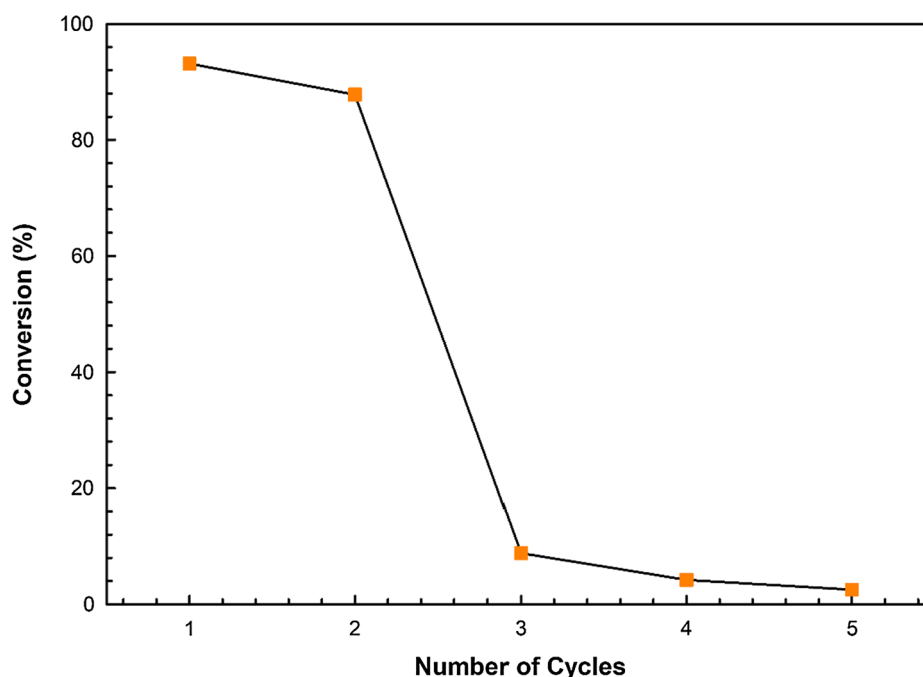


Fig. 11. Reusability of CBIW-800 catalyst for transesterification of Sunflower oil at optimum reaction conditions: catalyst loading = 1%, Temperature = 75 °C, reaction time = 60 min, methanol:oil ratio = 4.5:1, and stirring rate = 800 rpm.

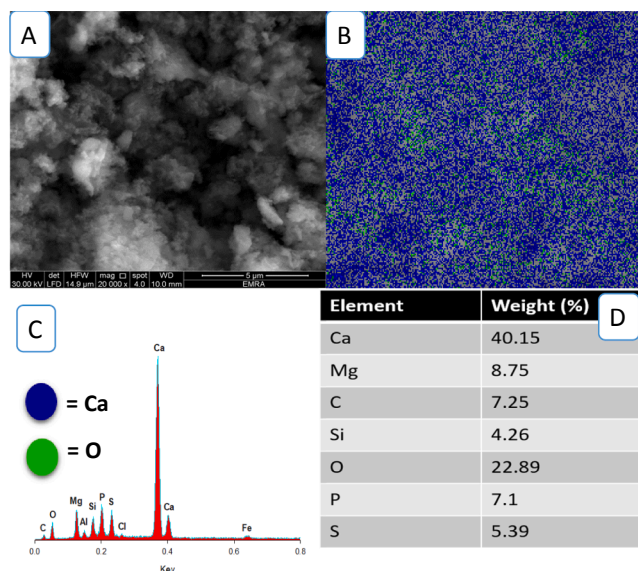


Fig. 12. (A) SEM images, (B) mapping EDX (CaO overlay), (C) EDX of reused sugarbeet industrial waste (UBIW) after the 2nd cycle, and (D) the estimated percentage of each component by using EDX data.

6:1, 7.5:1, 9:1, and 12:1 were used in several batches. With M:O molar ratio of 3:1, the conversion obtained was $70 \pm 3\%$, which increases to $93 \pm 2\%$ with increasing the molar ratio to 4.5:1. This means that the conversion % increase by nearly 34% for a 50% increase in the methanol amounts. While raising the molar ratio up to 6:1 shifts the conversion close to 100%, i.e., increase by 40% with raising the amount of methanol by 100% compared to (3:1 M ratio). Also, taking into consideration the cost of methanol and its recovery together with the dilution of sunflower oil by methanol causing a decrease in mass transfer rate and hence the reaction rate. So, 4.5:1 is exploited to be the optimum methanol:oil ratio.

Based on the obtained results, one can argue that, so far, the optimized reaction conditions are catalyst loading level = 1 wt%, reaction temperature = 75°C , reaction time = 60 min, and methanol:oil ratio = 4.5:1.

3.3. Catalyst reusability

The calcined sugarbeet industrial waste (CBIW-800) catalyst is recovered from the reaction mixture and reused in a new batch for 5 cycles. Note that, the optimum conditions were employed using the same sample of catalyst. Data are shown in Fig. 11. After each run, the reaction mixture was centrifuged and the separated catalyst was washed with ethanol followed by drying for 3 h at 80°C . Fig. 11 shows that, CBIW-800 catalyst keeps its catalytic activity for two consecutive cycles. Starting from the third cycle an appreciable deterioration in catalytic activity is observed possibly due to leaching of CaO catalyst in glycerol by-product leading to

the formation of calcium diglyceride which is reported by Kouzu et al. [40]. This is reflected in a decrease in CaO content in the reused catalyst from 74% down to 40%. Additionally, the aggregation of the particles (as observed in Fig. 12) is another factor that leads to losing the catalytic activity in the consequent cycles.

3.4. A comparative study with other systems in literature

Table 2 shows a comparison between the reported CaO-based catalysts (derived from natural sources) for the transesterification reaction. The optimum operating conditions are listed for each case and are compared with the conditions of the current study. Viriya-Empikul et al. [41] and Li et al. [18] utilized CaO obtained from eggshell waste and paper mill industry waste for transesterification of palm olein oil and peanut oil, respectively, into biodiesel with a yield of ca. 94% in 2 h and at 60°C in the presence of high catalyst loading (ca. 6–10 wt%) and a high methanol to oil ratio (15:1). On the other hand, Correia et al. [42] obtained a lower conversion of ca. 83% for transesterification of sunflower oil using crab shell waste (as CaO source) in 4 h at 60°C utilizing 3% catalyst loading. Also, Smith et al. [24] obtained a yield of ca. 97% utilizing bovine bone waste in 4 h and a catalyst loading of 8%. Whereas, in our case the optimum conditions were attained at milder operating parameters, e.g., a loading of only 1 wt% CaO catalyst and methanol:oil ratio of 4.5:1 give ca. 93% in a shorter time (1 h) at 75°C . This means that a saving of methanol in our case while maintaining a high conversion % with minimal use of chemicals and relatively saved energy.

4. Fuel properties

The properties of the produced biodiesel fuel (using CBIW-800 nanocatalyst) are determined according to ASTM methods, e.g., density at 15.56°C , kinematic viscosity at 40°C , total sulfur content, flash point, cloud point, pour point, and copper corrosion (shown in Table 3). That is, the obtained results are comparable with the American (ASTM6751) and European (EN14214) biodiesel standards. The properties of the produced biodiesel fuel are in good agreement with the specified biodiesel standards. Advantageously, the biodiesel fuel produced in this work shows low cloud and pour points as well as a high flash point. Thus, it can achieve better performance at low and high climatic conditions.

5. Conclusions

This work showed that sugarbeet agro-industrial residue is very active toward transesterification of sunflower oil into biodiesel. Thus it can be utilized as a cheap and environmentally friendly source of CaO-derived heterogeneous catalyst. The optimized calcination temperature was 800°C (CBIW-800). The lower temperature gives rise to the incomplete formation of active CaO-derived catalysts, causing low biodiesel conversion. The high catalytic activity of the prepared catalyst calcined at 800°C is attributed to its large surface area ($27.9\text{ m}^2\text{ g}^{-1}$)

Table 2

The review of CaO-rich waste catalysts used in transesterification reactions.

Catalyst	Feed stock	Catalyst pretreatment conditions		Transesterification reaction conditions				FAME Yield (Y) or Conversion (C) %	Ref.
		Calcination temperature ($^\circ\text{C}$)	Calcination time (h)	Temperature ($^\circ\text{C}$)	time (h)	Catalyst loading (wt. %)	M:O ratio		
Eggshell waste	Palm olein oil	800	2–4	60	2	10	18:1	94 (Y)	[41]
Crab shell waste	Sunflower oil	900	2	60	4	3	6:1	83 (C)	[42]
Bovine bone waste	Soybean oil	750	6	65	3	8	6:1	97 (Y)	[24]
Paper mill industry waste	Peanut oil	800	Not given	64	2	6	15:1	94 (C)	[18]
Sugar beet waste	Sunflower oil	800	2	75	1	1	4.5:1	93 (C)	This work

Table 3

Physicochemical properties of the obtained biodiesel in comparison with international biodiesel standards.

Test	Test method	Limits		**FAME
		*ASTM D6751	*EN 14214	
Density @ 15.56 °C (g/cm ³)	ASTM D-1298	–	0.86–0.90	0.88
Kinematic viscosity (mm ² s ^{−1})	ASTM D-445	1.9–6.0	3.5–5.0	8.88
Total Sulphur (wt %)	ASTM D-4294	0.05 max.	0.01 max.	0.015
Flash point (°C)	ASTM D-92	130 min.	101 min.	178
Cloud point (°C)	ASTM D-2500	−3 to +12	–	−3
Pour point (°C)	ASTM D-97	−15 to +16	–	−9
Copper corrosion	ASTM D-130	No. 3 max.	Class 1 max.	1a

* See Ref. [10,43].

** FAME: fatty acid methyl ester produced in this work via transesterification of sunflower oil using 1 wt% of the catalyst, reaction temperature of 75 °C for 1 h, and methanol:oil molar ratio of 4.5:1.

and small average particle size (33 nm) as well as its high basicity. The conversion (%) of sunflower oil to biodiesel (catalyzed by CBIW-800) was 93% obtained under relatively mild conditions (i.e. 1 wt% of the catalyst loading, reaction temperature of 75 °C for 1 h, and methanol:oil molar ratio of 4.5:1). The biodiesel produced from sunflower oil catalyzed by CBIW-800 revealed good fuel properties which compile the specifications set by American and European fuel standards (ASTM D-6751 and EN-14214).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2019.116481>.

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