New SrO based catalytic methods for biodiesel production from non-edible feedstock using microwave irradiation:

Implementation and adaptation to large-scale systems

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Ph.D. Thesis

Tradition of Excellence

Submitted to the Senate of Bar-Ilan University

Ramat-Gan, Israel December 2016

This work was carried out under the supervision of Prof. Aharon Gedanken, Department of Chemistry, Bar-Ilan University.

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Bar-Ilan University

NAME OF THE STUDENT: Alex Tangy

DEGREE AWARDED: Doctor of Philosophy in Chemistry

ACADEMIC UNIT: Department of Chemistry

TITLE OF THESIS: **New SrO based catalytic methods for biodiesel production from non-edible feedstock: Implementation and adaptation to large scale systems**

This is to certify that the thesis entitled "**New SrO based catalytic methods for biodiesel production from non-edible feedstock using microwave irradiation: Implementation and adaptation to large scale systems",** submitted by Alex Tangy to Bar Ilan University, Israel for the award of the degree of Doctor of Philosophy is a bona fide record of research work carried out by him under my supervision. The content of this thesis, in full or in part, has not been submitted to any other research organization for the award of a degree or a diploma.

Signature of supervisor

Prof. Aharon Gedanken

December, 2016

This thesis is dedicated to memories of my grandparents Mercedes and Max Tangy and Camille and Isaac Benchimol with a special mention of my grandmother Mercedes who left us this year.
Each of them has contributed to transmit idea and knowledge and to build my personality.

My parents Claire and Michel who afford me to fulfill my dreams.

My beloved wife, Shirley, and my daughter, Noa, who bring me each single day love, affection, and strength to achieve my goals.

ACKNOWLEDGEMENTS

I am indebted and am immensely grateful to the Almighty God for sustaining me to accomplish this task. Without His grace and mercies, this work would not have been realized.

This thesis would have not been possible without guidance and assistance of several individuals who one way or another appreciably contributed to the completion of this thesis.

I would like, first, to express my sincere gratitude to my research advisor, Prof. Aharon Gedanken, for mentoring, teaching, guiding, and giving me an opportunity to train myself and produce research work of high quality and productivity during the course of my Ph.D. program.

I cordially and sincerely thank Dr. Indra Neel Pulidindi and extend my gratitude to him for his valuable comments that helped me to improve the quality of this thesis. I appreciate his guidance, his continuous support and thoughtfulness, his technical assistance and precious discussions during all these last 4 years.

A special thanks to my friend Dr. Reuven Eitan for his help, support, and advices to overcome issues I have encountered during my Ph.D. studies.

I would like to thank all the members of Prof. Gedanken's laboratory for their help, encouragement, and friendship, with a special mention to Vijay Booshan Kumar for sharing with me his expertise on carbon dots.

I am also thankful to Prof. Nina Perkas and Prof. Yuri Koltypin, for their great help, and advices.
I express my thanks to Dr. Yaron Yehoshua and Dr. Yael Kinel-Tahan from Prof. Zvy Dubinsky lab, from the Faculty of Life Sciences for the research collaboration in the field of microalgae cultivation for biodiesel production.

I would like to thank my parents, Claire and Michel Tangy, and my brother David for all their love, support, and encouragement throughout the years. I would also like to express my deep gratitude and love to my cousin Dr. Jonathan Benchimol for supporting and encouraging me during all these years. Last but not the least; I warmly thank my lovely wife Shirley for her continuous love and support that helped me to overcome obstacles during the course of my Ph.D. study and sharing my challenges and frustrations. Without you, I could have never made it through this. You have been comprehensive and allowed me to come home late during most of my Ph.D. studies. You brought me the most beautiful gift: my daughter Noa. I am extremely lucky to have them in my life.

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Table of Contents

Abbreviations:

BET – Brunauer–Emmett–Teller
^{1}H NMR Spectroscopy – proton Nuclear Magnetic Resonance Spectroscopy
DLS – Dynamic Light Scattering
DMWO – Domestic Microwave Oven
EDS – Energy Dispersive X-ray Spectroscopy
ESEM – Environmental Scanning Electron Microscopy
EtOH – Ethanol
FAME – Fatty Acid Methyl Ester
FFA – Free Fatty Acid
FT-IR – Fourier Transform Infrared
GC-MS – Gas chromatograph coupled with a mass spectroscope
HRSEM – High-resolution scanning electron microscope
ICP – Inductively coupled plasma
MeOH – Methanol
MW – Microwave
NP - nanoparticle
SEM – Scanning electron microscope
$SrCO_3$ – Strontium carbonate
SrO – Strontium oxide
SrO/SiO_2 – SrO coated on millimetric silica beads
SrO-C dot – Carbon dots functionalized SrO
TEM – Transmission electron microscope
TGA – Thermogravimetric Analysis
WCO – Waste cooking oil

XRD – X-ray Diffraction

Units:

% : percent

θ : diffraction angle

°C : degree Celsius

g : gram

GHz : Giga hertz

h : hour

K : degree Kelvin

M : Molar (moles/liter)

mg : milligram

min : minute

mL : milliliter

nm : nanometer

s : second

t : time

T : temperature

W : watt

wt. : weight

List of figures:

List of tables:

Abstract

Science is appreciated if it transforms into real technology that could be used by common person. Energy demands and clean environment are haunting everyone. Energy sources are necessary for human existence, comfort, and progress. Limited crude petroleum resources and increasing awareness of the environmental impacts of fossil fuels motivate the search for new energy sources and alternative fuels. Biodiesel is a renewable, biodegradable, environmentally friendly, and non-toxic fuel, which has attracted considerable attention in the past decades. The feedstock cost and the production process are two major obstacles to large-scale biodiesel production. Microwave-assisted technology has been found to reduce significantly the reaction time and the production cost compared to conventional methods. Using waste vegetable oil or microalgae as a potential alternative feedstock for biodiesel production can significantly lower the production cost. Microalgae, also called 3rd generation of biofuel feedstock, have unique and dominant advantages compared to other feedstock. The current research addresses to solve the energy needs of common person in terms of transportation requirement in an environmentally friendly way by offering a fast method for the transesterification of cooked oil to biodiesel in a domestic microwave oven as well as a continuous flow reactor. SrO, a solid catalyst, was employed as heterogeneous and reusable catalyst for the transesterification reaction. The potential of SrO NPs coated on millimetric silica beads (SrO/SiO_2) in batch and continuous process, as well as carbon dots functionalized SrO (SrO-C dot) synthesized from $Sr(NO_3)_2$ precursor as solid based catalysts for biodiesel production showed improved performance for the transesterification of waste cooking oil and microalgae, respectively, compared to the conventional SrO catalyst using domestic microwave oven. The catalyst SrO/SiO_2 showed a conversion as high as 99.4% of waste cooking oil to FAME in just 10 s. Moreover, the catalyst could be easily separated and reused for 10 consecutive reaction runs with a loss of only 4.6%. Its high activity is attributed to the unique morphology of SrO particles on the silica bead surface at the nanometric level, resulting in well-dispersed active sites for the transesterification reaction. Moreover, homogeneous surface functionalization of carbon dots on SrO nanoparticles was used for the single step conversion of *Chlorella Vulgaris* to biodiesel in a microwave. High lipid conversion value of 97 wt. % and FAME yield value 45.5 wt. % were achieved using SrO-C dot composite catalyst in a short reaction time of 2.5 min. SrO-C dot catalyst showed improved performance for the transesterification of lipids compared to the conventional SrO catalyst (2.4 times). In addition to the batch process, the use of SrO/SiO_2 as promising catalyst in a fixed bed continuous flow microwave irradiation process with a conversion value of 93.3 wt. % while converting 2.46 L of feed (waste cooking oil and methanol) into biodiesel after 24.6 min is demonstrated. Thus, fast and efficient biodiesel production process based on the solid catalyst together with continuous microwave irradiation demonstrate the economic feasibility as well as an industrial adoptability of the process for large scale biodiesel production from cooked oil waste in a short time is developed.

1. Background and literature review

1.1 Global energy crisis, environmental pollution and demand for renewable energy

Due to rapid depletion of conventional energy sources or fossil fuels, like pretroleum, coal and natural gas, environmental concerns caused by their emissions, like greenhouse gas emissions (GHGs) [1], increasing energy demand and consumption generated by population expansion (**Figure 1**)[2], the conventional energetic system is considered to be unsustainable in the long term.[3]

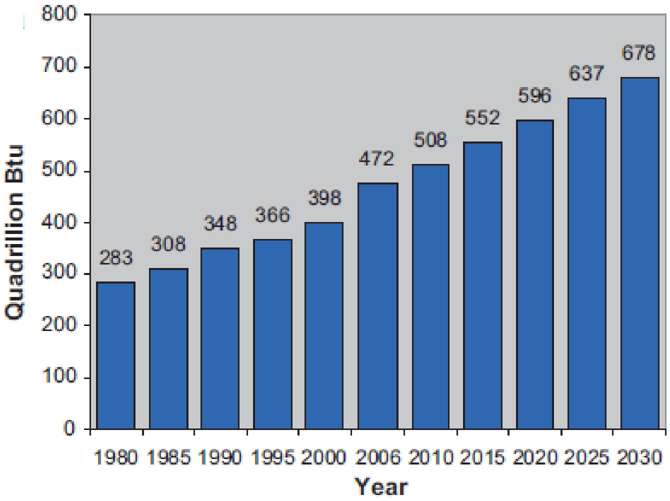


Figure 1 World marketed energy consumption.

Nowadays, more than 80% of the energy used in the world comes from fossil fuels. About 98% of CO_2 emissions are caused by fossil fuel combustion. **Figure 2** illustrated the percentage of world energy consumption in year 2013.[4]

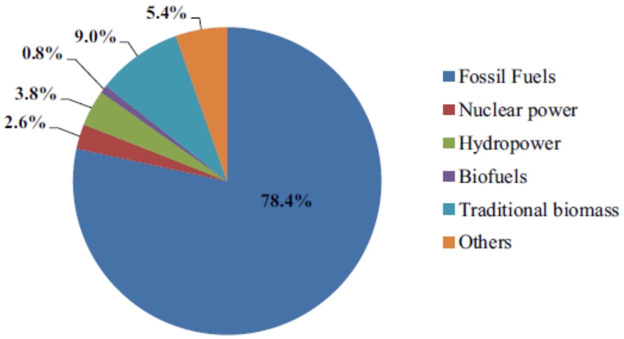


Figure 2: World primary energy consumption in 2013.

Energy generation from fossil fuels has been identified as the main reason of environmental pollution.[5] The rate of global CO_2 emission by end-used sectors from 1990 to 2035 is shown in **Figure 3**.[4] Therefore, shifting to renewable energy can help us meet the dual goals of reducing greenhouse gas emissions, and ensuring reliable distribution of energy.

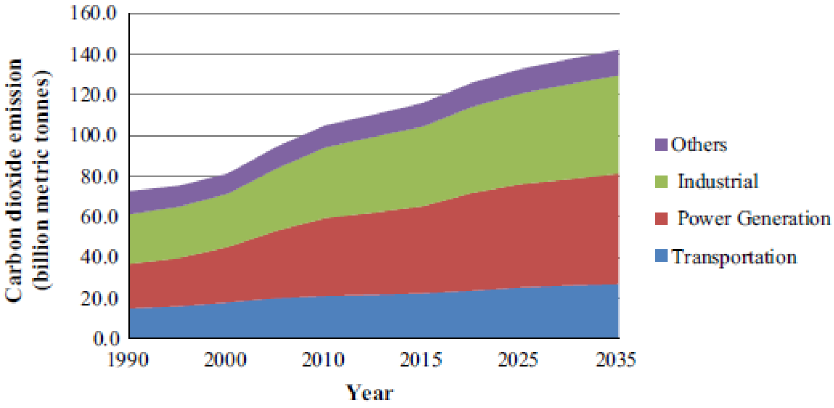


Figure 3: Global CO_2 emission from various sectors from 1990 to 2035.

Renewable energies are energy sources that are continually replenished by nature and derived directly from the sun (such as thermal[6], and photo-electric[7]), indirectly from the sun (such as wind[8,9], hydropower[10,11], and photosynthetic energy stored in biomass[12]), or from other natural movements and mechanisms of the environment (such as geothermal energy[13–15]). The modern renewable energy consists of 3.8% of hydropower, 0.8% of biofuels, and 5.4% of others energy sources including biomass, solar, geothermal heat, and wind energy for power generation.[4]

The transportation sector, representing 30 % of the world's total energy consumption, is the second largest energy-consuming sector after the industrial sector. Almost 60 % of world oil demand is required in the transportation sector that will probably be the strongest growing energy demand sector in the future. Transportation sector is currently and solely dependent on fossil fuels like petrol and diesel. The reserves are on the verge of exhaustion. The total world energy consumption is expected to grow by 56% between 2010 and 2040 (**Figure 4**).[16] Alternate fuels are necessary for meeting the demands for transportation applications. Therefore, great efforts has been devoted these last decades to develop renewable fuels that are environmentally acceptable, technically feasible as well as can fulfill the global energy demand.

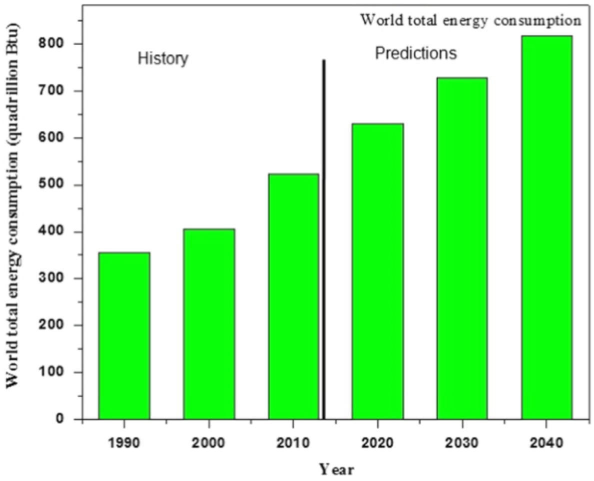


Figure 4 World total energy consumption; history and projection.

1.2Biodiesel as a potential alternative for transportation fuel

1.2.1 Biodiesel as alternative to fossil fuels

The main alternative to fossil fuel is biodiesel. Biodiesel is considered as an important renewable energy source because of its potential to fulfill the energy demand, reduce greenhouse gasses and global warming.[17] Biodiesel is a renewable liquid fuel for diesel engines. It is composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils, recycled cooking greases or oils, or animal fats.[18,19]

Vegetable oils have become attractive because of their environmental benefits and renewable nature with energy content close to diesel fuel. Therefore, vegetable oils are becoming widespread primary sources of biodiesel production. Vegetable oils need to be modified suitably for being substituted to petroleum diesel. The incompatibility of crude vegetable oils as fuel for engines is mainly due to its greater viscosity (27.2 to 53.6 mm^2/s) compared with that of the diesel fuel, which is 10–20 times higher than that of diesel for which the engines were designed (1.3 to 4.1 mm^2/s). However, vegetable oil cannot be an economically viable and sustainable feedstock for the demand based production of biodiesel and alternate feedstock need to be explored. This has been one of the objectives of the present research.

1.2.2 Biodiesel-Merits and demerits

Biodiesel have the main advantage to be used as fuel for transportation in its pure form or blended with petroleum diesel at any percentage with any or little modification of the engine[20], as the properties of biodiesel match generally that of petro-diesel. The production process is relatively easy and does not require expensive equipment. Therefore, biodiesel can be considered as the best alternative to petroleum diesel based on the cost of production. Biodiesel is also considered as a renewable, biodegradable, non-toxic and clean energy.[16] The emissions from vehicles that are using biodiesel contain both lower amount of hydrocarbons and CO_2 emissions, as the basic feedstocks consume CO_2 during its cultivation, and no aromatic compounds compared to conventional transportation fuels. Biodiesel also acts as a good lubricant for diesel engines. These advantages could therefore extend the engine's life. Biodiesel also has higher flash point, defined as the temperature of fuel flammability, which makes it safer to handle compared to diesel.[21] Other advantages of biodiesel are its availability without any reliance on external countries, renewability, higher combustion efficiency, higher cetane number, and higher biodegradability. Furthermore, the sulfur content of biodiesel is negligible and so no desulphurization process is required.[22] Moreover, biodiesel is the only alternate fuel that has obtained the clearance to be used as a transesterification fuel based on 1990 clean air amendment act.[23]

So, the use of biodiesel can be a solution to the problem of environmental pollution. Owing to these advantages, biodiesel is a promising alternative to petroleum-based fuels.

On the other hand, disadvantages of biodiesel include higher emission of nitrogen oxides (NOx gas)[24,25], lower energy content[26], less stability[27], decomposition upon thermal stressing of 275°C and above, higher pour points (the temperature at which biodiesel becomes semi solid and loses its flow characteristics). The most important concern of biodiesel it's his high cost compared to diesel due to high price of vegetable oils especially those of edible feedstock[28], which appears to be the primary factor preventing its more widespread use. Moreover, current worldwide production of vegetable oil and animal fat is not enough to replace liquid fossil fuel use. Biodiesel is a technologically feasible alternative to fossil diesel, but biodiesel costs 1.5–3 times more than fossil diesel. Regarding actual fuel costs, the current cost of biodiesel is comparable with that of gasoline.[29] The oxygen content of biodiesel is responsible for the higher NOx emission and CO_2 emission. General trends observed with biodiesel fuel are the increase in emissions of NOx and CO_2 approximately by 12% and 14% respectively.[21] However, the cost of biodiesel could vary depending on the source of feedstock. Biodiesel could also dissolve and degrade polymers containing in certain parts of the diesel engines. Nevertheless, the advantages of biodiesel overcome its disadvantages on the environmental aspects, making it a potential alternative to petroleum provided strategies for the fast and large-scale production of biodiesel are developed.

1.3 Transesterification reaction

Biodiesel is essentially produced from a chemical process known as transesterification. Transesterification, also called alcoholysis, is the displacement of alcohol group from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is employed instead of water. The reaction may be facilitated by catalyst using primary or secondary monohydric aliphatic alcohols having 1-8 carbon atoms.[30] This process enables the viscosity reduction of triglycerides. Typical transesterification reaction is described in **Figure 5**.[31] Transesterification is a reversible reaction consisting of mixing the reactants in the presence of an acid or a base catalyst to improve the reaction rate and yield, as the non-catalytic transesterification is too slow and energetically unfavorable.[32]

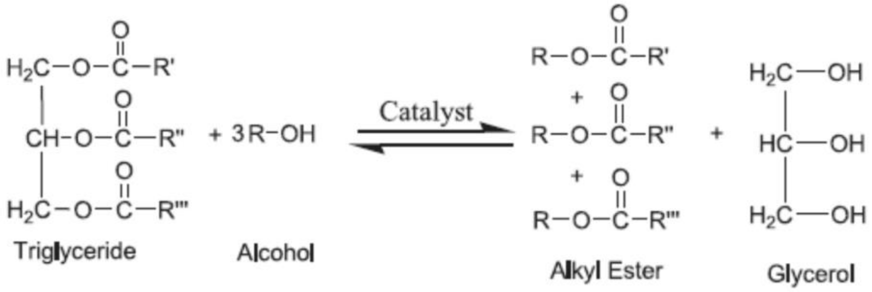
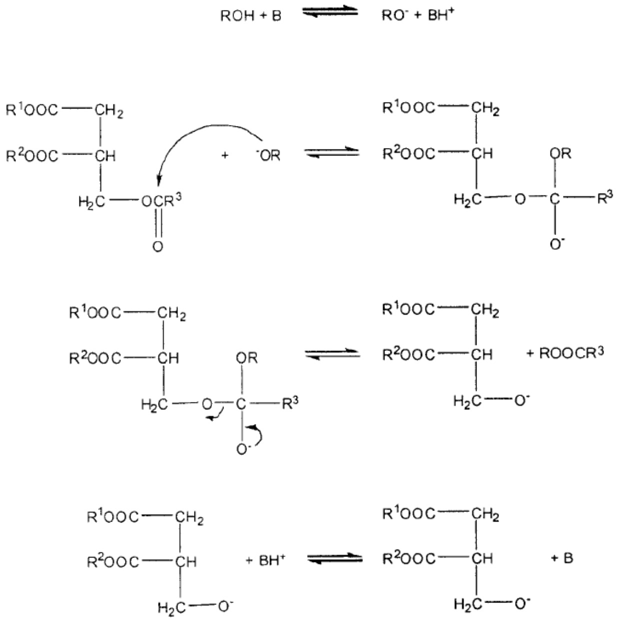


Figure 5: General transesterification process of triglycerides with methanol.

In a transesterification reaction, triglycerides react with, at least, threefold excess of an alcohol, typically methanol or ethanol, to shift the equilibrium towards the formation of fatty acid esters (FAE), the biodiesel. In fact, higher molar ratio between methanol and oil is needed to lead the equilibrium toward a maximum ester yield. The presence of a sufficient amount of methanol during the transesterification reaction is necessary to break the glycerin–fatty acid linkages.[33] Nevertheless, the reverse reaction is negligible, mainly due to the immiscibility of the products, namely, the fatty acid ester and the glycerol as byproduct. As a result, a two-phase system is formed when the FAME settles at the top of the reaction mixture.

The transesterification process consists of three successive reversible reactions [34]. The first reaction occurs between triglycerides and short-chains alcohol to produce diglycerides and an ester. In the second reaction, diglycerides (from the first reaction) react with alcohol to produce monoglycerides and a second ester. The third reaction occurs between the monoglycerides (from the second reaction) and alcohol to produce glycerol and an ester. Consequently, a mole of ester is liberated at each step. From these reactions, one molecule of triglycerides reacts with three molecules of alcohol to form three molecules of fatty acid alkyl esters and one molecule of glycerol.

Basic catalysts are known to accelerate the transesterification reaction more than acid catalysts and they are most often used commercially. Therefore, most of the research on the biodiesel production is focused on base catalyzed reactions. The mechanism of transesterification reaction in the presence of basic catalyst is described in **Figure 6**.[32] In the first step, base reacts with alcohol to produce an alkoxide and the protonated catalyst. The second steps involve the reaction between alcohol and the base catalyst to form an alkoxide ion, which attacks the carbonyl of the triglyceride molecule, resulting in the formation of a tetrahedral intermediate. The third step involves the rearrangement of the intermediate to give rise to an alkyl ester and diglyceride anion. In the last step, the catalyst is deprotonated and thus the active species, which react with another molecule of the respective alcohol, are regenerated. This process occurs three times until the formation of fatty acid ester and glycerol.[31,32]



R^1, R^2, R^3 = Different carbon chains of fatty acid

R = Alkyl group of alcohol

Figure 6: Mechanism of base catalyzed transesterification.

Like base catalyzed transesterification, acid transesterification reaction has three consecutive, reversible reactions. Unlike base catalysis, the carbon atom of the carbonyl group of the triglyceride becomes more electrophilic by the catalyst and more susceptible to be attacked by alcohol. This process is slower than the base mechanism.[35]

In addition to the type of catalyst (base vs. acid) and the molar ratio of alcohol to triglycerides, several parameters influence the biodiesel yield and affect the rate of the transesterification reaction including molar ratio of alcohol to oil, catalyst type and concentration, reaction temperature and time, and stirring.[36] Appropriate molar ratio of alcohol to oil is needed for the transesterification reaction: lower molar ratio than the optimum value could lead to a reversible reaction and then lower the biodiesel yield, when a higher molar ratio also reduces the yield and makes the separation process of esters and glycerol difficult.[37] The complexity evolving from the separation process might be because methanol has a polar hydroxyl group that can act as an emulsifier causing emulsification. Regarding the catalyst concentration, the use of more catalyst than the optimum value will not have any significant impact on biodiesel conversion and could even affect it in some cases due to mass transfer issue in the case of heterogeneous catalyst or side reactions when using homogeneous catalyst. Reaction temperature and time play a crucial role as an attempt is already made for accomplishing the transesterification reaction lowest possible temperature and time to reduce the viscosity of the oil in one hand and minimize the energy consumption in other hand. The commonly employed temperature ranges from room temperature to 65°C. Higher reaction temperature and time influence positively the transesterification reaction. The boiling point of methanol is 64.7°C and hence the transesterification reaction is carried out at lower temperature as a temperature higher than this may evaporate methanol and hinder the reaction to occur.[36] Higher temperature also favors saponification and hence must be avoided.[38] For optimum conditions, a molar ratio of 6:1 of alcohol to triglycerides should be used in the presence of base catalyst and under higher reaction temperatures but below the boiling point of the alcohol. Mixing is a very important criteria in the transesterification reaction for enhancing the contact between oils and methanol, as oils are immiscible with the alcohol solution.[19]

Nevertheless, biodiesel produced by transesterification process is completely miscible with commercial diesel in any blending proportion and its cetane number is found to be improved. Therefore, transesterification is the most suitable method for producing an environmentally friendly and safe fuel from unprocessed vegetable oil.

1.4 Homogeneous and heterogeneous catalysts

The presence of catalyst is necessary to increase the reaction rate and the transesterification reaction yield. The choice of catalyst for biodiesel production is evaluated based on its economic viability. The largely used catalysts for transesterification reaction in biodiesel production can be divided in two groups: homogeneous and heterogeneous catalyst and subdivided into acid or base catalyst.

1.4.1 Homogeneous catalysts

Homogeneous catalysts act in the same liquid phase as the reactants and products. They are commonly classified into acid and alkali catalysts. They are currently the most widely used catalyst for large scale production of biodiesel, owing to their low cost and less time required for oil conversion to biodiesel.[39]

The most common homogeneous acid catalysts used are sulfuric acid (H_2SO_4)[40–43] and hydrochloric acid (HCl)[44–46]. Despite the increase in the yield of the bio-diesel, the acid catalyzed reaction is 4000 times slower than the basic catalyzed reaction, and it also requires higher temperatures and pressures[32] due to the involvement of intermediate steps like formation of intermediate molecules which are susceptible to nucleophilic attack, whereas, the base catalyzed reaction proceeds on straight route at which alkoxide ion is initially formed and directly acts as a strong nucleophile.[34] Thus the strategy of a based catalyzed transesterification is appropriate for the demand-based production of biodiesel. However, much remains to be done and appropriate solid base catalysts to be developed as substitute to the conventional homogeneous catalysts like NaOH or KOH.

1.4.2 Heterogeneous catalysts

High-energy consumption and costly separation of the catalyst from the reaction mixture have inspired the development of heterogeneous catalysts. Heterogeneous catalytic process involves more than one phase, when usually the catalyst is a solid and the reactants and products are in liquid form. Due to the size of triglycerides molecules and the size of oil micelles formed in the reaction mixture (oil + alcohol) it is expected that the reaction occurs over the external surface of the solid catalyst.[47] Unlike homogeneous, heterogeneous catalysts are environmentally friendly, could be operated in a fixed bed reactor, are easier to be separated from liquid products, avoid the formation of soap and the catalyst can be reused several times.[16] Therefore, heterogeneous transesterification is a less expensive alternative to the current homogenous transesterification for biodiesel production, inducing lower energy consumption and leading to high purity of the products.[48] However, a higher molar ratio of alcohol to oil, larger amount of catalyst, longer time, and higher temperature are generally required when using heterogeneous catalyst for biodiesel production. As heterogeneous catalyst possess less active sites than homogeneous ones, evolving a slower kinetic reaction, the usage of excess methanol is one of the better options for improving the slow reaction rate of the transesterification reactions catalyzed by heterogeneous catalysts.[49] Additionally, their deactivation with time and several reuses occur systematically due to many possible phenomena, such as poisoning, coking, sintering, and leaching, leading to the increase of the cost process and possibility of product contamination. On the course of the transesterification reaction, the solid catalysts have a tendency to adsorb organic species, causing the inaccessibility of the active sites on the catalyst surface from the reaction medium. Finally, problems related to mass transfer always occur since the catalyst appeared in a solid phase and the reactants in liquid phases. Therefore, the kinetic of reaction is dependent on the diffusion between these phases.[31] Unlike homogeneous systems, in heterogeneous catalysis adsorption of reactants and desorption of products has to take place on the surface of the solid catalyst for the reaction to proceed at a faster rate.[35]

1.4.2.1 Heterogeneous acid catalysts

Heterogeneous acid catalysts are preferred over homogenous catalysts, because they do not dissolve in the alcohol and feedstock, hence they can be separated easily by filtration and can be reused. Such catalysts are more suitable for feedstocks having a high content of FFA, catalyzing, as homogeneous acid catalyst, both transesterification and esterification reactions simultaneously, and thus reduce the number of processing steps to biodiesel.[50,51] In heterogeneous acid catalysts, triglyceride is adsorbed on the surface of the catalyst by protonation of the carbon in carbonyl group which is to be attacked by alcohol in the liquid phase.[52] Despite their lower activity compared to homogeneous acid catalyst, they contain a multiple sites with different strength of Bronsted or Lewis acidity. These catalysts are less corrosive, less toxic, and generate less environmental issues than homogeneous ones.[53] However, the activity of solid acid catalysts requires extreme conditions of temperature and pressure and could lead to unfavorable side reactions.[50] Common types of solid catalysts comprise catalyst with sulfonic acid group[54–56], heteropoly acids[57–62], transition metal oxides[63,64], and acid zeolites[65].

1.4.2.2 Heterogeneous base catalysts

Heterogeneous base catalyst is preferred over acid catalyst for feedstocks with low FFA content, owing to its activity and strong basic sites. However, they are sensitive to water, moisture, and FFA. A small amount of moisture can initiate oil hydrolyzation to form soap and glycerol and thus, the catalytic activity might be reduced.[66] Therefore, when using a feedstock with low grade that contain high amount of FFA, pretreatment of the feedstock or esterification process is require prior to the transesterification with a base catalyst. In an attempt to reduce the production cost, a variety of catalysts, namely, anion-exchange resin[67,68], alkaline earth metal oxides[69–72], mixed metal oxides of alkaline earth group elements[73,74], rare earth metals[75], basic zeolites[76], spinels[77], hydrotalcites[78–80], and perovskites[81] are being tested for the industrial production of biodiesel. The common goals are always lessening the catalyst amount and lowering overall energy requirement of the process. The common problem associated with the heterogeneous biodiesel production process is its slow reaction rate compared with homogeneous catalysts, due to poor surface contact between triglycerides and alcohol during the reaction because of their reciprocal immiscibility.[82] In the presence of heterogeneous base catalysts, the reaction involves the active participation of methoxide species, formed upon adsorption of methanol on the catalyst surface, and then, the efficiency of the catalyst should be related to the rate of formation of methoxide anion.[83]

1.4.2.2.1 Alkaline earth metal oxides

Among the solid catalysts, alkaline earth metal oxides have higher basicity, lower solubility in alcohol and produce higher biodiesel yield.[84] However, leaching of metal oxide catalysts is accelerated in the presence of polar substances such as methanol, water and FFA.[85] Among the alkaline earth elements, beryllium (Be) and radium (Ra) are not used as catalyst for transesterification reactions because they are carcinogenic and radioactive, respectively.[86] The order of activity the remaining alkaline earth oxide catalyst is barium oxide (BaO) > strontium oxide (SrO) > calcium oxide (CaO) > magnesium oxide (MgO).[87] The basic strength of alkaline-earth metal oxide is related to the electronegativity of the conjugated metal cation. This is due to the increase in the ionic radii of alkaline-earth metals and an accompanied decrease in the electronegativity in this order, which reduced the attractive force of electrons for the conjugated metal cation.[87] This has improved the basic characteristic of the attaching oxygen anion on the alkaline-earth metal oxide. Various oxygen anions of low coordination number on the MO are considered to be responsible for the basicity.[49] The structure of metal oxides involves positive metal ions (cations) and negative oxygen ions (anions), which correspond to Lewis acid and Brønsted base sites, respectively. Basicity in alkaline earth oxides arise from M^{2+}- O^{2-} ion pairs present in different coordination environments, with strongest base sites occurring at low coordination defect, corner and edge sites, or on high Miller index surfaces.[88] The surface oxide anion is the basic site of the catalyst. In methanolysis of oils, these oxides provide sufficient adsorptive sites for methanol, in which the O–H bonds break into methoxide anions (CH_3O^-) and hydrogen cations (H^+) on basic sites of metal oxide catalyst surface (**Figure 7**)[66], leading to high activity of the catalyst. The methoxide anions then react with the triglyceride molecules to form the corresponding fatty acid methyl esters (FAME).[89] According to Lewis theory, the oxides of alkaline-earth metals are stronger bases than their hydroxides. Alkali earth metal oxides have very reactive surface with CO_2 and water and should be kept away from atmospheric contact with carbon dioxide to avoid carbonate formation.[35] Moreover, recent study have proved that feedstocks containing FFA could be responsible for the alkali earth metal oxide catalyst leaching into the reaction mixture.[90] Such catalysts would require an oil with no FFA and no water to attest the heterogeneity of the catalyst and to improve the biodiesel conversion at the end of the transesterification reaction.

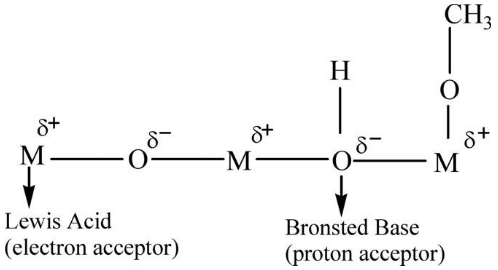


Figure 7: Mechanism of alkaline earth metal oxide catalyst in contact with methanol.

MgO have the lowest activity, the weakest basic strength and the lowest solubility in methanol among the alkaline earth metal oxide in the transesterification of triglycerides to biodiesel, and then, provide the slowest reaction rate.[83,91] The catalytic activity of CaO is high, its possess a long catalyst life time and its able to operate under mild reaction conditions.[48] Among alkali earth metal oxides, CaO has attracted many attentions for transesterification reaction these last decades thanks to its relatively high basic strength and low solubility in methanol. Tremendous research was done on the uses of CaO derived from several sources, as suitable catalyst for the transesterification reaction.[92–100] Interest in the use of CaO catalyst evolved as it could be prepared from cheaper and abundant materials like, sea sand[101], constructional lime[23,102], mollusk shell[103–105], egg shell[106–111], and limestone[112]. These natural sources are composed of calcium carbonates that are calcined in order to decompose it and produce CaO that can be used as a catalyst for the production of biodiesel. However, severe leaching of CaO was observed after the first run, affecting its reusability and long-life durability.[113] Moreover, the catalytic activity of CaO still remain low relative to SrO and BaO that exhibit excellent catalytic performance for the transesterification process.[70,114–116] Although BaO is active in transesterification reaction, however, it forms highly toxic barium complex compounds and highly dissolve in methanol compared to CaO and SrO.[93] The loss of active component will reduce the catalytic activity of repeated use of BaO and consequently will decrease the biodiesel production yield.[87] Therefore, BaO is not suitable for bio-diesel production. While Ca and Mg are the most widely used alkaline earth metals in solid base catalysis for transesterification reaction, the basic strength of catalyst is the key determinant in the reaction rate.[87] Therefore, SrO is a good potential candidate for biodiesel production.

1.4.2.2.1.1 Strontium oxide (SrO)

It has been reported that SrO can catalyze many chemical reactions, such as oxidative coupling of methane[117,118], selective oxidation of propane[119], nitroaldol reactions and mixed tishchenko reactions[120], Michael addition[121], and transesterification[37]. Pure SrO possesses the highest base site density of the alkali earth oxides, stronger than H_= 26.5 as indicated by hammett indicator method[122], a measure of the basicity/acidity of solid base catalyst, and a comparable base strength to that of BaO. Despite its lower surface area (1.05 m^2/g)[37] compared to Mg and Ca oxides and the partial solubility of the metal ion in methanol[123], SrO is a suitable catalyst for the transesterification process thanks to its high basicity, strong base sites, relative low lixiviation tendencies in biodiesel and high selectivity towards the transesterification reaction. SrO present superior activity than homogeneous base catalyst.[37,124] All these parameters represent the contributing factors of catalyst choice for an optimal biodiesel productivity.[125] The SrO catalyst derived from thermal decomposition of $SrCO_3$ at 1200°C was found to give high yield of FAME in a short time under mild temperature and pressure conditions.[37] Likewise, the long catalyst lifetime of SrO would maintain its activity even after being repeatedly used for 10 cycles, which could be a commercially viable way to decrease the costs of production for industrial application in the transesterification of triglyceride to biodiesel. Moreover, Koberg et al. showed that the transesterification of cooked oil to biodiesel in a microwave domestic oven can be completed using commercial SrO as catalyst in only 10 sec.[124] Such achievement, at this shorter time, is probably due to the product ratios that fit quickly the equilibrium constant. The short reaction time minimizes the input energy that is consumed for the biodiesel production. Additionally, the loading of SrO into ferric composite oxide enhance the stability of grafted sulfate ions and the catalytic reactivity of the active sites in the esterification of oleic acid with methanol for the production of biodiesel, due to the high chemical and thermal stability of the sulfate ions bonded on Sr cations.[126] Previous study shows that SrO could be recycle and reusable 10 times with an observation of only 2-3% losses on its activity at the 10th cycle.[127] The reason for the loss of 2–3% in conversion might be due to the loss of the catalyst during SrO recycling. These results confirm the stability and the sustainability of SrO activity, which is of great importance for industrial application. However, SrO is highly hygroscopic and have a strong tendency to react with CO_2 and water in air to form $SrCO_3$, mostly derived from the chemisorption of CO_2 onto the basic sites, and $Sr(OH)_2$ and loses its catalytic ability, due to their lower basic strength than the corresponding metal oxide.[93,128] Despite a similar catalytic activity between SrO and $Sr(OH)_2$, the later could be partially dissolved in the reaction medium, releasing OH^- ions, and then it will not act as fully heterogeneous catalyst.[124] To reactivate the catalyst, it must be calcined at temperatures higher than 1000°C.[129] As well, SrO, as other basic catalyst, is very sensitive to the presence of FFA containing in most of low grade feedstocks and/or water.[123,130] Therefore, both FFA and water should be removed prior the transesterification reaction with SrO in order to obtain optimum conversion of triglycerides to biodiesel. To overcome the FFA and water issues, mixing SrO with acidic material like zirconium oxide[131,132] or acid zeolite[133] was found as an effective method for achieving in one pot esterification and transesterification of feedstocks presenting high amount of FFA and/or water and resulting in high conversion to biodiesel. Another effective process to remove impurities like FFA and water consist of washing the oil with low concentrated homogeneous base catalyst like KOH[124] and drying the feedstock prior the transesterification reaction.

The catalyst activity of SrO occur on its surface and the reaction mechanism is as follows (**Figure 8**)[37]: In the beginning, surface O^{2-} extracts H^+ from CH_3OH to form surface $CH3O^-$ (step (2)), which is strongly basic and has high catalytic activity in the transesterification reaction. In the second step, the carbonyl carbon atom of the triglyceride molecule attracts a methoxide anion from the surface of the SrO to form a tetrahedral intermediate (step (3)), where R_1 represents the chain of alkyl group. In the third step, the tetrahedral intermediate picks up H^+ from the surface of the SrO (step (4)). The tetrahedral intermediate also can react with methanol to generate methoxide anions (step (5)).[134] In the last step, rearrangement of the tetrahedral intermediate results in the formation of biodiesel (step (6)).[37]

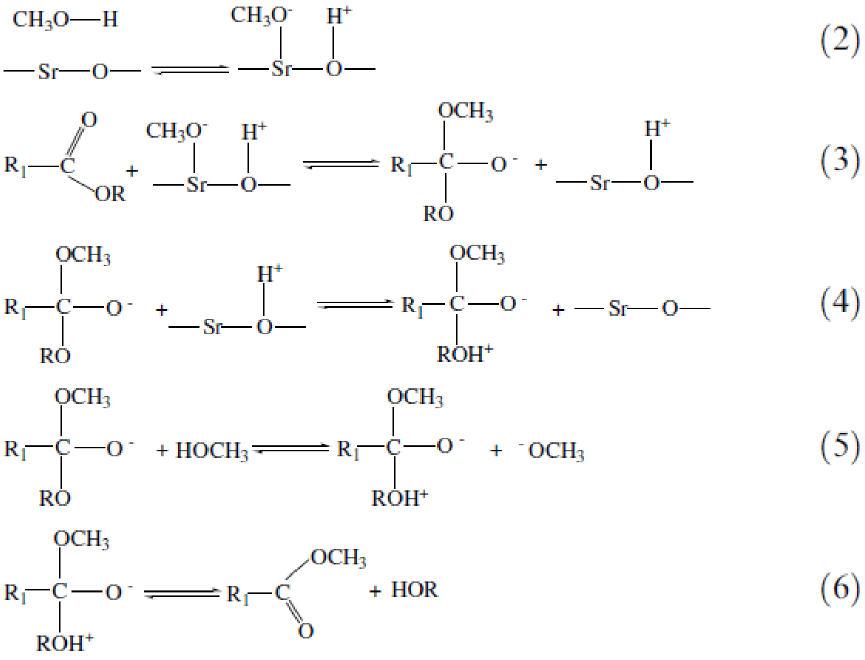


Figure 8: Mechanism of SrO catalyzed transesterification.

In order to increase the number of SrO active sites and/or to increase the surface area of the catalyst, great efforts were done recently to synthesize SrO on a suitable material support.[81,123,130,133] Such process involves a modification of the surface morphology and the texture of SrO. The homogenized dispersion of SrO in reaction medium will be also promoted after supporting it on a proper material.

~~**Table 1** summarize~~ M~~m~~ost of the ~~researchs~~ developments made on biodiesel production using SrO catalyst for transesterification reaction as bulk, or as mixed metal oxide, or as supported catalyst, using different sources of heating are summarized in Table 1.

Table 1.~~:~~ Literature review on biodiesel production using SrO based catalyst for transesterification reaction

Catalyst	**Feedstock**	**Reaction conditions**	**Biodiesel yield (wt. %)**	**Reference**
Ba–Sr/ZSM-5 (6 wt.% Sr based on ZSM-5 wt and 4 wt.% Ba based on the Sr wt catalyst amount)	Sunflower oil	Conventional heating; T = 60°C; **3 h**; MeOH: oil molar ratio = 9:1; 3 wt.% catalyst amount; Stirring: 500 rpm	87.7	133
Cu/SrO (CuO: 10 wt. %)	Hempseed oil	Hydrothermal heating; T=180°C; **3 h**; MeOH: oil molar ratio = 12:1; 3wt.% catalyst amount; 3 MPa	96	135
MgO - SrO (5 mmol Sr/g)	Palm olein oil	Conventional heating; T = 60°C; **30 min**; MeOH: oil molar ratio = 9:1; 5 wt. % catalyst amount	97.3	49
Sr/Ca (molar ratio : 0.5)	Palm oil	Conventional heating; T = 65°C; **30 min**; MeOH: oil molar ratio = 9:1; 5 wt.% catalyst amount	98.31	136
Sr/CaO (Sr: ~ 17 wt. %)	Cottonseed oil Waste frying oil	Conventional heating; T = 60°C; **2 h**; MeOH: oil molar ratio = 12:1; 3.5 wt.% catalyst amount	97.3 96.7	137
Sr/hydroxyapatite (2.5 mmol Sr/g	Soybean oil	Conventional heating; T = 70°C; **5 h**; MeOH: oil molar ratio = 9:1; 5.6 wt.% catalyst	85	138

support)		amount		
Sr/$Mg_{0.72}Al_{0.2}$ oxide (Sr: 1.5 wt. %)	Rice bran oil	Conventional heating; T = 60°C; **3 h**; MeOH: oil molar ratio = 20:1; 1.5 wt. % catalyst amount	56	139
Sr/MgO (2.5 mmol Sr/g support)	Soybean oil	Conventional heating; T = 65°C; **30 min**; MeOH: oil molar ratio = 12:1; 5 wt.% catalyst amount	93	140
Sr/NiO (molar ratio : 1)	Macaw oil	Conventional heating; T = 65°C; **5 h**; MeOH: oil molar ratio = 9:1; 2 wt.% catalyst amount	97	141
Sr/ZnO (2.5 mmol Sr/g support)	Soybean oil	Conventional heating; T = 65°C; **5 h**; MeOH: oil molar ratio = 12:1; 5 wt.% catalyst amount	94.7	142
Sr/ZrO_2 (Sr: ~ 7wt. %)	Waste cooking palm oil	Hydrothermal heating; T = 113.7°C; **89 min**; MeOH: oil molar ratio = 30:1; 2.1 wt.% catalyst amount	86.7	143
Sr_2TiO_4 (molar ratio Sr/Ti: 0.8)	Soybean oil	Conventional heating; T = 60°C; **15 min**; MeOH: oil molar ratio = 15:1; 1wt. % catalyst amount	98	144
$Sr_3Al_2O_6$ nanocomposite	Soybean oil	Conventional heating; T = 60°C; **61 min**; MeOH: oil molar ratio = 25:1; 1.3 wt. % catalyst amount	95.7	145
$SrAl_2O_4$	Rapeseed oil	Hydrothermal heating; T = 160°C; **2 h**; MeOH: oil molar ratio = 6:1; Catalyst amount: 1.95 g	89	77
Sr-cinder ($SrAl_2Si_2O_8$ and $Sr_5Al_8O_{17}$)	Soybean oil	Hydrothermal heating; T = 180°C; **1 h**; MeOH: oil molar ratio = 24:1; 4 wt. % catalyst amount	97.1	123
SrO	Fried vegetable oils	Catalytic bed sytem; T = 65°C; **40 min**; MeOH: oil molar ratio = 6:1; 5 wt.% catalyst amount; Flow rate of 100 mL/min	85	146

SrO	Camelina Sativa oil	Conventional heating; T = 60°C; **120 min**; MeOH: oil molar ratio = 12:1; 0.5 wt.% catalyst amount	82	[70]
SrO	Babassu oil Castor oil	Conventional heating; T = 65°C; **1 h**; MeOH: oil molar ratio = 6:1; 1 wt.% catalyst amount	97.2 96.4	[129]
SrO	Olive oil	Conventional heating; T = 65°C; **15 min**; MeOH: oil molar ratio = 6:1; 5wt. % catalyst amount	82	[130]
SrO	Palm oil	Conventional heating; T = 65°C; **3 h**; MeOH: oil molar ratio = 15:1; 3 wt. % catalyst amount	~ 92	[147]
SrO	Soybean oil	Conventional heating; T = 65°C; **30 min**; MeOH: oil molar ratio = 12:1; 3wt. % catalyst amount	95	[37]
SrO	Babassu coconut oil	Fixed bed reactor; RT (~25°C); **3 h**; Oil: MeOH weight ratio = 5:1; 1.5 wt.% catalyst amount	98.54	[148]
SrO	Waste cooking oil	Microwave irradiation; T = 60°C; **10 s**; MeOH : oil molar ratio = 6:1; 1.8 wt.% catalyst amount	99.8	[124]
SrO	Castor seed *Jatropha* seed	Microwave irradiation; T = 60°C; **5 min.**; 30 wt.% catalyst amount; $CHCl_3$:MeOH (1:2 v/v)	99.95 99.7	[127]
SrO	*Nannochloropsis sp.*	Microwave irradiation; T = 60°C; **5 min.**; 30 wt.% catalyst amount; $CHCl_3$:MeOH (1:2 v/v)	99.9	[149]
SrO	Rapeseed oil	Supercritical MeOH conditions: hydrothermal heating; T = 220°C; **10 min**; MeOH: oil molar ratio = 40:1; 1wt. % catalyst amount	> 90	[150]
SrO	Palm oil	Ultrasound heating; T = 65°C;	93.37	[151]

		30.7 min; MeOH: oil molar ratio = 9:1; 2.5 wt.% catalyst amount; 130W; Pulse on: 9 s and pulse off: 1 s		
SrO	Palm oil	Ultrasound heating; T = 65°C; **60 min**; MeOH : oil molar ratio = 9:1; 3 wt.% catalyst amount; 50% amplitude	95.2	114
SrO – CaO (Sr/Ca wt. ratio- 1 : 6)	*Jatropha* oil	Ultrasound heating; T = 65°C; **30 min**; MeOH: oil molar ratio = 10:1; 6 wt.% catalyst amount; 210W	95.4	152
SrO/Al_2O_3 (SrO: 2 wt. %)	Rapeseed oil	Ultrasound heating; Supercritical EtOH; **30 min**; T = 350°C; EtOH : oil molar ratio = 12:1; 2 wt.% SrO amount; Flow rate of 300 mL/min; 30 MPa	97.46	153
SrO/SiO_2 (molar ratio Sr/Si: 6)	Olive oil	Conventional heating; T = 65°C; **10 min**; MeOH: oil molar ratio = 6:1; 5wt. % catalyst amount	95	130
SrO/SiO_2 (wt. ratio Sr/Si: 2)	*Nannochloropsis sp.*	Microwave irradiation; T = 60°C; **2 min.**; 60 wt.% catalyst amount; $CHCl_3$:MeOH (1:2 v/v)	99.9	154
SrO/SiO_2 (molar ratio Sr/Si: 6)	*Chlorella vulgaris ESP-31*- 22.7 wt.%	Conventional method; T = 45°C; **6 h.**; 5.5 wt.% catalyst amount; MeOH : oil molar ratio= 424:1	81.8	155
$SrTiO_3$	Palm kernel oil	Hydrothermal heating; T = 170°C; **3 h**; MeOH: oil molar ratio = 20:1; 10 wt. % catalyst amount	99.9	81
$SrZrO_3$	Soybean oil	Conventional heating; T = 60°C; **3 h**; MeOH: oil molar ratio = 12:1; 3wt. % catalyst amount	98	131
$SrZrO_3$ (2 : 1 atomic ratio)	Waste cooking oil	Conventional heating; T = 75°C; **7 h**; EtOH: oil molar ratio = 12:1; 5 wt. % catalyst amount; Stirring: 400 rpm	99.61	132

Owing to the great potential of SrO, proper design of the catalyst[156] will allow in near future to move from laboratory scale to industrial and commercial biodiesel production, replacing the homogeneous base catalyst used nowadays in large-scale production for industry.

1.5 Feedstock for biodiesel production

The cost of feedstocks for biodiesel production represents 70–95% of the total production cost. Globally, there are more than 350 oil-bearing crops identified as potential sources for biodiesel production. Therefore selecting the cheapest feedstock is a vital issue to ensure low production cost of biodiesel.[157] The properties of biodiesel depend on the physico-chemical properties of feedstock and the production method.[158] A variety of feedstocks containing fatty acids, divided into different categories, such as vegetable oils or edible oils, non-edible oils, waste oils, animal fats, and algal lipids, have been evaluated for the production of biodiesel. It is very important to consider some parameters when comparing different feedstocks. Among the parameters, the most important ones are: availability of land, cultivation practices, energy supply and balance and, emission of greenhouse gases.

1.5.1 Vegetable oil

Vegetable oils and animal fats are considered an inexhaustible renewable source of energy. On the other hand, use of edible oil as feedstock gives rise to certain concerns like food crisis and subsequently, the price of edible oil raises, making the biodiesel production more expensive than petroleum. Moreover, the large-scale usage of vegetable oils for biodiesel production evolve a constant increase of starvation, deforestation, and usage of arable land.[16] Therefore, great efforts have been devoted during the last decade to employ non-edible oils, waste cooking oils, and microalgae as feedstock for biodiesel production to overcome these issues.

1.5.2 Waste cooking oil (WCO)

The residual obtained after using oil for the cooking purposes is generally discarded with no further application, causing also environmental damage[159]. Among the common used non-edible vegetable oils for biodiesel production, like jatropha seed oil[160–163], castor seed oil[164–167], karanja oil[108,168], linseed oil[169], cottonseed oil[170] that generally require extraction of oil before the transesterification process, WCO could be use as it or with pretreatment, depending of its composition and of the type of the catalyst used. Moreover, the use of WCO as feedstock for biodiesel production can offer an interesting alternative to achieve a more sustainable biodiesel production worldwide, avoiding the use of edible oils in fuel applications.[171] The price of waste edible oils, like cooked oils, is estimated to be 2–3 times cheaper than the virgin vegetable oil. Therefore, the use of cost-effective WCO can be a way to improve the economy of biodiesel production and its commercial production at an industrial scale.[157] The amounts of WCO generated by homes and restaurants are increasing rapidly due to the tremendous growth in human population. Moreover, the increment in food consumption has also contributed to the production of huge amounts of WCO.[29] Estimations on the amounts of annually generated WCO worldwide would account for a total of more than 15 million tons per year.[29] Using the wastes from cooking oil as a source of bio-diesel are not only economical, but also will affect positively the quality of the environment, because nowadays most of the used cooking oil is discharged into the city sewage system, causing water pollution and blockages in water drainage systems, which require extra work to clean. Moreover, water and soil pollution disturb the aquatic ecosystem in addition to being a human health concern.[172] Despite the feasibility of recycling WCO, it is believed that such process would cause cancer because of the toxic contents produced when the oil is oxidized.[29]

WCO have different physiochemical properties from those of refined and crude vegetable oils because of the physical and chemical changes, mainly due to thermolytic, oxidative and hydrolytic reactions that take place during frying at a temperature of $160 - 200°C$ for relatively long period of time. Their properties depend on their composition and the degree of heating. A thermolytic reaction occurs in the absence of oxygen at high temperatures. A series of alkanes, alkenes, lower fatty acids, symmetric ketones, oxopropyl esters, CO, and CO_2 are produced from the saturated fatty acids in the oil. From the unsaturated fatty acids, diametric compounds such as dehydrodimers, saturated dimers, and polycyclic compounds are formed. Oxidative reaction occurs when oxygen in air meets the oil and reacts mainly with unsaturated fatty acids, resulting in the formation of various oxidation products. In the case of hydrolytic reaction, the steam produced during the processing of food containing water causes the hydrolysis of triglycerides, resulting mainly in the formation of FFA.[173] WCO contain generally high amounts of free fatty acids (FFA) compared to edible oils (5–20% w/w)[174], due to the presence of heat and water that accelerate the hydrolysis of triglycerides. Therefore, the transesterification reaction may be greatly affected and the conversion of WCO to biodiesel will be complicated, as FFA undergoes saponification in the presence of basic catalyst. Soap formation deactivates the catalyst activity, thus lowering the yield of biodiesel produced. Water and heat hinder also the separation of fatty acid esters and glycerol. Particularly, the viscosity of the oil increases considerably, because of the formation of dimeric, polymeric acids and glycerides in used cooking oils.[175] Hence, experimental conditions used in the transesterification reaction will influence the viscosity of the biodiesel. Different viscosities are due to the incomplete reaction of the WCO, leaving conjugated or free glycerol in the alkyl ester phase. In fact, the presence of glycerides changes the apparent viscosity of alkyl esters.[175] Nevertheless, the engine performance of biodiesel obtained from WCO is better than that of diesel fuel while the emissions produced by the use of biodiesel are less than those of diesel fuels except that there is an increase in NOx.[158]

The use of base catalysts in the transesterification of cooked oil is limited because of the formation of soap during the reaction of fatty acid esters containing water with the catalyst. In addition, catalyst efficiency is reduced, the fatty acid esters yield is also reduced, and then, the separation of glycerol is difficult. To reduce the high FFA content in the oil, several pretreatment techniques of WCO have been proposed. The most common technique consists of a two-step transesterification process required to convert the FFA oils to its mono-esters. The first step, acid catalyzed esterification, aimed to reduce the FFA content of the oil to less than 2%. The second step, alkaline catalyzed transesterification process converts the products of the first step to its mono-esters and glycerol.[176–178] Other processes consist of esterification with ion-exchange resins[67], neutralization with alkalis followed by soap separation by a decanter or centrifugation[124], and extraction with polar liquids along with acid esterification and distillation of FFA. To eliminate water content, a WCO sample is often heated to above 100°C. Then, the suspended solids, phospholipids, and other impurities commonly found on such oils after several reuses can be washed away with hot water or removed by centrifugation and paper filtration.

A summary of the recent developments in the catalytic processes for the conversion of waste cooking oil into biodiesel in batch and continuous flow process is presented in Table 2.

Table 2.~~:~~ Catalytic processes for the conversion of waste cooking oil (WCO) to biodiesel

Catalyst	**Reaction conditions**	**Batch/ Continuous**	**Conversion of WCO to biodiesel (wt. %)**	**Reference**
NaOH	Conventional heating; T = 50°C; **30 min**; MeOH : oil molar ratio = 7.5:1; 0.5 wt.% catalyst amount	Batch	96	179
KOH	Conventional heating; T = 50°C; **30 min**; MeOH: oil molar ratio = 9:1; 1 wt.% catalyst amount	Batch	99.46	180
KOH	Conventional heating; T = 65°C; **1 h**; MeOH: oil molar ratio = 7.5:1; 1.4 wt.% catalyst	Batch	99.38	181
NaOH	Conventional heating; T = 65°C; **45 min**; MeOH: oil molar ratio = 9:1; 0.72 wt.% catalyst amount	Batch	92.05	182
KOH	Conventional heating; T=60°C; **2 h**; MeOH: oil molar ratio = 10:1; 4wt.% catalyst amount	Batch	100	183
NaOH	Helicoidal; reactor; T = 60°C; **75 min**; MeOH : oil molar ratio = 6:1; 0.6 wt.% catalyst amount	Continuous	89.5	184
KOH	Hydrodynamic cavitation reactor; T = 60 °C; **30 min**; MeOH: oil molar ratio = 6:1; 1 wt. % catalyst amount	Batch	≥ 96.5	185
NaOH	Microwave irradiation; **3 min**; MeOH: oil molar ratio = 15:1; 1 wt.% catalyst amount	Batch	97.2	186
$NaOCH_3$	Microwave irradiation; 4.47 min; MeOH: oil molar ratio = 11.62:1; 0.68wt.% catalyst amount	Continuous	97.13	187
NaOH	Microwave irradiation; T = 78°C; **30 s**; EtOH : oil molar ratio = 12:1; 3 wt.% catalyst amount	Continuous	97	188
NaOH	Ultrasound heating; **150 s**; MeOH: oil molar ratio = 8.6:1; 0.5 wt.% catalyst amount; 1 L/min	Continuous	90	189
NaOH	Ultrasound heating; **2 min**; MeOH-EtOH (50%-50%): oil molar ratio =	Batch	98.7	190

	9:1; 1 wt.% catalyst amount; 300W			
KOH	Ultrasound heating; T=45°C; **40 min**; MeOH : oil molar ratio = 6:1; 1 wt.% catalyst amount; 200W	Batch	89.5	191
KOH	Ultrasound heating; ultrasonic amplitude of 56 %, vibration pulse of 62 % and flow rate of 50 mL/min	Continuous	91.6	192
Tris-dodecyl cerium (III)	Conventional heating; T = 100°C; **1 h**; MeOH : oil molar ratio = 6:1; 10 wt.% catalyst amount	Batch	91.6	193
Mo-Mn/γ-Al_2O_3-15 wt % MgO	Conventional heating; T = 100°C; **4 h**; MeOH: oil molar ratio = 27:1; 7.5 wt. % catalyst amount	Batch	91.4	194
Encapsulated mixed lipase from B. subtilis and B. cepacia	Conventional heating; T = 35°C; **60 h**; MeAcetate : oil molar ratio = 12:1; 2 g catalyst loading	Batch	93.61	195
Novozyme 435 the immobilized form of Pseudozyma Antarctica lipase B in a macroporous resin	Conventional heating; T = 40°C; **24 h**; EtOH: oil molar ratio = 6:1; 5 wt. % catalyst	Batch	89.5	196
KOH/TZT (treated zeolitic tuft)	Conventional heating; T = 50°C; **2 h**; MeOH: oil molar ratio = 11.5:1; 6 wt. % catalyst amount	Batch	96.7	197
Cu doped ZnO nanocomposite	Conventional heating; T = 55°C; **50 min**; MeOH: oil molar ratio = 8:1; 12 wt. % catalyst	Batch	97.71	198
Tri-potassium phosphate	Conventional heating; T = 60°C; **2 h**; MeOH : oil molar ratio = 6:1; 4 wt.% catalyst amount	Batch	97.3	199
Acidic ionic liquid from 1-allyl-1H-imidazole, 1,3-propyl	Conventional heating; T = 60°C; **20 h**; MeOH : oil molar ratio = 25:1; 5 wt.% catalyst amount	Batch	87.58	200

sulfonic acid lactone and H_2SO_4 on silica-gel				
Hydrated lime	Conventional heating; T = 60°C; **2h**; MeOH : oil ratio (vol.) = 0.17; 3.6 wt.% catalyst amount	Batch	100	201
CaO derived from Mereterix mereterix	Conventional heating; T = 60°C; **3 h**; MeOH : oil molar ratio = 6.03:1; 3.2 wt.% catalyst amount	Batch	97.74	202
Oil palm ash	Conventional heating; T = 60°C; **30 min**; MeOH : oil molar ratio = 18:1; 5.35 wt.% catalyst amount	Batch	71.74	203
Sea sand	Conventional heating; T = 60°C; **6 h**; MeOH: oil molar ratio = 12:1; 7.5 wt. % catalyst	Batch	95.4	101
CaO supported on activated carbon	Conventional heating; T = 60°C; **8 h**; MeOH : oil molar ratio = 25:1; 295 mm packed bed height	Fixed bed reactor	94	204
Snail shell	Conventional heating; T = 60°C; **8 h**; MeOH : oil molar ratio = 6.03:1; 2 wt.% catalyst amount	Batch	99.58	205
Mg-Al-Na mixed oxides	Conventional heating; T = 60°C; **8 h**; MeOH : oil molar ratio = 9:1; 7 wt.% catalyst amount	Batch	67	206
Egg shell	Conventional heating; T = 65°C; **1 h**; MeOH: oil molar ratio = 12:1; 5 wt.% catalyst amount	Batch	94.52	110
KBr impregnated CaO	Conventional heating; T = 65°C; **1.8 h**; MeOH: oil molar ratio = 12:1; 3 wt. % catalyst	Batch	83.6	207
$Zn_{1.2}H_{0.6}PW_{12}O_{40}$ Nanotubes	Conventional heating; T = 65°C; **12 h**; MeOH : oil molar ratio = 28:1; 2.5 wt.% catalyst amount	Batch	97.2	208
$Zr_{0.7}H_{0.2}PW_{12}O_{40}$ with nanotube structure	Conventional heating; T = 65°C; **14 h**; MeOH : oil molar ratio = 20:1; 2.12 wt.% catalyst amount	Batch	98.5	209
$Al_{0.9}H_{0.3}PW_1$	Conventional heating; T = 65°C; **14 h**;	Batch	96.1	210

$_2O_{40}$ nanotubes	MeOH : oil molar ratio = 34:1; 3 wt.% catalyst amount			
Heteropoly acid	Conventional heating; T = 65°C; **14 h**; MeOH : oil molar ratio = 70:1; 10 wt.% catalyst amount	Batch	88.6	211
β-$K_2Zr_2O_5$	Conventional heating; T = 65°C; **2 h**; MeOH : oil molar ratio = 10:1; 4 wt.% catalyst amount	Batch	96.85	212
Waste coral fragments	Conventional heating; T = 65°C; **2 h**; MeOH : oil molar ratio = 15:1; 100 wt.% catalyst amount	Batch	98	213
CaO and ZrO_2 mixed oxides	Conventional heating; T = 65°C; **2 h**; MeOH : oil molar ratio = 30:1; 10 wt.% catalyst amount	Batch	92.1	214
Waste ostrich- and chicken-eggshells	Conventional heating; T = 65°C; **2 h**; MeOH: oil molar ratio = 12:1; 1.5 wt.% catalyst amount	Batch	96	215
Calcined scallop shell	Conventional heating; T = 65°C; **2 h**; MeOH: oil molar ratio = 6:1; 5 wt. % catalyst	Batch	86.0	104
Waste mud crab shells and cockleshells	Conventional heating; T = 65°C; **3 h**; MeOH : oil molar ratio = 13:1; 5 wt.% catalyst amount	Batch	98	216
CaO	Conventional heating; T = 65°C; **3 h**; MeOH : oil molar ratio = 6:1; 5 wt.% catalyst amount	Catalytic bed system	92	146
Ba meliorated construction site waste marble	Conventional heating; T = 65°C; **3 h**; MeOH : oil molar ratio = 9:1; 3 wt.% catalyst amount	Batch	88	102
$Cs_{0.6}Zr_{0.4}O_2$/ Al_2O_3	Conventional heating; T = 65°C; **3 h**; MeOH: oil molar ratio = 30:1; 3 wt.% catalyst amount	Batch	90	217
Ba doped CaO derived from waste shells of T striatula	Conventional heating; T = 65°C; **3 h**; MeOH: oil molar ratio = 6:1; 1 wt.% catalyst amount	Batch	>98	218
Chicken	Conventional heating; T = 65°C; **4 h**;	Batch	89.33	219

bone	MeOH: oil molar ratio = 15:1; 5 wt. % catalyst; agitation speed of 500 rpm			
Mono lacunary phosphotungstate anchored to MCM-41	Conventional heating; T = 65°C; **6 h**; MeOH: oil molar ratio = 8:1; 6wt.% catalyst amount	Batch	90	220
KF supported $Mg_3Al_{0.6}La_{0.4}$	Conventional heating; T = 65°C; **8 h**; MeOH: oil molar ratio = 12:1; 3 wt.% catalyst amount	Batch	98.9	221
$KHCO_3$ loaded in Al_2O_3	Conventional heating; T = 65°C; **90 min**; MeOH : oil molar ratio = 6:1; 1.5 wt.% catalyst amount	Batch	96.8	222
p-toluenesulfonic acid doped polyaniline	Conventional heating; T = 70°C; **3 h**; MeOH: oil molar ratio = 10:1; 4 wt.% catalyst amount	Batch	97.1	223
Sr:Zr mixed oxide	Conventional heating; T = 75°C; **7 h**; EtOH: oil molar ratio = 12:1; 5 wt. % catalyst amount; Stirring: 400 rpm	Batch	99.61	132
$FeCl_3$-modified resin	Conventional heating; T = 78°C; **3 h**; EtOH: oil molar ratio = 4:1; 10.97 wt. % catalyst	Batch	92.13	224
KF-Impregnated Clam Shells	Conventional heating; T=65°C; **2 h**; MeOH: oil molar ratio = 9:1; 4wt.% catalyst amount	Batch	95.77	225
Potassium methoxide	Hydrodynamic cavitation reactor; **30 min**; MeOAc : oil molar ratio = 12:1; 1 wt.% catalyst amount	Batch	90	226
Basic ionic liquid [TBP][OH]	Hydrothermal heating; T = 100°C; **3 h**; MeOH: oil molar ratio = 21:1; 5 wt.% catalyst amount	Batch	82	227
Pyrolyzed Rice husk	Hydrothermal heating; T = 110°C; **15 h**; MeOH: oil molar ratio = 20:1; 5 wt.% catalyst amount	Batch	87.57	228
WOx/Al_2O_3	Hydrothermal heating; T = 110°C; **2 h**; MeOH : oil weight ratio = 0.3:1; 1 wt.% catalyst amount	Batch	97.5	229
Sulfonated carbon mi-	Hydrothermal heating; T = 110°C; **4 h**; MeOH: oil molar ratio = 10:1; 10%	Batch	89.6	230

crospheres	catalyst amount			
Sr/ZrO_2	Hydrothermal heating; T = 115.5°C; **87 min**; MeOH : oil molar ratio = 29:1; 2.7 wt.% catalyst amount	Batch	79.7	231
SO_4^{2-}/ZrO_2	Hydrothermal heating; T = 120°C; **4 h**; MeOH : oil molar ratio = 9:1; 3 wt.% catalyst amount	Batch	93.6	232
Silica sulfuric acid	Hydrothermal heating; T = 120°C; **8h**; MeOH: oil molar ratio = 20:1; 4 wt.% catalyst amount	Batch	98.66	233
Zinc aluminate	Hydrothermal heating; T = 150°C; **2 h**; MeOH: oil molar ratio = 40:1; 10 wt.% catalyst amount	Batch	>95	234
SO_4^{2-}/SnO_2-SiO_2	Hydrothermal heating; T = 150°C; **3 h**; MeOH : oil molar ratio = 15:1; 3 wt.% catalyst amount	Batch	92.3	235
Barium-modified montmorillonite K10	Hydrothermal heating; T = 150°C; **5 h**; MeOH: oil molar ratio = 12:1; 10.97 wt. % catalyst	Batch	83.38	236
Active clay-based catalyst	Hydrothermal heating; T = 150°C; **5 h**; MeOH: oil molar ratio = 15:1; 3.5 wt.% catalyst amount	Batch	96	237
$Mn_{1.4}Zr_{0.35}Al_{0.6}O_3$	Hydrothermal heating; T = 150°C; **5h**; MeOH: oil molar ratio = 14:1; 2.5 wt.% catalyst amount	Batch	93	238
CuO-CeO_2	Hydrothermal heating; T = 160°C; **20 min**; 30% MeOH; 1% wt./v catalyst	Batch	92.59	239
Metakaolinite	Hydrothermal heating; T = 160°C; **4 h**; MeOH : oil molar ratio = 23:1; 5 wt.% catalyst amount	Batch	95	240
TiO_2–MgO	Hydrothermal heating; T = 160°C; **6 h**; MeOH : oil molar ratio = 50:1; 10 wt.% catalyst amount	Batch	92.3	241
Activated carbon supported KF	Hydrothermal heating; T = 175°C; **1 h**; MeOH : oil molar ratio = 8.85:1; 3 wt.% catalyst amount	Batch	83	242
Mg_{1-x} $Zn_{1+x}O2$	Hydrothermal heating; T = 188°C; **4h15**; MeOH : oil molar ratio = 9:1; 2.55 wt.% catalyst amount	Batch	80	243

Ferric–Manganese Doped Tungstated Zirconia NPs	Hydrothermal heating; T = 200°C; **4h**; MeOH: oil molar ratio = 25:1; 4 wt.% catalyst amount; 600 rpm	Batch	96	244
Ionic liquid [HMim][HSO$_4$]	Hydrothermal heating; T = 255°C; **45 min**; 9.62 MPa; 0.35 mL catalyst	Batch	97.6	245
SO4 $^{2-}$/Zr-SBA-15	Hydrothermal heating; T=160°C; **12 h**; MeOH: oil molar ratio = 30:1; 10wt.% catalyst amount	Batch	91.7	246
SrO	Microwave irradiation; T = 60°C; **10 s**; MeOH : oil molar ratio = 6:1; 1.8 wt.% catalyst amount	Batch	99.8	124
Zr-SBA-15/bentonite	Packed bed reactor; T = 210°C; **30 min**; MeOH: oil molar ratio = 50:1; 28 g catalyst amount	Continuous	96	247
Zinc stearate immobilized on silica gel (ZS/Si)	Parr reactor; T = 200°C; **10 h**; MeOH : oil molar ratio = 18:1; 3 wt.% catalyst amount	Batch	98	248
Waste egg shell	Reactive distillation system; T = 65°C; **7 h**; MeOH: oil molar ratio = 4:1	Continuous	93.48	249
Egg shell	RT; **11 h**; MeOH: oil molar ratio = 6:1; 5.8 wt.% catalyst amount	Batch	94.52	109
BaO	Simultaneous microwave and ultrasound irradiations: **2 min**; MeOH: oil molar ratio = 6:1; 0.75 wt. % catalyst amount; 200W (100/100 MW/US).	Batch	93.5	250
Modified coal fly ash	Ultrasound heating; **1.41 min**; MeOH: oil molar ratio = 10.71:1; 4.97wt.% catalyst amount	Batch	95.57	251
Hydrotalcite	Ultrasound heating; **60 min**; MeOH: oil molar ratio = 15:1; 8 wt. % catalyst amount; ultrasound amp. 55%	Batch	76.45	80
Sulfonated carbon derived from cyclodextrin	Ultrasound heating; T = 117°C; **8.8 min**; MeOH: oil molar ratio = 20:1; 11.5 wt. % catalyst	Batch	90.8	252
K_3PO_4	Ultrasound heating; T = 50°C; **90 min**; MeOH: oil molar ratio = 6:1; 3 wt.%	Batch	92	253

	catalyst amount			
Na-silica waste sponge	Ultrasound heating; T = 55°C; **30 min**; MeOH: oil molar ratio = 9:1; 3 wt.% catalyst amount	Batch	98.4	254
Calcium diglyceroxide	Ultrasound heating; T = 60°C; **30 min**; MeOH: oil molar ratio = 9:1; 1 wt.% catalyst amount	Batch	93.5	255
Novozym 435 (lipase B from Candida antarctica; immobilized on macroporous polyacrylic resin beads)	Ultrasound heating; T=60°C; **4 h**; Dimethyl carbonate: oil molar ratio = 6:1; 10 wt.% catalyst amount; 200W	Batch	86.61	256

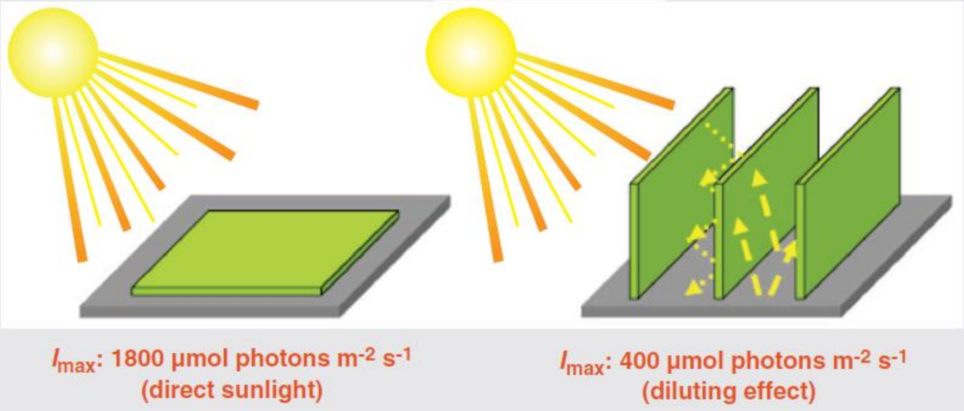
The potential for biodiesel production from WCO is still limited, as the estimation of WCO generation can meet less than 30% of the world's biodiesel demand.[174] Therefore, the remaining amounts of biodiesel production need to be provided from other feedstocks.

1.5.3 Microalgae

Algae are another sustainable source of triglycerides. Algae are a large and diverse group of simple aquatic organisms that are mostly microscopic. ~~Microalgae are unicellular photosynthetic microorganisms that are deficient of cell types found in land plants.[4] Microalgae are photosynthetic microorganisms capable of converting sunlight, atmospheric CO_2 and wastewater into a variety of high energy molecules, including fatty acids (FA) and triacylglycerols (TAGs), the major feedstock used for biodiesel or FAME production.[257,258] Microalgae, also called third generation fuel, are considered one of the most promising feedstocks for biofuels.[259] The productivity of these photosynthetic microorganisms in converting CO_2 into carbon-rich lipids greatly exceeds that of agricultural oleaginous crops ($6.9*10^4$ cells/mL/h)[260], without competing for arable land and food crops.[261] The microalgae efficiency is also high, with biofuel yields up to 12000L/ha, which is much higher than terrestrial plants.[262] Microalgae can be grown on fresh or salt water, and even in a wastewater environment.[258] Microalgae represent a large~~

~~number of different photosynthesis species in both heterotrophic and autotrophic. The autotrophic microalgae species can fix inorganic carbon from CO_2, to form mainly carbohydrates, in which the carbohydrate can be converted into fermentable sugars for further conversion to bioethanol by selected microbial.[263] The heterotrophic microalgae species take up organic molecules and convert into mainly lipids, which are used in biodiesel production.[4] Phototrophic cultivation is the most common way of microalgae cultivation. The photosynthesis required two sources, which are solar radiation and carbon sources. The light is needed for carbon fixation and for increasing the growth rate of microalgae, resulted in high production of microalgae biomass. However, low intensity of light will inhibit the photosynthesis process. The carbon source is a vital for the growth of microalgae.[260] The higher concentration of carbon will result in faster growth rate and higher biomass productivity, but has the tendency to reduce the pH in the cultivation medium that may inhibit the growth of microalgae. Concentration of nitrogen and carbon to nitrogen ratio are also crucial to determine the growth rate of microalgae. As a result, selecting right cultivation system for microalgae biofuels production highly depends on the type of microalgae strain, applied technology, and biological conversion process.[4] Microalgae are known to produce high oil and biomass yields, can be grown on non-arable land and do not compete with common food resources. Recent advances present opportunities to develop microalgae as feedstock for biodiesel production in a sustainable and economical way within the next 10 to 15 years.[264,265] Microalgae can be cultivated from several aqueous systems such as open ponds, closed pounds, photo-bioreactors, or hybrid photo-reactors. The most common cultivation technologies are ponds and photo-bioreactors. Microalgae cultivation systems are usually classified into open or closed systems depending on their cultivation conditions. In open systems, microalgae are cultivated in open area environment such as ponds, lagoons, deep channels, and others. In closed systems, microalgae are cultivated in vessels with transparent wall and exposed under sunlight or artificial radiation to facilitate photosynthesis.[266] Among the different types of open ponds used for microalgae cultivation, such as raceway, shallow ponds, or circular ponds, the most common open system is raceway pond due to its potential to produce large quantity of microalgae. However, the problem with raceway pond system is the difficulty to control the surrounding environment condition, like temperature and pressure, which will directly affect the microalgae biomass productivity. The highest~~

~~biomass production rate obtained with raceway pond are 60-100mg/L/day of dry microalgae weight.[267] Photo-bioreactors technologies are closed systems designed to overcome the problems associated with open pond system. Photo-bioreactors will allow the cultivating of single species microalgae for longer period than open raceways and able to produce large quantity of microalgae biomass. Photo-bioreactors are more practical and productive in order to cultivate microalgae due to the effective controlled conditions cultivation (pH, temperature,~~ ~~CO_2~~ ~~concentration, etc.) and the reduction of the risk of contamination. The two main factors that affect reactor efficiency are the total illuminated surface area of the reactor and culture volume. The lower these values, the more efficient and cost effective the reactor. In order to reduce the light intensity at the reactor surface, loading the reactor units vertically could be an efficient way as shown in **Figure 9** and **Figure 10**.[264,268] Narrow spacing in the panels minimizes loss of light to the ground surface.~~



~~**Figure 9:** The principle of light dilution. The light intensity (I), striking closely spaced vertical panels, is much lower than the intensity striking a horizontal reactor on the same surface.~~ (our emphasis is not on algae cultivation and harvesting rather on the conversion so please delete these aspects) and focus more on the catalytic conversion of algae to biodiesel

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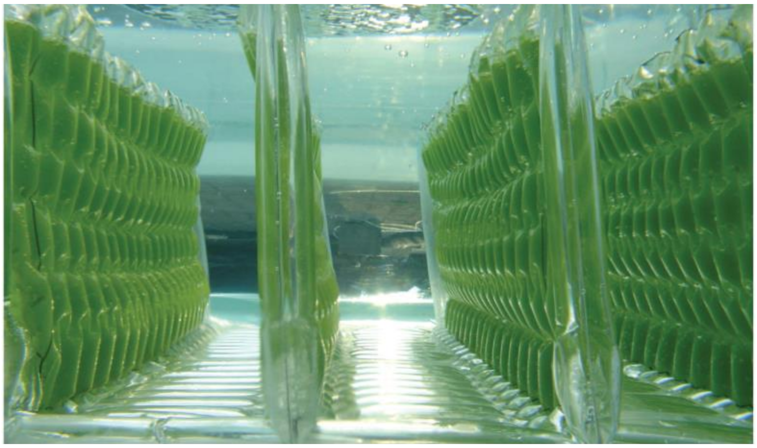
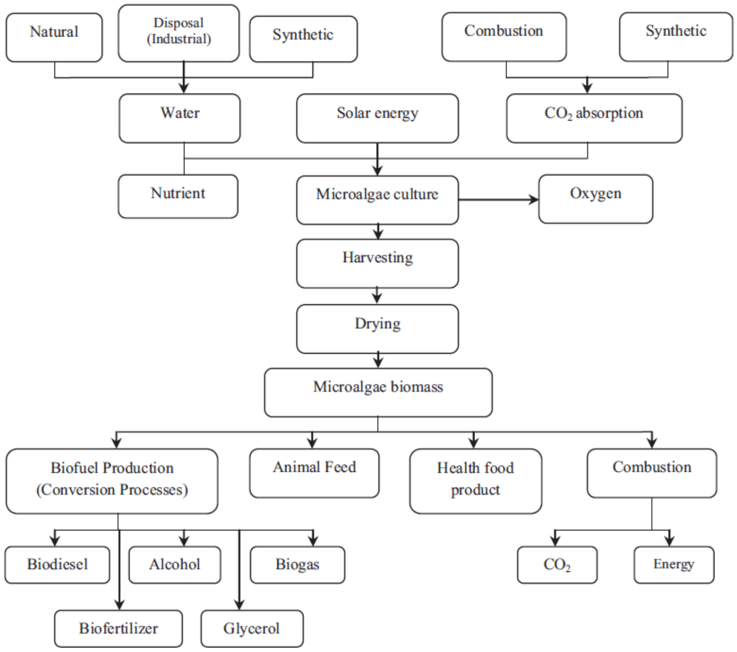


~~**Figure10 :** Development of low-cost photo-bioreactors. Flat-panel reactors from Proviron, Belgium~~

~~Open raceway ponds are more productive per unit illuminated area than flat-plate reactors, but they require six times more volume than closed photo-bioreactors to produce the same amount of algae.[262] However, capital costs are much higher than open systems.[269] Microalgae have the highest growth rates among all the photosynthetic organisms.[270] Approximately 46 tons of oil/hectare/year can be produced from diatom algae.[271] These characteristics make them an attractive source of biodiesel production. However, microalgae have low biomass concentrations and need controlled environment with specific physical and chemical conditions for an optimal cultivation and harvesting.[270] Therefore, the cultivation of microalgae remain costly in comparison with common crops used for biodiesel production.~~

Algal biomass contains macromolecular proteins, polysaccharides, and lipids, along with inorganic components.[272] Only the lipid contents are extracted and generally targeted to produce biodiesel whereas carbohydrates are extracted to produce ethanol.

Biodiesel production from microalgae is mainly divided into 3 main stages: a) cultivation, b) harvesting, and c) lipid extraction and transesterification for biodiesel production. ~~A process flow of biofuels derived from microalgae biomass is shown in **Figure 11**~~.[4]



~~**Figure 11** : Flow diagram of biofuels production from microalgae~~ (delete the flow chart)

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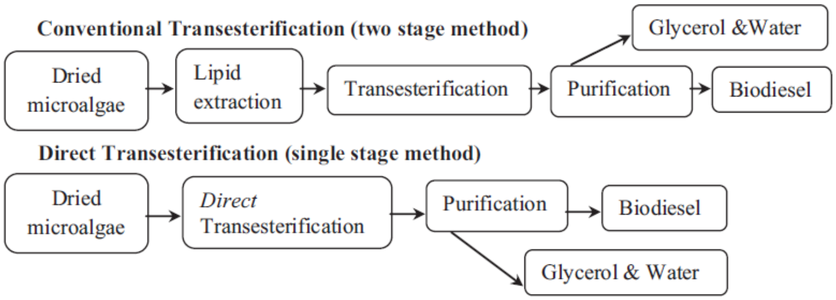
~~Harvesting process is usually costly and accounted about 20-30% of total biofuels production cost. Therefore, it is important to choose appropriate harvesting methods to minimize the overall cost. The harvesting methods are highly dependent on the type of microalgae, cells density and desired target products. Algal cultures are very dilute, usually around 1% for autotrophic growth up to 10% for heterotrophic growth, and dewatering is necessary prior to biomass use.[258] Harvesting of microalgae can be divided into two step process. The first step is bulk harvesting where biomass is separated from the bulk culture, such as flocculation, flotation or sedimentation. The second step is to concentrate the biomass slurry via techniques like centrifugation and filtration.[273,274] Dehydration process is an immediate process after harvesting which is important for dried microalgae biomass production. The most common drying methods that are usually used are sun drying, low-pressure shelf drying and, freeze-drying (lyophilized). Sun drying process is the cheapest among all dehydration methods, but requires large surfaces area and very time consuming. Consequently, harvesting and dewatering methodologies require high energy consumption,~~

~~such as centrifugation and tangential filtration, representing until 57% of the final biomass cost, and compromise the overall net energy ratio.~~[~~258~~]

The lipids produced by microalgae are usually between 12 and 22 carbons long and can be saturated or unsaturated. For biodiesel production, saturated fatty acids between 12 and 16 carbons are desirable.[258] The lipid content of microalgae is dependent on the microalgae species and cultivation conditions. This means that the microalgae could be tailored such that the lipid content is maximum leading to higher yields of biodiesel. ~~Microalgae have the capability to grow rapidly and could accumulate large amounts of natural lipid, which is approximately between 20 and 70 % of lipid content from the dry biomass.~~[~~4~~] ~~The growth of rich lipid microalgae requires a long period of microalgae starvation of nitrogen, rising the energy consumption during the cultivation step. Faced with stresses such as nutrient deprivation, algae store chemical energy in the form of oils such as neutral lipids or triglycerides.~~[~~264~~]

The usual method for extracting lipids from the whole algae biomass consists of mixing the microalgae with an organic solvent or adopt other methods like the use of a functional membrane coated with a cationic polymer[275] or the use of ionic liquids.[276] This strategy of extracting the lipids from the rest of the components of algae is cumbersome and increase the operation cost. Thus strategies for the insitu isolation of lipids and their conversion to biodiesel are developed (add references). ~~Due to the low performance of aliphatic alcohols such as methanol as lipids extractants from microalgae, the incorporation of a co-solvent like chloroform could accelerate lipids extraction; improve the mass transfer as well as the performance of direct transesterification process. Extracted microalgae lipids are then converted to biodiesel by transesterification using alcohol and catalyst. Recently, a combination of lipid extraction and biodiesel conversion in a one step process, called direct (in-situ) transesterification, was reported.~~[~~149~~] ~~This methodology simplifies the production process and improves the biodiesel yield compared to conventional extraction because of the elimination of a lipid extraction step that involves lipid loss and reduces the number of stages in the biodiesel production process as shown in~~ ~~**Figure 12**.~~[~~4~~] ~~Direct transesterification has several advantages, like the cell disruption, lipid extraction and transesterification reaction in single step and was proven to be favorable over conventional methods.~~[~~277~~] ~~The conventional two-step preparation of biodiesel from microalgae display several disadvantages in comparison to~~ ~~*in situ*~~ ~~transesterification,~~

~~including the operation complexity, a longer process time, a high energy consumption and a relatively high cost, which restricted the commercial production of biodiesel from microalgae. Higher biodiesel yield is obtained in direct transesterification than in a two stages process.[17,20] Moreover, direct transesterification provides energy-efficient and economical routes for biodiesel production.[279]~~



~~**Figure 12:** Conventional transesterification and direct transesterification method~~ (delete)

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Transesterification of microalgal oils for biodiesel production has been carried out by both homogeneous and heterogeneous catalysis. A brief summary, pros, and cons of the state of the art processes for the conversion of microalgal lipids from different species into biodiesel are presented in **Table 3**.

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Table 3: State of the strategies for the production of biodiesel from microalgae

Catalyst	**Micro algae species - oil content**	**Reaction conditions (Lipid extraction method; Transesterification reaction: heating source strategy; temperature; time; catalyst amount; MeOH : oil molar ratio)**	**Biodiesel yield (wt. %)**	**Reference**
H_2SO_4	*Chlorella* algae – 15 wt.%	*In situ* transesterification: conventional heating; 60°C; **4 h**; 20 wt.%; 801:1	98.44	40
H_2SO_4	*Chlorella pyrenoidosa* - 20 wt.%	Hexane; MW irradiation; 90°C; **30 min**.; 3 vol. %; 8:1	86.74	280

H_2SO_4	*Chlorella sp.*- 12 wt.%	*In situ* transesterification: conventional heating; 60°C; **19 h**.; catalyst : lipid molar ratio = 0.35:1; 600:1	92	281
H_2SO_4	*Enteromorpha compressa*	Ultrasonic irradiation; T = 65°C; **1h30**; 10 wt.% catalyst amount; MeOH: algal biomass ratio = 5.5:1; 30 vol% of THF as a co-solvent	98.89	282
H_2SO_4	*Nannochloropsis oceanica*	Conventional method; T = 95°C; **1h30**; 0.3 g H_2SO_4; $CHCl_3$:MeOH = 1:2 (v/v)	91.1	283
KOH	*Chlorella vulgaris*	MW irradiation; T = 60°C; **15 min**.; 1.5 wt.% catalyst amount; MeOH: lipid molar ratio = 10:1	84.01	284
KOH	Inoculum *Nannochloropsis sp.,*	MW irradiation; T = 60°C; **4 min.**; 2 wt.% catalyst amount; MeOH : algae ratio = 12:1 (wt./vol)	80.13	285
NaOH	*Chlorella sp.*	MW irradiation; 350 W; **6 min**.; 2 wt.% catalyst amount; EtOH: algae molar ratio = 500:1	96.2	286
NaOH	*Chlorella vulgaris*	Lipid extraction: Folch method; incubator shaker; T = 60°C; **10 min.**; 96 wt.% catalyst amount; MeOH : oil molar ratio = 925:1	96	287
NaOH	*Chlorella vulgaris ESP-31*- 26.3 wt.%	Conventional method; T = 45°C; **15 min.**; 0.5 wt% catalyst amount; hexane/ MeOH/ sample = 12 mL/8 mL/2 g	97.2	288
NaOH	*Nannochloropsis sp.*	Conventional method; T = 60°C; **75 min**.; catalyst : lipid molar ratio of 0.15:1; MeOH: lipid molar ratio = 600:1	77.6	289
NaOH	*Nannochloropsis sp.* – 38.31 wt.%	Lipid extraction: MW irradiation (5 min., 65°C) using MeOH – hexane in the ratio of 1:2 (% v/v) as solvent; MW irradiation; T = 65°C; **10 min.**; 0.2 g of catalyst; MeOH : hexane (1:1 v/v)	86.41	290

$Ca(OCH_3)_2$	*Nannochloropsis oculata*	Conventional method; 80°C; **3 h**.; 3 wt.% catalyst amount; MeOH : oil molar ratio= 30 :1	99	[291]
$CaMgO/Al_2O_3$	*Chlorella protothecoides*	Ultrasonic irradiation (5 min.) using Bligh and Dyer method; Microreactor; 60°C; **3 h**; 10 wt.%; 60:1	85.3	[292]
CaO/Al_2O_3	*Nannochloropsis oculata*	Hexane; conventional heating; 50°C; **4 h**; 2 wt.%; 30:1	97.5	[293]
CH_3COCl	*Nannochloropsis gaditana* - 11.1 wt%	Bligh and Dyer method; hydrothermal; 100°C; **1h45**; 5 % (v/v); 171.1:1 (mL.g-^{1})	100	[294]
Free lipase NS81006 and Novozym 435	*Chlorella protothecoides*	Bligh and Dyer method; conventional heating; 45°C; **6 h**; 5 wt.%; 5:1	97	[295]
Ion exchange resins	*Nannochloropsis gaditana* – 42 wt.%	Hydrothermal method; T = 100°C; **4 h**; 0.8 wt.% catalyst amount; MeOH: lipid weight ratio = 40:1	90	[296]
KF/CaO	*Chlorella vulgaris* – 21.13 wt. %	Combination of ultrasound and MW irradiation; T = 60°C; **45 min**.; 12 wt.% catalyst amount; MeOH: lipid molar ratio = 8:1	93.07	[297]
Li_4SiO_4	Dry microalgae powder - 30 wt.%	Lipid extraction: MW irradiation (40 min.) using n-hexane / iso-propanol (2:1) as solvent; conventional heating; T = 68°C; **4 h**; 3 wt.% catalyst amount; MeOH : oil molar ratio = 18:1	76.2	[298]
Mg/Al hydrotalcites	*Chlorella protothecoides* CS-41	Conventional method; T = 66°C; **4 h**; 1.7 wt.% catalyst amount; MeOH: lipid molar ratio = 6.4:1	90.3	[299]
Mg–Fe LDH	*Chlorella protothecoides CS-41*	Conventional method; T = 60°C; **1.5 h**.; 2 wt.% catalyst amount; MeOH : oil molar ratio= 6:1	88	[300]

Mg-Zr	*Nannochloropsis sp.*- 46.43 wt.%	Conventional method; T = 65°C; **4 h**; 10 wt.% catalyst amount; MeOH: lipid weight ratio = 10:1; volume ratio MeOH : CH_2Cl_2 = 2:1	28	301
Novozyme 435	*Aurantiochytrium sp.* KRS101- 56.8 wt.%	Conventional method; T = 50°C; **12 h**.; enzyme to biomass ratio of 30% (w/w); DMC to biomass ratio of 5:1 (v/w)	89.5	302
Rhizopus oryzae lipase	*Nannochloropsis gaditana*	Incubation; T = 35°C; **72 h**.; 70 wt% lipase/lipid ratio; MeOH: lipid molar ratio = 11:1; 10 mL t-butanol/g Lipid.	83	303
Sand dollar	*Nannochloropsis oculata*	Conventional method; T = 60°C; **3 h**.; 3 wt.% catalyst amount; MeOH : oil = 30:1	90	304
SrO	*Nannochloropsis sp.*	MW irradiation; T = 60°C; **5 min.**; 30 wt.% catalyst amount; $CHCl_3$:MeOH (1:2 v/v)	99.9	149
SrO/SiO_2	*Chlorella vulgaris ESP-31*- 22.7 wt.%	Conventional method; T = 45°C; **6 h**.; 5.5 wt.% catalyst amount; MeOH : oil molar ratio= 424:1	81.8	155
TiO_2-CaO	*Hydrodictyon reticulatum* - 41.4 wt.%	Conventional method; TiO_2-CaO molar ratio 0.25T = 50°C; **8.5 h**.; 5.12 wt.% catalyst amount; MeOH : oil molar ratio= 15.68:1	86.4	305
Waste shell of Angel Wing	*Nannochloropsis Oculata* – 29.2 wt.%	Lipid extraction: ultrasonic irradiation (5 min.) using Bligh and Dyer method; conventional heating; T = 65°C; **1 h**; 9 wt.% catalyst amount; MeOH : oil molar ratio = 150:1	84.11	306
WO_3/ZrO_2	*Scenedesmus sp.*- 29 wt.%	Ultrasonic irradiation; Lipid extraction solvent: hexane; T = 50°C; **20 min.**; 4 wt.% catalyst amount; MeOH : oil molar ratio = 60:1	71.37	307

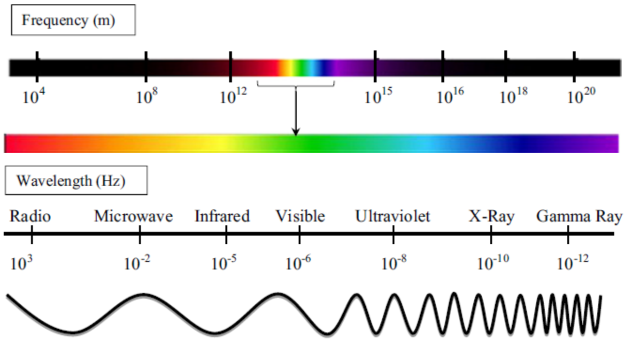
Although microalgae have high potential to produce biodiesel with high conversion and replace the current fossil fuels, challenges to commercialize the production at large scale need to be overcome. The main challenge is the cost for the biodiesel production from microalgae that is high. Low cost with high efficient and low contamination harvesting techniques are non-negligible obstacles faced by the current stages of microalgae cultivation. Extracting the oil from the dried microalgae is another challenge; even though the microalgae are recognized of high lipid contents, but oil extraction is not as predicted.

Beside or because of the production limitations mentioned above, in a practical point of view, if, for example, all transport fuels were to be replaced by biodiesel in Europe, the scale of microalgae production needs to increase at least three orders of magnitude, with a decrease in the cost of production by a factor of 10. Consequently, large scale of biodiesel production from microalgae is challenging in both economic viability and energetic balance.[259] Therefore, the main objective ~~targeted~~ in this arena is to reduce production costs and energy requirements while maximizing lipid productivity and increasing the biomass value by making use of all algal biomass components. For cost, energy reduction and maximization of lipid productivity cell properties, bioreactor design, efficiency in supply, and use of nutrients and resources need to be improved, and to make use of all biomass ingredients, a biorefinery infrastructure needs to be established in addition to the development of innovative strategies for the single step catalystic conversion of algal biomass to biodeisel .[264]

1.6 Microwave irradiation as effective heating source for biodiesel production

1.6.1 Principles of microwave irradiation

Microwave (MW) irradiation is a potential technique for accelerating chemical reactions by several orders of magnitude. ~~MW is a non-ionizing radiation, specifically electromagnetic waves that can be transmitted, reflected, or absorbed. MW irradiation is an electromagnetic irradiation in the range of wavelengths from 0.01 to 1 m and corresponding frequency range of 0.3 to 300 GHz (**Figure 13**).~~[308] Generally, most of the microwaves irradiations operate at a frequency of 2.45 GHz.



~~**Figure 13:** The electromagnetic spectrum~~ (delete the figure; this is present in several text books)

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~~A MW heating process can be divided into two stages: the input electrical energy is first converted to MW energy, and then the microwave energy, in the form of electromagnetic waves, is absorbed by dielectric media and converted to effective heat. A macroscopic consequence of the whole process is the rising temperature of the heating media.[309] Microwaves, as an energy source, produce heat by the interaction of the electric field of radiation with the materials at molecular level without altering the molecular structure, due to their low energy content.[310]~~ The microwave-absorption ability of a certain material depends on its dielectric properties, including dielectric constant and dielectric dissipation factor, which yet may be varying with temperature and microwave frequency.[309] MW have a selective heating function, depending on the polarity of the heated material. Non-polar molecules are inert in their contact with MW electric fields while polar molecules with high dielectric constant and low molecular weight can selectively absorb MW energy.[311] This selective heating of certain compounds may lead to the formation of microzones with a temperature much higher than the overall recorded temperature of the reaction bulk mixture. These high temperature microzones are called “hot spots” (above 1200° C).[312] Thus, a rapid enhancement of temperature is produced which may lead to an increase in the acceleration of chemical reaction rate.[313] ~~Dielectric properties are defined as frequency of applied electric field of the MW and temperature dependent of the sample. The dielectric loss factor is related to the electromagnetic energy dissipation in the material. Interaction between MW energy and the mixture occurs through two major mechanisms: dipolar rotation and ionic conduction.[314] These mechanisms by which MW energy can interact~~

~~with the material, depending if the material possesses or not a dipole moment at the molecular level. If a molecule, especially the solvent, possesses a dipole moment, then, the interaction between the material and the applied electrical field generated by the microwaves during irradiation will lead to the heating of the material due to its net polarization. Because of the dipole moment, the molecules will be reoriented and aligned with the electric field through continuous oscillations of the dipole moment molecules, resulting in friction, and thus, heat. In ionic conduction, the electric field of the MW will generate the movement of the ions from side to side through the dissolved charged particles. When the electric field direction changes, the larger ions dissipate their kinetic energy as heat as they slow down and change direction via friction at molecular levels. Consequently, collisions and friction between the moving molecules is created and generated heat again. In addition, because of the molecular collisions at high frequency, the molecules do not have enough time to relax and the generated heat can be, for short times, much greater than the overall temperature of the bulk reaction mixture, obtaining instantaneous localized superheating. Both mechanisms contribute to localized superheating leading to high temperature and pressure gradients. At the same time, the probability of molecular encounters increases by accelerating the molecular/ionic movement, which leads to increased reaction rates.[315] Nevertheless, the mechanisms of interaction and their efficiency in term of heat production are strongly dependent on the structure of materials, type and strength of chemical bonds between atoms.[316] MW acceleration of chemicals is strongly dependent on the reaction mixture or the solvent having a dipole moment.~~

~~The electromagnetic energy (average power) absorbed by the volume V of a dielectric material, which is converted into heat, is obtained from Maxwell's equations, and is given by equation 1:~~

~~$P = \omega \varepsilon_0 \varepsilon''_{ef} E^2_{rms} V$ (eq.1)~~

~~Where P is the power (W) absorbed by the material,~~

~~ε_0 is the vacuum permittivity (=8.85 *10^{-12} F/m),~~

~~ε''_{ef} is the dielectric loss factor – the thermal conversion of electromagnetic energy~~

~~E^2_{rms} is the root mean square of the applied oscillating electrical field (V/m) with frequency~~

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~~f ($\omega = 2\pi f$) over the volume V (m^3) of the sample.~~

~~Another factor that can be used to explain the dielectric heating is the loss tangent, which depends~~

~~on relaxation time (τ), as is defined as: $\tan\delta = \varepsilon''_{eff}/\varepsilon'$ (eq. 2) (ε' is the relative dielectric constant – the storage of electromagnetic energy in the material) and is an important parameter in describing the dielectric response of materials in terms of, for example, the penetration depth (Dp), the distance at which the amplitude of the electrical field is restrained to 1/e = 0.369 of its initial value at the surface of the material.[314] The microwave absorption ability of a material is directly proportional to its dissipation factor.~~

1.6.2 Microwave assisted transesterification reaction

MW efficiency may relate to the ionic nature of the transition state of the transesterification reaction. The mixture contains fatty acid and alcohol, which have polar and ionic components, and hence MW irradiation can play an active role in heating the reactants to the required temperature quickly and efficiently. Therefore, MW is coupling with the reacting molecules and causing the acceleration of the chemical reaction.[316] The microwave interaction with the reaction compounds (triglycerides and methanol) results in a large reduction of activation energy due to an increased dipolar polarization phenomenon.[279] Likewise, methanol is known to be very active under a specific frequency of the microwave, which increases its collision probability with other reactant. For a reaction rate, $K = A \times e^{-\Delta G/RT}$ (Arrhenius equation describing the reaction rate by two factors: ΔG, which is Gibbs free energy of activation and A, which is the pre-exponential factor), the constant A, which describes the molecular mobility, is increased under microwave irradiation due to the increased vibration frequency of the molecules at the reaction interface.[317] Methanol is more polar than other alcohols because of its smaller molecular size and the shorter distance between the poles, which allows it to rotate and realign faster. Furthermore, the smaller molecules also have a higher dipole moment.[318] Presence of methanol in transesterification reaction helps also to decrease catalyst requirement to less than ten-fold under MW irradiation.[315] However, triglycerides, as the non-polar materials, are unaffected by the variations in frequency and temperature. In addition, the MW radiation can also break the immiscible two-phase interface between triglycerides and methanol. Therefore, under microwave heating, the kinetic reaction degree of methanol will be more intense than the conventional heating, which leads to the increase of the reaction order.[319] ~~Because the mixture of oil, methanol, and catalyst contains both polar and ionic components, rapid heating is observed upon MW irradiation, and because the energy interacts with the sample on a molecular level, very efficient heating can be obtained. In addition, because the MW photons interact with the molecules at a very fast rate, the molecules do not have time to relax and the heat generated can be, for short times, much greater than the overall recorded temperature of the bulk reaction mixture. In essence, there will be instantaneous localized superheating. The mass transfer resistance is counteracted by high reaction temperature caused by MW in the case of heterogeneous catalyst. Asakuma et al.[320] further attributed the positive effect of MW on transesterification to factors other than heating efficiency. Firstly, the conformal isomer of the triglyceride has a lower dipolar moment under MW irradiation and consequently a lower activation energy. Secondly, the vibration around the C=O bond is stronger under MW irradiation, thereby facilitating the reaction. Finally, the conformal isomer has a planar structure, which is more easily accessible for the nucleophile attack.~~

MW heating compares very favorably over conventional methods where heating can be relatively slow and inefficient because transferring energy into a sample depends upon convection currents, thermal conductivity, and radiation of heat energy from the surfaces of the reactor to the reactants; it is, therefore, a slow and inefficient heat transfer of the reaction mixture. The reason for the short reaction time under MW is due to the higher temperature obtained under MW of the super-heated liquids.[173]

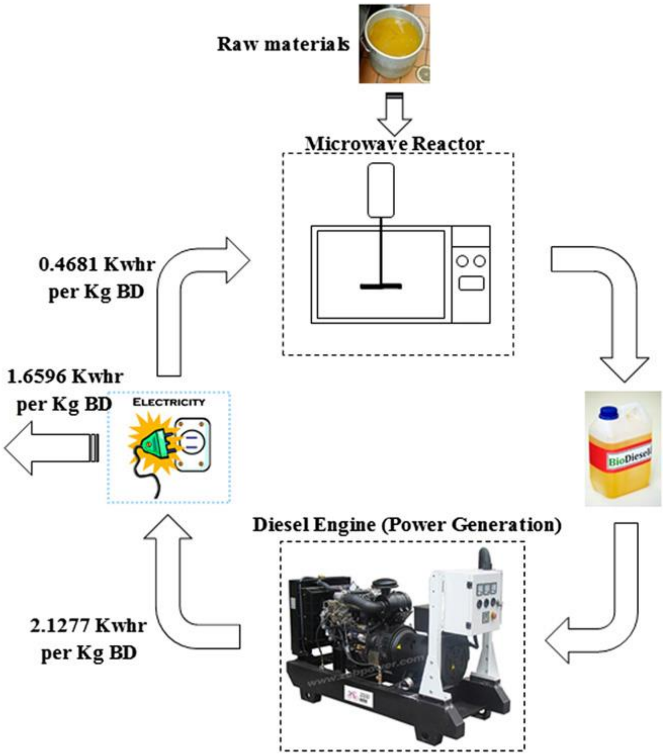
~~MW irradiation is commonly used for accelerating and enhancing chemical reactions because it provides the energy directly to the reactant, reducing the reaction time from hours to minutes or even a few seconds in some cases.[124] When 30-60 s were sufficient for MW heating, 30-60 min were required for conventional heating to achieve comparable biodiesel yields. This large difference in reaction time can be attributed to the limitations of conventional heating in which the energy is first utilized to increase the temperature of the reaction vessel and the higher temperature of the reaction vessel results in higher heat losses to the ambient.[321] Therefore, heat transfer is more effective compared to conventional heating and the reaction can be completed in a much shorter time, using lower oil/methanol ratio, and reducing drastically the energy consumption. The short reaction time is allowed due to the higher temperatures achieved under MW irradiation,~~

~~which affected the formation of spatial hot spots at higher temperatures than would have occurred at the average temperatures observed under a conventional reaction. The reaction conversion is more dependent on the final temperature than the residence or reaction time. However, the temperature is significantly influenced by MW power, components absorption ability and residence time.[312] The decreasing rate of dielectric constant decays as the temperature rises, which is related to the kinetic energy of molecules. Therefore, the response to the changing electric field is faster, which increases the realignment process, enhancing the dipolar rotation of molecules and the dielectric constant of the material compared to lower temperature.[318]~~ Direct production of biodiesel from microalgae biomass of Nannochloropsis by MW and ultrasound radiation was reported by Koberg et al.[149] MW and ultrasound radiation with the aid of SrO catalyst were compared to identify the most effective technique. It was observed that a direct transesterification reaction using microwave irradiation resulted in a higher biodiesel yield of 37.1% in 5 min at 60 °C, while only 20.9% yield can be obtained in the same reaction time by using the sonication technique. Additionally, Cheng et al.[322] have reported that the kinetic rate of converting wet microalgae into biodiesel via the two-step method using conventional heating is approximately six times slower than that via the one-step method using MW irradiation. Thus, MW irradiation is one of the best methods for reducing the reaction time and obtaining higher yields in the production of biodiesel. It enhances the speed of the reaction and makes the separation process easier in comparison to conventional heating.

1.6.3 Energy consumption of microwave-assisted biodiesel production

MW requires less energy input for heating compared with the conventional heating method. The conventional heating takes longer time for preheating and reaction, consuming tremendous energy, which depends on the thermal conductivities of the materials. In the microwave-assisted process, energy can penetrate within materials.[315] The energy required by the conventional method is found to be around 23 times greater than that by the MW irradiation.[321] Furthermore, Motasemi et al.[323] show that for the production of one kg biodiesel, 0.4681kWh electrical energy has been used in a simple MW-assisted biodiesel production system. On the other hand, according to Chauhan et al.[324] the brake specific fuel consumption, which measures the efficiency of an engine in case of biodiesel, was found to be about (average) 0.47 kg/kWh. As a result, an average of 2.1277 kWh electrical energy can be produced from one kg biodiesel, while production of one kg biodiesel needs only 0.4681 kWh electricity~~, as shown in **Figure 14**~~.[325] Thus, using MW-assisted production of biodiesel can save the energy significantly. ~~This system has the potential for production of 1.6596 kWh extra electrical energy per kg biodiesel, which it proves the sustainability of system. Consequently, the energy consumption is greatly reduced when using MW irradiation as heating source for transesterification reaction.[323]~~

~~Then, MW irradiation is an efficient heating method to strengthen the chemical reaction, improve the reaction rate, shorten the reaction time, and reduce significantly the energy consumption in comparison with conventional heating.~~



~~**Figure 14 :** Energy payback of microwave-assisted biodiesel production system~~

1.6.4 Microwave-assisted continuous flow process for biodiesel production

~~However, t~~The use of MW batch reactors for industrial production is limited due to the penetration depth of MW that is only few centimeters into the absorbing materials, which means that a homogeneous field of MW intensity is extremely difficult to achieve in large volume reactors. Depending on the dielectric properties of the liquid reaction mixture, the penetration depth is about 10^{-2} to 10^{-3} m and, therefore, the heating is dominated by convective heat-transfer at larger liquid volumes. Another limitation is the specific security measures that should be taken into account when MW is used at high intensities (power up to 5000 W), requiring sophisticated cooling systems, thereby increasing the complexity, cost, and size of the reactor.[326]

In order to move from laboratory to industrial scale, the extension of the MW-heating methodology to continuous-flow processing, as an alternative of the penetration depth issue, has been used in previous researches. Successful scale up of pharmaceutically relevant reaction in a commercial continuous flow microwave reactor (Flow SYNTH) resulting in the production rates of 1-6 L/h were reported. Substantial manufacture capability (processing of 30 kg raw material) was achieved.[327] Such microwave reactor has attracted attention in the synthesis of organic reactions, allowing scale-up and energy efficiency of the reaction.[328–332] Upscaling microwave technology to higher production scales, from multi-gram to kilogram scale, has become a major topic for industrial chemists. [333]

~~There are several reports in literature related to the use of continuous flow MW irradiation technique for the large-scale production of biodiesel from several feedstocks using conventional homogeneous catalysts like KOH and NaOH. For example, using a 9 mm diameter coiled tube in a household microwave and a flow rate of 19.8 L/h at an average outlet temperature of 78 °C with a maximal power of 800 W and NaOH as catalyst, Lertsathapornsuk et al. [188] investigated MW assisted continuous biodiesel production from waste frying palm oil. It has been reported that continuous conversion of waste frying palm oil to ethyl ester was 97% at ethanol to oil molar ratio of 12:1 with catalyst loading of 3% NaOH (in ethanol) and 30 s residence time. In addition, the energy consumption for MW assisted continuous transesterification process was about 269 kJ/L, while the energy consumption for conventional heating process was 799 kJ/L. Barnard et al.[316] studied the continuous-flow preparation of biodiesel from used vegetable oil using a commercially available multimode MW apparatus in a 4 L non-agitated continuous tank with a flow rate of 7.2 L/min and a 1:6 molar ratio of oil/alcohol. A 98.9 % conversion was obtained in 30 s at 50 °C using a maximum power of 1600 W in a large multimode microwave cavity. Energy consumption calculations suggest that the continuous-flow MW methodology for the transesterification reaction is more energy-efficient than using a conventional heated~~

~~apparatus. Quantitatively, the MW process has an energy requirement of 26.0 kJ/L of biodiesel as compared to 94.2 kJ/L required for the conventional mode of heating. Continuous-flow microwave-induced transesterification reaction conducted by Terigar et al. using a 2 L cylindrical Teflon beaker lead to a biodiesel yield as high as 99.3 % in 10 min at 73 °C using ethanol and 0.6 wt. % NaOH as catalyst from soybean and rice bran oil.[334] The reaction mixture was pumped into the microwave reactor at a constant flow rate of 100 mL/min and was pumped out using a peristaltic pump. Encinar et al. successfully converted soybean oil to biodiesel with a yield as high as 97 wt. % with 1.5 wt.% KOH in a Teflon tubing reactor of 150 mL coiled into the microwave oven. This oven is a household microwave, 700 W, which was modified with two holes at the top oven for inlet and outlet.[312] A 2,45 MHz microwave generator having a maximum power of 6 kW and a partially modified 10 L conventional stainless steel vessel by Kim et al. allowed an accelerated conversion of 95% in 5 min using KOH as catalyst.[335] Mohd et al.[187] studied the optimization of WCO transesterification in a continuous MW assisted reactor (CMAR) using sodium methoxide ($NaOCH_3$) as catalyst. The custom-built CMAR employed an integrated proportional integral derivative controller for accurate control of temperature and reactant flow rate. The reactor is connected to three tanks for storing the reactant and product. The feed flow rate is controlled using two solenoid metering pump. The optimum WCO conversion (97.13%) was found at 11.62: 1 methanol to oil molar ratio, 4.47 minutes of reaction time and 0.68 wt. % of catalyst loading at 720W of MW irradiation power. Finally, Choedkiatsakul et al.[336] got recently an ester content of 99.4% using a commercial FlowSynth microwave reactor for the continuous production of biodiesel from palm oil. Such improvement was obtained in 1.75 min residence time at a methanol to oil molar ratio of 12, MW heating power of 400 W, 70°C and 1 wt. % NaOH loading. The energy consumption of only 0.1167 kWh/L of biodiesel was required.~~

~~Therefore, ~~U~~u~~se of MW irradiation as heating source allow improvement of extraction and acceleration of chemical reactions such as those of hydrolysis and esterification as well as offering a fast and easy route to biodiesel production. Typical advantages include enhancement of the reaction rate and improvement in the separation process. Consequently, the most optimize heating source for biodiesel production was found to be the MW irradiation.[149]

The combination of MW-assisted heterogeneous catalysis and continuous processing may have strong industrial potential for FAME production.[124]

In our current research, we could successfully transform the batch MW irradiation process of biodiesel production to a continuous flow process overcoming the limitation of up scaling. This has opened a new avenue for up scaling and the possibility of developing a commercial process for biodiesel production is high.

1.7 Nanocatalytic technology for biodiesel production

The activity of the catalyst has been reported to be dependent on the particle size. Smaller catalyst particles, in the nanometer range, are expected to exhibit higher rate of reaction than micrometric ones, and consequently higher conversions of biodiesel due to increased external surface area to volume ratio. Nanocatalyst has high selectivity due to nano-dimensional pores on the surface. The nanoparticle tends also to reduce the diffusion limitations. Nanocomposites have gained attention in biomass conversion to chemicals and fuels, as they possess a large surface area with enhanced interaction between the reactant and catalyst.[337] Moreover, the nanometric size of the catalyst provides shorter paths to access active sites for molecules, which reduces the internal diffusion significantly.[338] For example, in contrast to bulk CaO, which is hardly active, nanocrystalline powder of this material are capable of producing biodiesel with 99% conversion of the triglyceride. In addition, this type of nanocatalyst has also shown good recycling characteristics lasting up to five reuses.[339] Tremendous researches were conducted this last decade to synthesize both acid and basic catalysts in nanometer size for transesterification reaction from edible and non-edible feedstocks, affording FAME conversion higher than 95% and reusability several times.[198,291,340–347] It was shown that to obtain similar biodiesel conversion, the amount of nanocatalyst required is only 30% of that of common catalysts, and additionally, the reaction is less affected by the moisture of the oil and not influenced by FAA content.[339,348,349] ~~Hsiao et al. have showed that use of CaO nanoparticles as catalyst improves the biodiesel conversion by more than 31 time compared to bulk CaO under same reaction conditions.[338,350] Moreover, extraction of oils from non-edible oils could be enhanced and accelerated by the use of catalysts having nanometric dimensions.[351,352] However, utilization of powdered catalyst in catalytic reactions is problematic because~~

~~powder form presents several disadvantages like high pressure drop, high mass/heat transfer, poor contact efficiency, and complex separation processes from the media.~~

~~The heterogeneous catalysts are generally in the form of powders with diameter ranging from nano- to micrometer. The volatility of nanomaterials involves possible health risks caused by inhalation of small particles as well as treatment issues. Utilization of powders in catalytic reactions renders their recovery and purification challenging, and energy intensive is needed for the subsequent separation operation. The separation processes represents more than half of the total investment in equipment for biodiesel production.[156] In addition, the active phase of the powdered catalyst may not be uniformly distributed on the support but rather form localized aggregates leading to low contact of active surface in the catalyst.~~

Thus, the efficiency of the catalyst and its feasibility at industrial scale might be improved by making use of the new inventions in the nanoscale materials. ~~Designing a catalyst on a support with millimetric dimension seems to be an appropriate solution to overcome problems associated with the powdered catalysts. The mechanical strength and shape of the catalyst is the key issue for the millimetric heterogeneous catalysts. Additionally, supported catalyst in spherical form can offer shape dependent advantages such as minimizing the abrasion of catalyst in the reaction environment. It is further highlighted that high mechanical strength is crucial for long term stability of catalyst. Therefore, easy handling, separation and reusability are the main strength which could response to select the spherical millimetric catalyst.[66] Moreover, such catalysts could be adapted for a catalytic bed system. Such technique doesn't require the separation of the catalyst at the end of the reaction process. The limiting step will be the deactivation of the catalyst. Therefore, the fabrication of structured catalyst with a support having a macroscopic form could be the most appropriate and optimal solution for industrial applications.~~

~~For an optimal design of the material support, several properties are required:~~

~~- Inertness: support materials should have no catalytic activity leading to undesirable side reactions.~~

~~- Stability at high temperature reactions and regeneration conditions.~~

~~- Shape, preferably, spherical in order to minimize the resistance to transport of reactants and products.~~

~~- Low cost.~~

~~Materials with low surface area are generally useful in supporting very active catalytic components in reactions where further side reactions may affect the activity and selectivity.[156]~~ Microwave based and sonochemical driven strategies offer simplified pathway for the production of new catalytic materials that revolutionaize the conversion of biomass to biofuels.

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~~1.7.1 Synthesis of nanomaterials under microwave irradiation~~

~~MW-assisted chemical reactions have shown superiority over other synthetic techniques in the fields of organic, inorganic, and analytical chemistry.[317] As compared to conventional synthetic methods, use of MW heating processes showed a dramatic reduction of reaction times, increased product yields, and a higher purity of products because of reducing unwanted side reactions. The reduction of heating time during the synthesis process is due to an extremely rapid kinetics of crystallization (one to two orders of magnitude) and to the formation of novel or metastable phases.[353] With no direct contact between the chemical reactants and the energy source, MW-assisted chemistry is energy efficient, and enables rapid optimization of procedures.[354] MW provides uniform heating of reagents, solvents, and products. This homogeneous MW heating also provides uniform nucleation and growth conditions, leading to uniform nanomaterials with small sizes. Due to rapid and homogeneous MW heating, a better crystallinity can be obtained.[355] Another thermal effect specific to MW irradiation is the formation of hot spot: when some solids heated by MW are involved in the reaction system, hot spots are created on the solid liquid surfaces. The uniform formation of hot spots also accelerate the reduction of metal precursors and the nucleation of the metal cluster, leading to uniform nanostructures with small sizes. In recent years, MW-assisted synthesis has established as a modern way of producing different nanomaterials in order to influence positively both size distribution and material properties. Therefore, the use of MW-assisted synthesis offers unique opportunities in the generation of nanomaterials of uniformly small size, which is not easily achievable via other synthesis techniques. The rapid consumption of starting materials in kinetically driven reactions reduces the formation of agglomerates in MW-assisted methods for nanomaterials with narrow size distribution. In the general synthesis of nanoparticles via a bottom-up approach, the reduction of inorganic salts and their subsequent capping is the common procedure.[356] The use of MW has already been demonstrated as well to be a~~

~~suitable deposition technique for anchoring NPs on solid supports, enabling homogeneous dispersion of the NPs on the support.[357–360] H_2O is the most commonly used solvent for the synthesis of inorganic nanostructures. In the case of MW-assisted preparation of nanostructures in aqueous solution, polar molecules such as H_2O try to orientate with the electric field, in the MW frequency range. When dipolar molecules try to re-orientate with respect to an alternating electric field, they lose energy in the form of heat by molecular friction.[361] Tuval et al.[360] suggested that coating under MW irradiation might be obtained for substrates that show high slope in the temperature–time plots, which are referred to as 'thermal runaways'. This phenomenon, where solids are heated to very high temperatures in a very short time, would create hotspots on their surfaces. At these hotspots, local reactions can occur, leading to the formation of NPs that will eventually be deposited on their surfaces. Using MW irradiation as heating source, it is possible to synthesize NPs with exact parameter control in a short time and change particle properties and particle size as required. Moreover, these last decades, Nps synthesis in large-scale process was able using MW-assisted continuous flow process method, enabling scale of NPs yield from grams to kilograms.[353,362,363] Constant conditions, which can be easily tuned under MW, are crucial during nucleation and nanomaterial growth and augment the reaction rate.~~

~~1.7.2 Synthesis of nanomaterials using sonochemical technique~~

~~Ultrasound has proven to be a very useful tool in enhancing the reaction rates in a variety of reacting systems. Acoustic cavitation is the physical phenomenon responsible for the sonochemical process. Ultrasound is defined as sound of a frequency beyond that to which the human ear can respond. The normal range of hearing is between 16 Hz and about 18 kHz and ultrasound is generally considered to lie between 20 kHz to beyond 10 MHz like any sound wave, ultrasound alternately compresses and stretches the molecular spacing of the medium through which it passes, causing a series of compression cycles.[364] The main event in sonochemistry is the creation, growth, and collapse of a bubble formed in the liquid. The stage leading to the growth of the bubble occurs through the diffusion of solute vapour into the volume of the bubble. The last stage is the collapse of the bubble, which occurs when a large negative pressure gradient is applied to the liquid so that the distance between the molecules exceeds the critical molecular distance necessary to hold the liquid intact, the liquid will break down and voids (cavities) will be created, i.e., cavitation bub-~~

~~bles will form.[365] During the collapse of bubble, very high temperatures (5000–25,000 K)[366] are obtained/reached causing the breaking of chemical bonds. Since this collapse occurs in less than a nanosecond, very high cooling rates (in excess of 1011 K/s) are also obtained. This high cooling rate hinders the organization and crystallization of the products. The formation of nanostructures is the result of the fast kinetics which does not permit the growth of the nuclei. In each collapsing bubble, a few nucleation centres, whose growth is limited by the short collapse, are formed. If, in contrast, the precursor is a non-volatile compound, the reaction occurs in a 200 nm ring surrounding the collapsing bubble.[367] The temperature in this ring is approximately 1900 °C[368], which is lower than the temperature inside the collapsing bubble, but higher than the temperature of the bulk. In almost of the sonochemical reactions leading to inorganic products, nanomaterials were obtained. They vary in size, shape, structure, and in their solid phase (amorphous or crystalline). But, these reactions were always nanometric size.~~

2. Research Goals

2.1. Research importance and major goal

~~The demand for alternate energy sources is increasing exponentially. Population explosion and depleting fossil fuel reserves prompt vigorous research into alternate fuel sources. Transportation section is currently and solely dependent on fossil fuels like petrol and diesel. The reserves are on the verge of exhaustion. Alternate fuels are necessary for meeting the demands for transportation applications. Biodiesel, a biofuel, is an alternative to fossil fuels and an immediate substitute for the currently used transportation fuels. Biodiesel is considered as the less expensive renewable energy resource. Moreover, its use does not require major modification in the physical structure of the current transportation vehicles. However, the industrialization process for biodiesel production remains a challenge due to the high production cost compared to petroleum. Despite encouraging research that has been conducted during the last decade to optimize the production process of biodiesel using non-edible feedstock instead of edible ones, by decreasing the process time from several hours to several seconds, and by decreasing the energy consumption of the process, these processes could not be up-scaled and the catalyst cost remained expensive. The present research is aimed at solving the above specified problems with~~

~~specific research targets and objectives specified below.~~ The main goal of this research is to develop a large scale utility for the sustainable and demand based production of biodiesel. Towards fulfilling this goal, a continuous flow microwave irradiation process is exploited for the conversion of waste cooking oil into biodiesel. The potential of microalgae as promising feedstock for is also examined. Another main goal of this study is to design innovative solid based catalysts for the conversion of microalgae and waste cooking oil into biodiesel.

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2.2. Minor goals

2.2.1 Screening of feedstock based on cost as well as feasibility ~~of~~ forconversion to biodiesel in large scale

~~The replacement of fossil fuel with biodiesel is feasible only if it encounters two basic requirements: first, is its easy availability and environmentally adoptability, and second being economically reasonable.~~ The price of biodiesel mainly depends on the cost of feedstocks, which makes up 70–95% of the total production cost.[157] As much as possible, the biodiesel feedstock should fulfil two requirements for production of biodiesel; these are low production costs and large production scale. Actually, most of industrial biodiesel production is made from edibles feedstock~~s~~. However, since vegetable oils are vital constituents of human food consumption and their limited availability can lead to an increase in price of the oil in the market, which will obviously increase also the price of biodiesel. ~~Moreover, the viability of such feedstocks for biodiesel production is challenging because of the conflict with food supply, and risk of starvation in several undeveloped countries.~~ Therefore, the use of non-edible oils can be a way to improve the economy of biodiesel production and its commercial production at an industrial scale. Globally waste cooking oil is generated in ton quantities globally. Nowadays, it is estimated that more than 60% of the WCO produced is improperly disposed.[157] Inappropriate disposal of WCO have a negative impact on the environment. Its price is estimated to be 2–3 times cheaper than any other vegetable oils. Therefore, producing biodiesel from WCO can play a vital role in meeting the energy demands of the growing population as well as diminishing the pollution caused by its non-appropriate disposal. Nevertheless, converting the same in an economical viable and fast way is a challenge, mainly due to high content of FFA and water containing in such feedstock~~s~~. The objective of this study is to develop a catalytic process for the conversion of waste cooking oil into biodiesel in large scale. ~~To overcome the issues encountered with WCO and scale-up the biodiesel production from such attracting feedstock, appropriate pretreatment of WCO was evaluated prior to its transformation to biodiesel in a continuous flow MW irradiation with catalytic bed reactor. Extending the batch process of microwave irradiation to a continuous process could produce large quantities of biodiesel that could indeed meet the increasing demand for the transportation fuel. For moving from milliliter to liter scale, the transesterification reaction was first optimized under domestic MW oven (DMO). However, the sustainability of the biodiesel production process being developed is also governed by feedstock.~~ Even though waste cooking oil is an abundant and inexpensive source, the estimation of WCO generation doest not exceed 30% of the world's biodiesel demand.[174] Therefore, to make the process sustainable, the remaining amounts of biodiesel production need to be provided from other non-edible feedstocks. ~~Then,~~So ~~our~~ the objective ~~was to explore other possible renewable feedstocks as well.~~is further extended to evaluate the feasibility of the single step conversion of Marine microalgae ~~are an appealing sustainable candidate~~to biodiesel. Microalgae have the potential to produce 25 to 220 times higher triglycerides than terrestrial plants without competing with arable lands or food crops.[262] Producing biodiesel from microalgae in a single step by reducing significantly the energy consumption generally required for both extraction and transesterification was evaluated and optimized during my research studies using appropriate catalyst. The lipids in the algae was extracted in situ into the solvent (chloroform) contained in the reaction mixture in addition to methanol and catalyst and simultaneously the extracted lipids are converted to biodiesel.

2.2.2 Designing economically feasible, easily reusable, and environmentally friendly catalyst for the biodiesel production process in a continuous flow microwave system

Catalyst is another major component that adds to the process cost of biodiesel production apart from the feedstock. SrO is a suitable catalyst for the transesterification process ~~thanks~~ owing to its high basicity, strong base sites, relative low lixiviation tendencies in biodiesel and high selectivity towards the transesterification reaction. Basic catalysts, despite their sensitivity to FFA and water, operate in moderate conditions compared to acid catalyst, reducing the cost of biodiesel production process. Previous researches in our laboratory indicated that for a microwave-based process SrO based catalyst are the best offering fast reaction rates for the transformation of vegetable oil, marine algae, and other terrestrial biomasses.[172] SrO ~~have shown showing~~is a potential catalyst ~~the ability of~~ converting 99.8% of WCO to biodiesel in 10 s under domestic MW irradiation using commercial micro-powder of strontium oxide (SrO).[124] However, despite the reusability for several runs, the catalyst remain expensive. Additionally, demonstration of industrialization and commercialization of biodiesel production in optimal and cheapest conditions need to be done.

Initial studies were carried out with commercial SrO on MW assisted continuous flow system to optimize the transesterification ~~reaction~~ process conditions. Even though, SrO powder has been demonstrated to be an active catalyst in a batch process, for its industrial adoptability such a catalyst need~~s~~ to be used as a coating on an inert solid material, reducing the process cost by substantial reduction in the utilization of SrO and scaling-up of the process. Therefore, ~~in addition to the~~as a substitute to the use of commercial SrO catalyst, ~~we had synthesized~~ SrO deposited on millimetric silica beads (SrO/SiO_2) catalyst was synthesized using strontium nitrate $(SrNO_3)_2$ precursor and MW irradiation with success in a batch process. Such low cost, fast, and green methodology for the synthesis of this hybrid solid base catalyst present several advantages over commercial SrO. SrO/SiO_2 as solid and reusable catalyst is particularly appealing for use in a fixed bed continuous flow microwave reactor for biodiesel production. The micrometer size of the supported catalyst eliminates the mass flow constraints as well as pressure drops in a batch process as well as in a continuous flow industrial process and the possibility of this system being a candidate for industrial utility is high. The cost reduction is due to the effective utilization of the catalyst by the homogeneous dispersion of the active sites on the glass beads. Owing to the peculiar properties attributed to the nano-dimension of the synthesized SrO, like high reactivity, lower amount of SrO is needed for the complete~~ing~~ conversion of WCO to biodiesel. Moreover, such a catalyst contributes to the increase of mass and heat transfer, improves the contact between the liquid medium and the catalyst surface, and facilitates its separation from the product~~s~~ mixture either by filtration or by centrifugation. In addition, depositing the catalyst on solid support~~s~~ can help prevent possible health risks caused by inhalation of fine powders. In addition, catalysts supported on spherical beads can offer shape-dependent advantages such as minimizing the abrasion of the catalyst in the reaction environment.

The idea behind the use of a continuous flow reactor for biodiesel production is to transform the batch process to an industrial operation. Such a study could lead to the development of a startup plant for biodiesel production and could cater to the energy needs of Israel in particular. Therefore, regarding the aspects of feedstock, catalyst, and faster technology based on microwave irradiation, and a flow process, the probability of a startup plant on biodiesel production is high and realizable. Currently, the minimum cost of bus fare for transport is 6.60 NIS. Such price could be cut down and used by common person for purchasing a packet of milk for the family. One of the ways of such cost reduction in transportation sector is by developing an economically viable process for the production of biodiesel, which could be an alternative to the current fossil-based fuels. Thus, the objective of the research is to reduce the transportation expenses for the consumer.

2.2.3 Developing a catalytic process for the production of biodiesel using micro algal biomass as feedstock

Combining MW irradiation and SrO catalyst for the conversion of microalgae to biodiesel allow high reduction of production costs and energy consumption compared to conventional heating method and even ultrasonication irradiation.[149] Such achievement is the consequence of enhancement of cell~~s~~ disruption of the algae and efficient lipid extraction under MW irradiation in relatively shorter time. Therefore, lipid productivity can be maximized and the utilization efficiency of the biomass can be increased by making use of all algal biomass components and by reducing the process time. However, the existence of both microalgae, catalyst dispersed in methanol, and biodiesel at the end of the transesterification reaction when a heterogeneous catalyst is used leads to diffusion constraints of various components present in the medium relative to the case when a homogeneous catalyst is used. This leads to lowering of the reaction rate. The reaction takes place in the interfacial region between the catalyst, lipids, and methanol. Thus, a highly active catalyst is required to increase the area of interaction/contact between the two phases.

The use of metal-oxide as a host matrix for carbon dots (C-dots) has the potential to open a new technological gateway for the development of catalysts due to the novel inherent characteristics of carbon nanostructures as well as nanometal-oxides. It is expected that replacing the commercial micron-sized catalytic particles by nanosized particles of SrO and C-dots can lead to further improvement in the transesterification rate of the conversion of algal biomass. C-dots have dimensions of 10 nm or less, so that the mobility of the internal electrons is restricted within the nanoscale dimensions in all directions. Therefore, C-dots may be a promising catalytic material because of their high chemical stability and multifunctionality. C-dot-modified by SrO (SrO-C-dots) could enhance the reduction of energy consumption during the transesterification reaction by completing the conversion of microalgae to biodiesel in lesser time than commercial SrO in a single step of lipid extraction and transesterification. Unfortunately, up scaling of biodiesel production from microalgae remain very challenging and all attempts to achieve such a goal until ~~yet is~~now are unfruitful. The complex harvesting and processing procedures combined with insufficient production of algal dry mass and high cost of productivity are limiting factors for algal biofuel production. Additionally, an attempt was made in our laboratory to convert 1 kg of microalgae to biodiesel using MW assisted continuous flow system. Regrettably, the mixture ~~content~~ of the reaction medium was highly viscous and inappropriate for such technique, causing high pressure and high constrain of flowing, ~~which lead~~leading to the damage of the machine.

3. Novelty of the research

There are three novel aspects of the present doctoral research. The first one is to identify WCO as sustainable feedstock for large-scale production of biodiesel. The second novelty of the study is to develop state of the art catalyst for the conversion of waste cooking oil in a batch as well as in a continuous flow MW irradiation process. The catalyst, namely SrO/SiO_2, was highly active for transesterification of waste cooking oil and sustained the continuous flow of ~ 2.5 L of feed for ~ 25 min. The fixed bed catalyst comprise of 41.3 wt. % SrO deposited on millimetric silica beads prepared using a unique microwave assisted process. Owing to the large particle size of the support (silica beads), the nanoparticles of SrO were homogeneously distributed over the surface rendering the high catalytic activity. Moreover, industrial constraints in large-scale biodiesel production like the mass flow hindrances are effectively surmounted using the catalyst. Thus indeed a catalytic process for biodiesel production from non-edible feedstock that is adaptable to large-scale systems is brought to existence. This research could be termed both as innovative as well as breakthrough in the field of renewable energy. Apart from demonstrating the potential of waste cooking oil as a sustainable feedstock for the demand based production of biodiesel, attempts were further devoted to wards converting a more complex non-edible feedstock to biodiesel. Micro algal biomass, *Chlorella vulgaris*, was successfully transformed to biodiesel in a single step under MW irradiation in a batch process. The novelty of the study is that the biomass is used as received or harvested without any separate step of extraction of lipid component, the starting material for fatty acid methyl ester, FAME. Moreover, the biomass is used as such without any prior esterification of free fatty acids, FFA's, which would hinder the catalytic activity of the base (SrO) catalyst for transesterification. The problem posed by the FFA's of algae is surmounted by designing a novel composite catalyst based on SrO and Carbon dots (C-dots). The unique feature of the C-dots is that the material has a variety of oxygen function groups on the~~are~~ carbon nanoparticle surface structure. The carboxy and phenolic groups on the carbon dot structure would promote the *in-situ* transesterification of FFA's of algae into esters and the basic component of the composite, SrO, would promote the transesterification of the lipid fraction of the algae leading to the formation of biodiesel. Thus, a single step and efficient conversion of micro=~~-~~algae to biodiesel is demonstrated. The research results form a founding stone for the upcoming biorefinery.

4. Experimental methodology

4.1. Materials and methods used in the present research

4.1.1. List of materials and chemicals used during the research

Table 4: Feedstocks used for biodiesel production

Feedstock	Place of purchase
Waste cooking oil (WCO)	Restaurant
Crude dried solid microalgae biomass ~~of~~ (*Chlorella Vulgaris*)	Prof. Zvy Dubinsky Laboratory (Faculty of Life Sciences, Bar-Ilan University, Israel)

Table 5: Materials used as catalyst or for its preparation

Material	Place of purchase
Strontium oxide (SrO) (99.5%)	Alfa Aesar

Strontium nitrate $(SrNO_3)_2$ (≥99.0%)	Sigma Aldrich
Sodium carbonate (Na_2CO_3)	Sigma Aldrich
Silica gel (1-3 mm)	Sigma Aldrich
Silica gel (3-6 mm)	Sigma Aldrich
Ethylene diamine (EDA) ($C_2H_8N_2$) (+99%)	Acros Organics
Potassium Hydroxide (KOH)	Alfa Aesar
Sodium Hydroxide (NaOH)	Alfa Aesar

Table 6: List of solvents used in this research

Solvent	Place of purchase
Methanol (CH_3OH)	Bio-Lab
Chloroform ($CHCl_3$)	Bio-Lab
Polyethylene glycol-400 (PEG-400, 99.998%)	Sigma Aldrich
Isopropyl alcohol (C_3H_8O)	Bio-Lab
Acetone	Bio-Lab
Ethanol	Bio-Lab

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4.1.2. Pretreatment of WCO

WCO was filtered through a USA standard testing sieve of mesh size 250 µm to remove residues and impurities. The acid value of the cooking oil was determined by a titrimetric method and was found to be 3.6 mg KOH/g. The titration of WCO was made by dissolving 20 g of WCO in 75 mL of a solvent that is a 1:1 v/v mixture of distilled water and EtOH that is first neutralized with the 0.02 M aqueous NaOH solution until the appearance of a slight pink color. The sample is then added and the solution is vigorously shaken during the titration process until the reappearance of the pink color, as in the neutralization of the solvent. The acid number of oils was calculated through equation (2) where A is the titrant.

$$Acid\ Number = \frac{(A-B)\times C \times 56.1}{m} \times \left(mg\,\frac{KOH}{g}(sample)\right) \text{ ……Equation (2)}$$

Where B is the titrant solution volume, in mlL~~,~~ used in titration of a blank. C is the concentration of the titrant solution in M, and m is the mass of the sample in grams.[369] To avoid the saponification FFA and the hydrolysis during the transesterification reaction, FFA and water were removed from the cooking oil before the transesterification reaction. The cooking oil was mixed with a solution of KOH to remove the FFA in the form of soap. The soap was separated from the oil content by centrifugation. Then, the cooking oil was heated at 110 °C to evaporate the water.

4.1.3. Cultivation and harvesting of *Chlorella vulgaris*

Freshwater microalgae *C. vulgaris* cultures were grown as a part of our collaboration in the laboratory of Prof. Dubinski in a 3 L sterile flask using a Bristol medium, with air bubbling, under 70 µmol of photons m^{-2} s^{-1} and continuous LED light, at 22 °C with three replicates. After a week, the algae are transferred outdoors to a 30 L flat-panel photobioreactor (PBR). The light, temperature, oxygen, and pH were monitored with a computerized system for 12 days. The light is monitored with a Li-COR QUANTUM sensor; LDO sensors (HACH LANGE) monitor the temperature and dissolved oxygen; the pH was monitored by pHD sc Digital Differential pH/ORP sensors (HACH LANGE). The daylight (12 h) reached up to 2,200−2,500 µmol photons m^{-2} s^{-1}. The temperature reached up to 29−42°C at noon and 16−24°C at night. The pH range was 6.1−7.8. During the first 7 days of the experiment, the initial inoculum reached maximum culture density. The nutrient deficiency diverted the biosynthesis toward lipid accumulation in the algae cells. The algal culture was harvested by centrifugation and freeze-dried in a lyophilizer.

4.1.4. Heating instrumentations for the preparations of the catalysts and transesterification reaction

4.1.4.1. Domestic microwave oven (DMWO)

The preparation of SrO/SiO_2 and the transesterification reaction in batch mode were conducted under DMWO irradiation. The DMWO was operated at 2.45 GHz in a batch mode. The output of the DMWO reactor was 1100 W. The MW oven was operated at 70% power (cycle mode of 21 s on and 9 s off), a cycle mode function provided by the DMWO's manufacturer. The microwave oven was modified, to have a provision for the distillation column passing through the MW oven (for enhanced safety of operation) and with a stirring facility during the reaction. The modification was performed by replacing the bottom part of the oven by a rounded aluminum plate. The plate was carefully attached to the framework in such a way as to allow for magnetic stirring (**Figure 15**).

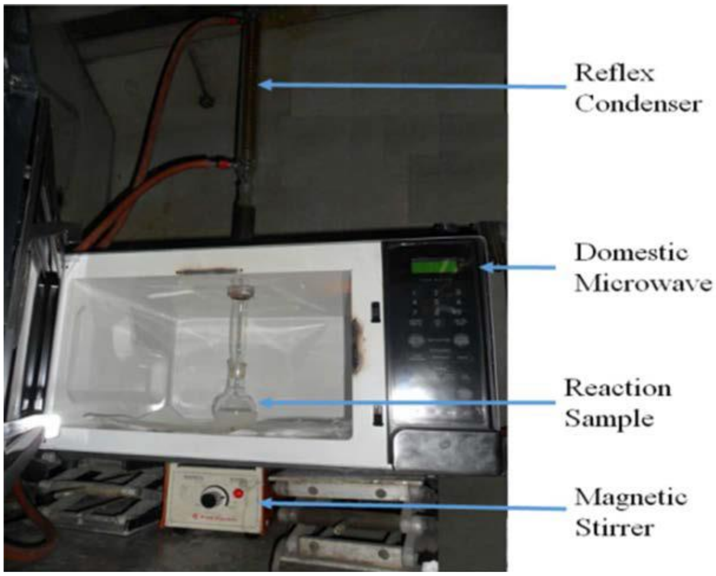

Figure 9~~15~~: Modified domestic microwave oven (DMWO)

4.1.4.2. Microwave assisted continuous flow reactor

The transesterification reaction of WCO to biodiesel in large-scale process was carried out with a continuous-flow process on a FlowSYNTH microwave system (Milestone FlowSYNTH ATC-F0 300 continuous-flow microwave reactor, **Figure 16**). The FlowSYNTH system is a continuous-flow microwave reactor with 1000W available power with a magnetron able to deliver power in 1 W increments, heating a vertically mounted 200-mL flow reactor capacity running through the center of the cavity. The mixture is pumped in at the bottom of the reactor and out at the top, passing through a microwave cavity. A high-pressure membrane pump from the base upwards through the column to the top pumps the reaction mixture. In-line sensors allow continuous monitoring of the reaction temperature. Homogeneity of the temperature along the entire length of the reactor is ensured by a magnetically driven paddle-stirrer. An Archimedean screw provides agitation and helps maintain plug flow characteristics, while reducing back mixing. The reaction mixture is stirred mechanically inside the microwave cavity by means of a stir shaft equipped with three paddles. These paddles fit the agitator aid heating through conduction. The reactor is also equipped with a pump, to enable flow of the reaction solution through the reactor. The temperature of the reaction mixture is measured both in the microwave cavity and after exiting the cooler by by in-line thermocouple sensors. An external touch-screen terminal controls the FlowSYNTH, controlling process conditions such as temperature, power, and feed flow rate via software process control. The reaction chamber, with 190 mL working volume, is mounted vertically in the microwave cavity. The reaction mixture exits through a back pressure regulator which regulates the pressure of the system/solvent, although in principle this is not needed when operating below the solvent boiling point. The maximum working conditions for the reactor are 200 °C, 30 bar and 1000 W. The reaction mixture is pumped continuously through the reaction vessel under microwave heating. The peristaltic pump enables flow rates from 0.06 to 3400 mL/min. The continuous-flow process facilitates the large-scale production of biodiesel in a shorter time than the conventional biodiesel production process.

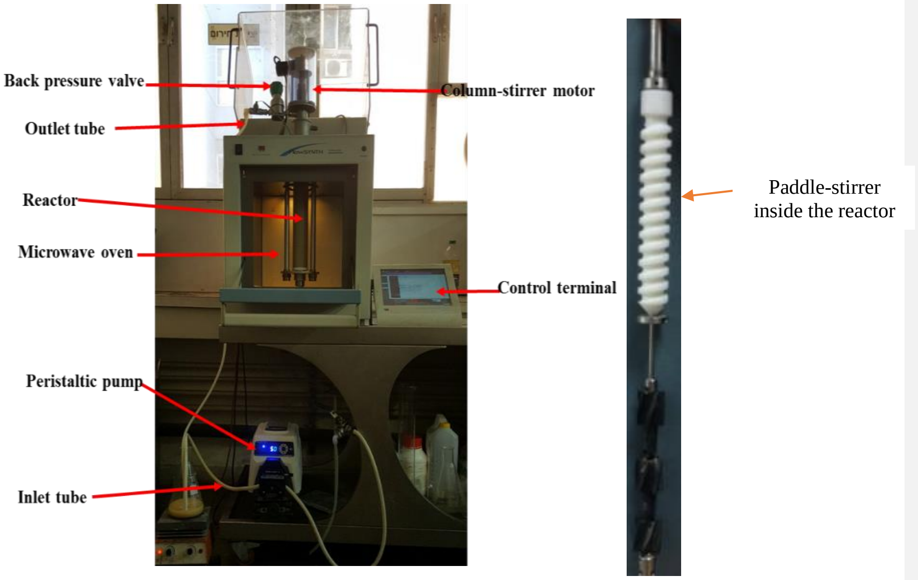

Figure 10~~16~~: Experimental setup for the continuous-flow biodiesel production based on microwave irradiation~~. Stirring shaft with three Weflon15 blades for the tubular reactor of the FlowSYNTH (the outlet and inlet marked are for the experiments using commercial SrO as the catalyst; however, the inlet and outlet are reverted when the biodiesel production is carried out using a fixed-bed reactor packed with the SrO/SiO_2 catalyst).~~

4.1.4.3. Ultrasonication irradiation

The preparation of SrO-C-dots was carried out under ultrasonic irradiation (Sonics and Materials Inc., USA, model VCX 750, frequency 20 kHz, AC voltage 230 V, 70 % amplitude). The tip of an ultrasonic transducer made from titanium rod was immersed in the reaction liquid which is driven to vibration by a piezoelectric, transducer which vibrates when subjected to an alternating current electric field. A typical ultrasonic probe is shown in **Figure 17**. The mixture was dipped in a water/Si-oil bath at 70 °C.

Figure 11~~17~~: Typical sonochemical apparatus

4.2. Synthesis of SrO based catalyst

4.2.1. Preparation of SrO/SiO_2

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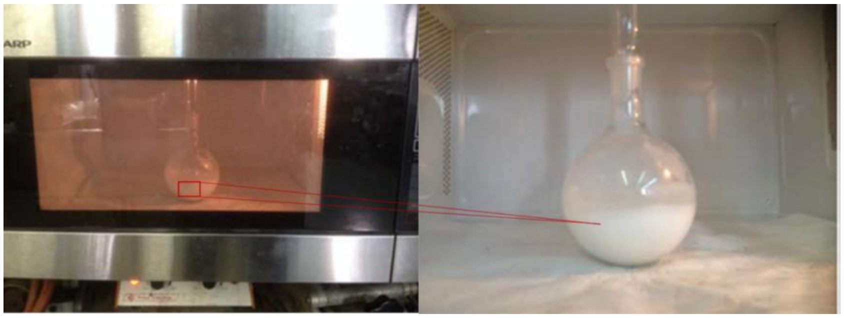
The deposition of SrO on SiO_2 gel consists of dissolving equal molar amounts of $Sr(NO_3)_2$ and Na_2CO_3 in water under vigorous stirring. Optimized catalyst preparation was obtained by dissolving 4.23 g of $Sr(NO_3)_2$ and 2.11 g of Na_2CO_3 into 100 mL of water taken in a 250 mL round-bottom flask at RT. 10 mL of ethylenediamine (EDA) were then added. Subsequently, 6 g of SiO_2 gel beads (3–6 mm particle size) was added to the solution and irradiated under DMWO (**Figure 18**). The optimized irradiation time of the slurry under DMWO was 30 s. After having been cooled, the residual solid mass was separated by centrifugation from the supernatant, washed with EtOH three times, and subjected to drying under vacuum overnight. The optimum calcination temperature and time of the obtained material $Sr(CO_3)_2/SrO$ ($Sr(CO_3)_2$ deposited on SiO_2 beads) was 900 °C for 4 h in air, yielding in situ deposition of SrO NPs on SiO_2 beads (SrO/SiO_2).



~~**Figure 18:** Pictorial representation SrO/SiO_2 preparation under DMWO~~ (delete; this fig is similar to fig 15)

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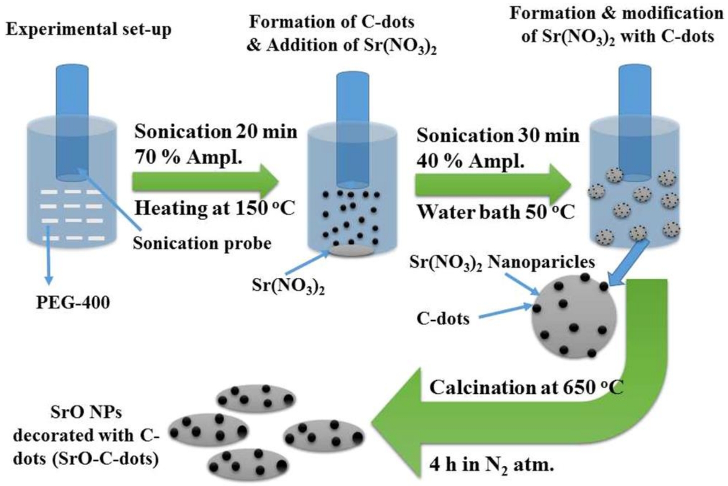
4.2.2. Preparation of SrO-C-dots

The synthesis of SrO-C-dots ~~(**Figure 19**)~~ was performed as follows: firstly, 20 mL of polyethylene glycol (PEG-400) was transferred into a quartz test tube. The tip of an ultrasonic transducer was dipped in the solution, about 2 cm above the bottom of the test tube for 2.5 h, leading to the formation of C-dots. Subsequently, 10 g of $Sr(NO_3)_2$ was added to the test tube, and the sonication was continued for another 30 min in a hot water bath at 50°C. Then, the product mixture was centrifuged. The $Sr(NO_3)_2$-C-dot nanoparticles were washed with double-distilled water and acetone (1:1) and then dried in vacuum at room temperature. The dried product was subjected to calcination for varying periods of time to determine the optimal conditions for the decomposition of $Sr(NO_3)_2$.



~~**Figure 19:** Schematic overview of the sonochemical synthesis of the $Sr(NO_3)_2$–C dot composite~~ (delete; this is present in our manuscript that is present in the subsequent sections of the thesis)

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4.3. Transesterification reaction

4.3.1. Transesterification reaction of WCO using SrO/SiO_2 as catalyst in batch mode

The transesterification reactions were carried out in a 50 mL round-bottom flask. A typical batch process of the transesterification reaction comprises of taking 15 g of WCO, 4 mL of MeOH, and 0.5 g of catalyst, SrO/SiO_2, and irradiating the content in MW for 10 s at 70% (cycle mode of 21 s on and 9 s off) power. This means that the actual irradiation time is only 7 s during the reaction. First, SrO/SiO_2 was dispersed in MeOH with high magnetic stirring to ensure a good dispersion of the catalyst into the MeOH. WCO was subsequently added, and the mixture was irradiated for 10 s. At the end of the reaction, the temperature of the mixture was measured by a pyrometer (Fluke, 65 Infrared thermometer) and was found to be 60 °C. The mixture was then centrifuged, and three distinguished layers were observed: the top layer was composed of FAME and excess MeOH, the middle one was SrO/SiO_2, and the bottom layer was glycerol~~ (**Figure 20**)~~. Then, the top layer was extracted, and a rotary evaporator removed the excess MeOH. The catalyst was then separated in order to recycle it and study the catalyst activity and stability. To each sample, cooking oil and MeOH were added in the same amounts used for the initial reaction.

~~**Figure 20:** Typical digital image of the product obtained from the transesterification reaction~~ (not very informative; present in the supplementary of one of our publications)

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4.3.2. Transesterification reaction of WCO using SrO as catalyst in MW assisted continuous flow process

A typical transesterification process in the flow system consists of feeding a mixture of WCO and methanol (different mole ratios, 1:6 – 1:12) and a SrO catalyst (5 – 8.75 g) at different flow rates (100 – 300 mL/min). The effect of various reaction parameters such as the stirring shaft rotation velocity, mole ratio of WCO to methanol, amount of catalyst, reaction time, reaction temperature, flow rate of the feed and microwave power on the conversion of waste cooking oil into biodiesel was evaluated.

4.3.3. Transesterification reaction of WCO using SrO/SiO_2 as catalyst in MW assisted continuous flow process

In the case of SrO/SiO_2 (41 wt% SrO/SiO_2), 15 g of the catalyst is packed in the microwave reactor system using a permeable membrane at its bottom that only enables the liquid product, but not the solid catalyst, to pass through. The feed (WCO and methanol) flows from the top of the fixed bed of the catalyst packed in the reactor, under the optimized process parameters found using SrO as catalyst.

4.3.4. *In-situ* transesterification reaction of *Chlorella Vulgaris* using SrO-C-dots as catalyst in batch mode

A typical batch process of the transesterification reaction consists of taking 1 g of dried microalgae mixed with 10 mL of chloroform, 5mL of MeOH (1:2 v/v), and 0.3 g of SrO−C-dots and irradiating the content in a microwave oven for a certain time. First, the catalyst was dispersed in MeOH by high magnetic stirring to ensure good dispersion of the catalyst into the MeOH. The microalgae and chloroform were subsequently added, and the mixture was irradiated. At the end of the reaction, the temperature of the mixture was measured with a pyrometer and was found to be 60 °C, owing to the presence of the condenser, which allowed the cooling of the reaction. After the completion of the reaction, the samples were centrifuged and filtered under vacuum to separate the methanol−chloroform phase that contained the FAME from the residual microalgae, the glycerol, and the catalyst. The solution of methanol−chloroform was evaporated in a rotary evaporator, and the FAME content was determined gravimetrically. The oil content was expressed by its weight relative to the weight of the microalgae biomass.

4.4. Characterization methods

4.4.1. Analysis of WCO

Gas chromatography – Mass spectra (GC-MS) analysis (Varian 431-GC, 220-MS) using a VF-5 ms column allowed the determination of the chemical composition of FAME produced from WCO. Various components present in FAME were identified by comparison of the retention time and mass spectra with library data of mass spectra compounds. The GC–MS conditions used are detailed in **Table 7**.

Table 7: Experimental conditions adopted for GC-MS analysis of the biodiesel samples for the identification of various components in the FAME

GC-MS conditions			
Injection mode		Splitless	
Injector temperature		250 °C	
Split ratio		20	
Constant column flow mode		1 mL/min	
Carrier gas		Helium	
Column oven temperature progress			
Temperature (°C)	**Rate (°C/min)**	**Hold (min)**	**Total (min)**
70	-	1	1
180	35	1	5.14
220	3	0.67	19.15
280	45	0.5	20.98
Column: VF-5 ms			
Length		30 m	

Diameter	0.25 mm
Film thickness	0.25 µm
MS	
Ionization mode EI auto	EI auto
Start m/z 50	m/z 50
End m/z 350	m/z 350

4.4.2. Characterization of SrO based catalysts

4.4.2.1. X-ray Diffraction (XRD)

Powder X-ray diffraction (PXRD, Bruker AXS Advance powder X-ray diffractometer (Cu Kα radiation; λ = 0.154178 nm))~~)~~ analyses were conducted to probe the crystallographic nature of ~~SrO~~ of the solid based catalysts. ~~obtained from the decomposition of $SrCO_3/SiO_2$ and $Sr(NO_3)_2$-C-dots. XRD patterns were collected using a Bruker AXS Advance powder X-ray diffractometer (Cu Kα radiation; λ = 0.154178 nm) operating at 40 kV/30 mA with a 0.02 step size and 0.0019 step size per 0.5 s in the range of 10−80° (2θ) for identifying SrO compound in SrO/SiO_2 and SrO-C-dots, respectively. The phases were identified using the power diffraction file (PDF) database (JCPDS, International Centre for Diffraction Data). The crystallite size of SrO from SrO/SiO_2 was estimated from by Scherrer equation choosing the most intense signal and finding the full width at half maxima in the XRD patterns. Then, the parameters λ and θ (in radians) were substituted in the Scherrer' equation: $L = 0.9\lambda/B \cos \theta$, where L is the crystallite size, λ is the X-ray wavelength, B is the line broadening, and θ is the Bragg angle in radians.~~

4.4.2.2. Thermogravimetric analysis (TGA)

The precise decomposition temperature of $SrCO_3$ from $SrCO_3/SiO_2$, a reaction intermediate for the generation of SrO from $Sr(NO_3)_2$, was deduced from TGA. The TGA curves were recorded using a Q500 Thermogravimetric Analyzer (TGA) in the temperature range of 25−1000 °C in the air atmosphere at a heating rate of 10 °C/min.

~~For the temperature decomposition of $Sr(NO_3)_2$− C-dot to SrO− C-dot, the TGA curves were recorded using TGA-GC-MS (EI/CI) Clarus 680/Clarus SQ 8C by PerkinElmer over~~

~~the temperature range 25– 900 °C in both nitrogen and air atmospheres at a heating rate of 10 °C/min~~

4.4.2.3. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy (Nicolet (Impact 410) FT-IR spectrophotometer) ~~identifies~~ is used to evaluate the chemical composition of **the solid base catalysts**. ~~The vibrations of different chemical species, such as functional groups of molecules, occur in defined ranges of infrared spectrum. Therefore, particular peak in the spectrum can be assigned to a specific chemical moiety. FT-IR spectra **of both catalysts** were recorded in KBr pellet mode on a Nicolet (Impact 410) FT-IR spectrophotometer under atmospheric conditions. The samples were scanned in the range of 400 – 4000 cm^{-1}.~~

4.4.2.4. Electron microscopy

The imaging and morphology of both SrO/SiO$_2$ and SrO-C-dots catalysts and their respective elemental mapping were evaluated using a high-resolution scanning electron microscopy (HR-SEM) having a JEOL-JSM 700F instrument and an LEO Gemini 982 field emission gun SEM (FEG-SEM). ~~Due to the low conductivity of SrO, the catalysts were coated with iridium (Ir). Elemental analysis was carried out using Energy-dispersive X-ray analysis (EDAX) in conjunction with the HR-SEM instrument.~~

Transmission electron microscope (TEM) images of SrO particles from SrO/SiO$_2$ particles as well as SrO–C-dot particles were taken with JEM-1400, JEOL to visualize their morphology. TEM images ~~of the SrO–C-dot particles~~ were obtained using a Tecnai G2 (FEI, Oregon USA), a high-contrast/cryo TEM equipped with a bottom CCD 1 Kx1 K camera. ~~to visualize and evaluate the shape, size, and surface morphology of the SrO–C-dots. Both samples for TEM were prepared by making a suspension of the particles in isopropyl alcohol, using water-bath sonication. Two small droplets of the samples were then applied on a TEM copper grid coated with a carbon film, and dried on a covered Petri dish in vacuum. The crystal structure of the SrO from SrO/SiO$_2$ was determined by selected area electron diffraction (SAED) crystallographic analysis.~~

4.4.2.5. Dynamic Light Scattering (DLS)

The dynamic light scattering (DLS) instrument was used to measure the size and size distribution of molecules and particles, dispersed in a liquid~~, typically in the submicron region. The particle-size distribution of the SrO−C-dot nanoparticles was measured by DLS particle-size analysis model using a ~~using a Zetasizer Nano SZ (Malvern Instruments Ltd., Worcestershire, UK) device.

4.4.2.6. Raman spectroscopy

Raman spectra of the SrO−C-dots were performed on a Renishaw inVia Raman microscope equipped with RL785 and RL830 Class 3B wavelength stabilized diode lasers and a Leica DM2500 M (Leica Microsystems) materials analysis microscope. ~~A powder sample was sprinkled on the glass slide, and the Raman spectra were recorded to confirm the presence of C-dots on the surface of SrO in the SrO−C-dot composite.~~

4.4.2.7. Brunauer−Emmett−Teller (BET) sorptometry

The specific surface area of the catalysts was measured by the BET method at 77 K under liquid nitrogen on a Micromeritics instrument (Gemini 2375) after the samples were evacuated at 25 °C for 12 h with an evacuator (Micromeritics, Flow Prep 060).

4.4.2.8. Inductively Coupled Plasma (ICP)

ICP analysis was carried out using Ultima 2, Jobin Yvon Horiba. This study was main used for the determination of SrO loading on SiO_2 beads as well as to know the content of SrO in the SrO-C dot composite catalyst.~~ is an analytical atomic spectrometer. It can identify most of the elements and quantify their concentration in ppm units (mg/L). The analysis is performed in aqueous homogeneous media.~~

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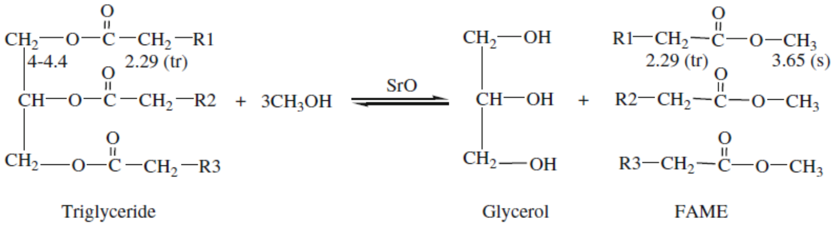
~~To evaluate the exact amount of SrO deposited on silica beads and the leaching of SrO from the SiO_2 surface after transesterification reaction of the catalytic bed process, ICP analysis was used. Typical methodology for this is comprised of taking a known amount of SrO/SiO_2 in concentrated HNO_3 and stirring at 50 °C on a magnetic stirring base for 1 h to dissolve the SrO coated on the silica beads. Subsequently, the silica beads were separated from the filtrate using Whatman (150 MM Φ) filter paper. The filtrate was analyzed for~~

~~Sr^{2+} ions using an inductively coupled plasma (ICP) spectrometer (Ultima 2, Jobin Yvon Horiba~~).

4.4.3. FAME analysis

After each production of FAME, the FAME product was analyzed by nuclear magnetic resonance (^1H NMR) spectroscopy. ^1H NMR is carried out on a Bruker 300 MHz NMR spectrometer. ~~analysis provided important information, like progress of the transesterification reaction. ^1H NMR spectroscopy enables the simultaneous detection of the product (FAME) and the precursor (oil), and as a result, the progress of the transesterification reaction can be monitored. Secondly, a ^1H NMR spectrum can identify whether the resulting product is pure or perhaps includes impurities such as glycerol, methanol, chloroform, acetone, or other extracted components in addition to the extracted oil phase. Thirdly, the conversion of FAME can be calculated. The conversion of oil to FAME might be calculated by the integration of ^1H NMR signals. The relevant signals chosen for integration were those of the methoxy groups in the FAME (3.65 ppm, singlet) and those of the α methylene protons present in all the triglyceride derivatives (2.29 ppm, triplet) of the oil (**Fig. 21**).[127] The decision to use the described signals resulted from the fact that selected signals are distinct, compared to other signals in the spectrum. As a result, the integration value can be estimated with a low percentage error in integration.~~



~~**Figure 21:** The transesterification reaction with relevant chemical shifts of protons in a transesterification reaction.~~ (delete)

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~~The equation (3) used to quantify the yield of transesterification was:~~

~~$Conversion\ (\%) = \frac{2I_{Me}}{3I_{CH_2}} \times 100 \ldots\ldots\ldots (3)$~~

~~The conversion ratio of the oil to the resultant fatty acid methyl ester was obtained by dividing I_{Me} (the integration value of the protons of the methyl esters) by I_{CH2} (the integration~~

~~value of the methylene protons). Factors 2 and 3 were derived from the fact that the methylene carbon possesses two protons and the methyl carbon has three attached protons.~~

~~The signals in the range of 4–4.4 ppm are attributed to the CH_2 groups (CH_2-O-COR) of triglycerides. The weak or absent intensity of these peaks along with the strong intensity of the methyl ester peak are a good indication of high yield of FAME.~~ (delete ; this information is present in all the three publications of ours)

~~Using the ^1H NMR technique it is difficult to identify other components in the biodiesel phase at lower concentration than < 3 wt. %. For more precision and accuracy, GC-MS technique is preferable and commonly used for determining the yield of biodiesel, despite its relative complexity.~~

5. Logical integration of the research publications

5.1. List of articles

I have published the following the research articles as first author:

(1) Alex Tangy, Indra Neel Pulidindi, and Aharon Gedanken, **SiO_2 beads decorated with SrO nanoparticles for biodiesel production from waste cooking oil using microwave irradiation**, *Energy & Fuels*, 2016, 30, 3151−3160.

(2) Alex Tangy, Indra Neel Pulidindi and Aharon Gedanken, **Continuous flow biodiesel production from waste cooked oil using microwave irradiation and supported SrO catalyst**, *Bioresource Technology*, 2016, 10.1016/j.biortech.2016.10.068.

(3) Alex Tangy, Vijay Bhooshan Kumar, Indra Neel Pulidindi, Yael Kinel-Tahan, Yaron Yehoshua and Aharon Gedanken, **In situ transesterification of *Chlorella Vulgaris* using carbon dot functionalized strontium oxide as heterogeneous catalyst under microwave irradiation**, *Energy & Fuels*, 2016, 10.1021/acs.energyfuels.6b02519.

5.2. Logical connection between the above articles in forming continuous structure of the thesis

The main objective of my doctoral research is to make the biodiesel production process sustainable and demand based by designing energy efficient, economically viable, and environmentally benign strategies. My first publication deals with the identification of the most viable feedstock for biodiesel production, namely, waste cooking oil (WCO). Tons of this feedstock are generated around the world each day and are an environmental waste. We have designed a novel methodology for the efficient~~ly~~ and quick conversion of this feedstock to biodiesel. To this end, a potential solid base catalyst comprising of the deposition of SrO nanoparticles on millimetric (3-6 mm) SiO_2 beads is produced under microwave irradiation in an aqueous medium. Conversion values of WCO to biodiesel as high as 99.4 wt. % were achieved using this catalyst in a transesterification reaction carried out in a batch process in a domestic microwave oven. Moreover, the reusability of the catalyst for over 10 repeated reaction runs without appreciable loss in catalytic activity was demonstrated. This is a breakthrough in the field of renewable energy research.

Another challenge is to make the above batch process of conversion of WCO to biodiesel into a continuous flow microwave irradiation process that facilities handling of large quantities of the feed and makes the biodiesel production process sustainable and profitable. Towards solving this problem, we have used the novel solid base catalyst ~~that we have developed~~ (41.3 wt. % SrO/SiO_2) in a fixed bed flow reactor. Interestingly, owing to the large size of the silica bead support (3-6 mm), several conventional process obstacles, like the mass flow constraints for the feedstock, as well as catalyst deactivation were successfully surmounted in the innovative strategy~~ we have developed~~. A conversion value of WCO to biodiesel as high as 99.2 wt. % was achieved with the reactor packed with 15 g of 41 wt. % SrO/SiO_2 catalyst in 8.2 min. with 820 mL of feed. Excellent performance of the fixed bed catalyst without loss in activity for a lifetime of 24.6 min. converting a feed of 2.46 L to FAME was observed. Thus, an industrially adoptable biodiesel production process is designed. These research results provide a foundation for the development of a pilot plant for the conversion of WCO to biodiesel.

Another major challenge facing the upcoming biorefinery is the bottle neck of the inflexibility of using multiple feedstock. Even though, large quantities of WCO are accessible, this feedstock alone could not meet the exponentially growing demand for biodiesel for transportation as well as industrial needs. So, in addition to the WCO, other appropriate~~ly~~ and abundant feedstock need to be explored and strategies for the conversion of such feedstock to biodiesel in an econ~~m~~om~~n~~ically feasible manner need to be developed. With this objective in mind, we have explored lipid rich micro algal biomass, *Chlorella vulgaris*, as feedstock for the production of biodiesel. In addition to the use of micro~~-~~algea as feedstock, another novelty of the work comprise of the design of a SrO-Carbon dot catalyst for the single step conversion of *Chlorella vulgaris* to biodiesel. The use of carbon dot in the composite catalyst is that no addition or prior pretreatment of the biomass is required for the conversion of free fatty acids to esters. The surface acid groups on the C-dots in the SrO-C dot composite promote the esterification of FFA’s to esters and in addition the SrO component of the composite promote the transesterification of lipids to biodiesel formation. Using this hybrid catalyst, a~~s~~ 2.4 fold enhancement in the rate of lipid conversion of biodiesel comparted to conventional commercial SrO catalyst is observed. FAME yields of 97 wt. % are observed in a short during of 2.5 min of microwave irradiation of the reaction medium using this hybrid catalyst.

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Thus, there is logical connection between the three research articles I have published.

6. Articles abstracts

6.1. Article 1

SiO$_2$ Beads Decorated with SrO Nanoparticles for Biodiesel Production from Waste Cooking Oil Using Microwave Irradiation

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Alex Tangy, Indra Neel Pulidindi, and Aharon Gedanken

Energy & Fuels, 2016, 30, 3151−3160

Energy sources are necessary for human existence, comfort, and progress. Limited crude petroleum resources and increasing awareness of the environmental impacts of using fossil fuels motivate the search for new energy sources and alternate fuels. Herein, a low cost, fast, and green methodology for the synthesis of a hybrid solid base catalyst, strontium oxide coated millimetric silica beads (SrO@SiO$_2$), is designed for the transesterification of cooking oil into biodiesel in a domestic microwave oven. The cost reduction is due to the effective utilization of the catalyst by the homogeneous dispersion of the active sites on the silica beads and their reusability. The catalyst synthesis process was optimized with respect to the amount of glass beads, microwave irradiation time, calcination time, and calcination temperature. Several methods for synthesizing SrO by minimizing energy consumption were investigated, and an optimized process for designing SrO@SiO_2 was developed. The SrO@SiO_2 catalyst produced under optimum conditions was characterized by TGA, XRD, FTIR, ICP, SEM, and TEM. XRD analysis indicated peaks typical of SrO alone. ICP analysis indicated 41.3 wt. % deposition of SrO on silica beads. The novel solid base catalyst thus generated was used for the transesterification of waste cooking oil. Conversion values as high as 99.4 wt. % in 10 s irradiation were observed from ^1H NMR analysis using this composite catalyst, indicating the feasibility of economical biodiesel production from cooking oil waste in a very short time.

6.2. Article 2

Continuous flow through a microwave oven for the large-scale production of biodiesel from waste cooking oil

Alex Tangy, Indra Neel Pulidindi, Nina Perkas, Aharon Gedanken

Bioresource Technology, 2016, DOI: 10.1016/j.biortech.2016.10.068

This report presents a method for producing large quantities of biodiesel from waste cooking oil (WCO). Preliminary studies on optimization of the WCO transesterification process in a continuous-flow microwave reactor are carried out using commercial SrO as a catalyst. The SrO catalyst can be separated and reused for five reaction cycles without loss in activity. Challenges like mass flow and pressure drop constraints need to be surmounted. SrO nanoparticles deposited on millimeter-sized (3–6 mm) silica beads (41 wt.% SrO/SiO_2) are prepared and evaluated as a substitute for the SrO catalyst. A WCO conversion value to biodiesel as high as 99.2 wt% was achieved with the reactor packed with 15 g of 41 wt% SrO/SiO_2 catalyst in 8.2 min with 820 mL of feed. Excellent performance of the fixed-bed catalyst without loss in activity for a lifetime of 24.6 min converting a feed of 2.46 L to FAME was observed.

6.3. Article 3

In-Situ Transesterification of *Chlorella vulgaris* Using Carbon-Dot Functionalized Strontium Oxide as a Heterogeneous Catalyst under Microwave Irradiation

Alex Tangy, Vijay Bhooshan Kumar, Indra Neel Pulidindi, Yael Kinel-Tahan, Yaron Yehoshua, and Aharon Gedanken

Energy & Fuels, 2016, DOI: 10.1021/acs.energyfuels.6b02519

The main goal of this study is to functionalize SrO with carbon dots (C-dots) and to explore the composite as a catalyst for fatty acid methyl esters (FAME) production using Chlorella vulgaris as feedstock. C-dots are synthesized by sonicating polyethylene glycol followed by sonochemical modification of $Sr(NO_3)_2$ (precursor for SrO) with C-dots. Sonication facilitates the adhesion of C-dots to the surface of $Sr(NO_3)_2$. The resulting material is calcined in an inert environment to form a SrO−Cdot composite. The effect of functionalizing SrO with C-dots on the transesterification of the lipids in the alga with methanol is studied. The optimization of a one-stage process of conversion of the lipid fraction of microalga Chlorella vulgaris into FAME using direct transesterification under microwave irradiation is illustrated. A lipid conversion value of 45.5 wt. % is achieved using the SrO−C-dot catalyst after 2.5 min of microwave (MW) irradiation. The catalyst displayed better activity than commercial SrO. Microwave irradiation accelerates the disruption of the microalgal cells and facilitates the release of lipid content into the reaction medium. The catalyst is characterized by a variety of physicochemical techniques. The FAME product obtained from the alga is quantified using ^1H NMR spectroscopy. The new catalyst, namely, SrO−C-dot nanoparticles (NPs), yielded 97 wt. % FAME from *Chlorella vulgaris* in 2.5 min of MW irradiation.

7. Incorporation of the research articles

7.1. Article 1

SiO2 Beads Decorated with SrO Nanoparticles for Biodiesel Production fromWaste Cooking Oil Using Microwave Irradiation

Alex Tangy, Indra Neel Pulidindi, and Aharon Gedanken

Energy & Fuels, 2016, 30, 3151−3160

Electronic Supplementary Information, ESI

SiO_2 beads decorated with SrO nanoparticles for biodiesel production from waste cooking oil using microwave irradiation

Alex Tangy,[a] Indra Neel Pulidindi,[a] and
Aharon Gedanken[a,b]*

[a]Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel and

[b]Department of Materials Science and Engineering, National Cheng Kung University, Tainan 70101, Taiwan

Tel: +972-3-5318315; Fax: +972-3-7384053; *E-mail: gedanken@mail.biu.ac.il

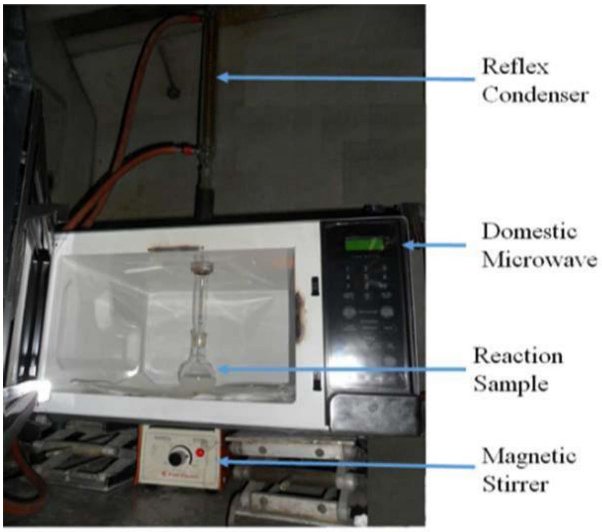


Figure S1. Modified domestic microwave oven

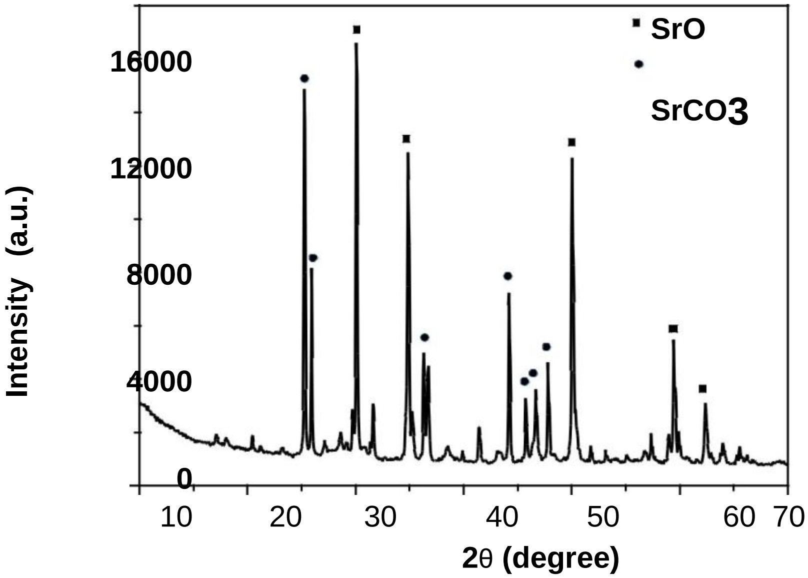


Figure S2. The XRD pattern of the material obtained after calcination of $SrCO_3@SiO_2$ at 900 °C for 2 h in air

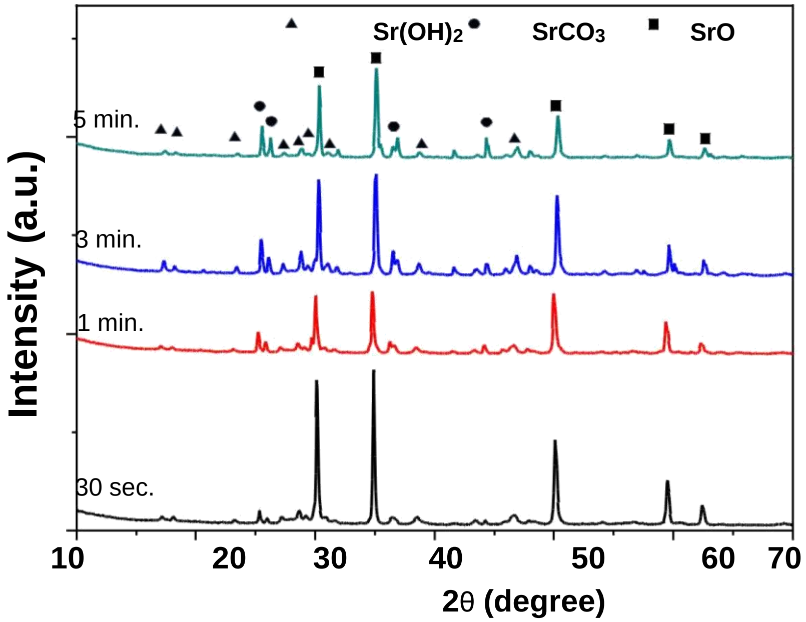


Figure S3. The effect of calcination temperature (900 °C, 3 h) on the conversion of $SrCO_3@SiO_2$ to $SrO@SiO_2$

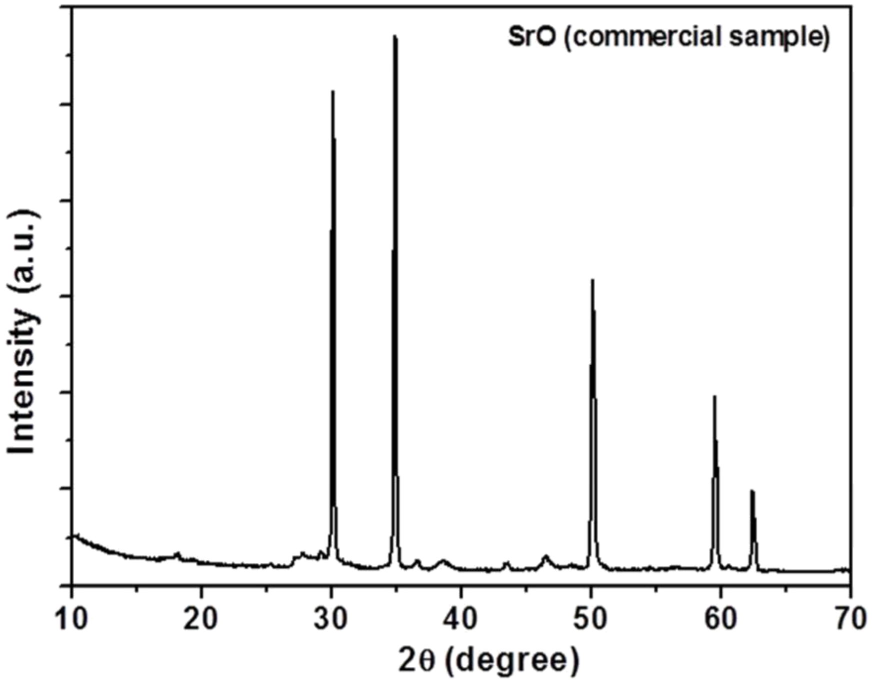
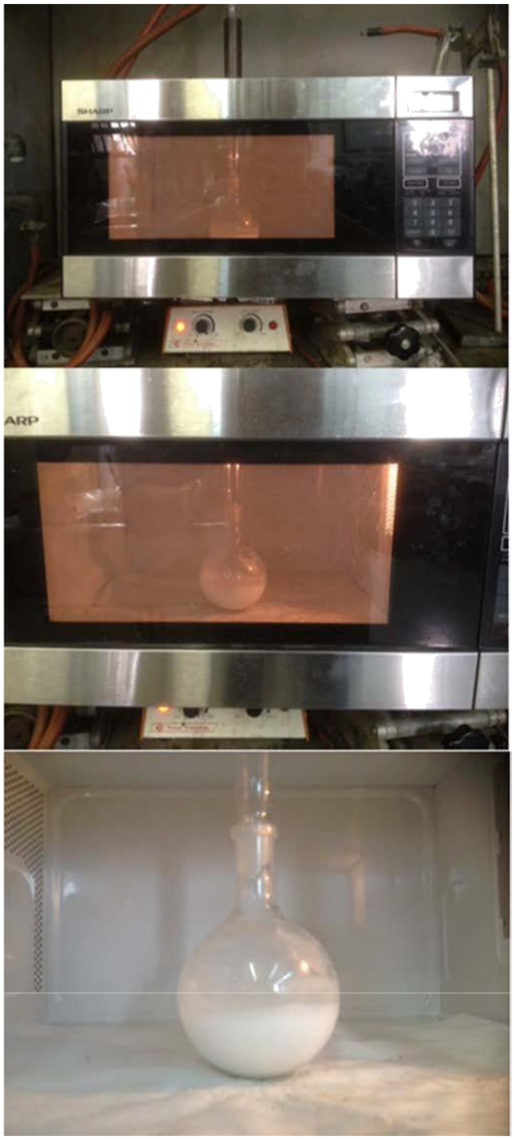


Figure S4. The XRD pattern of commercial SrO (standard) from Sigma-Aldrich



Pictorial representation of the catalyst (SrO@SiO$_2$) preparation under microwave irradiation

Figure S6. Product obtained from the transesterification reaction

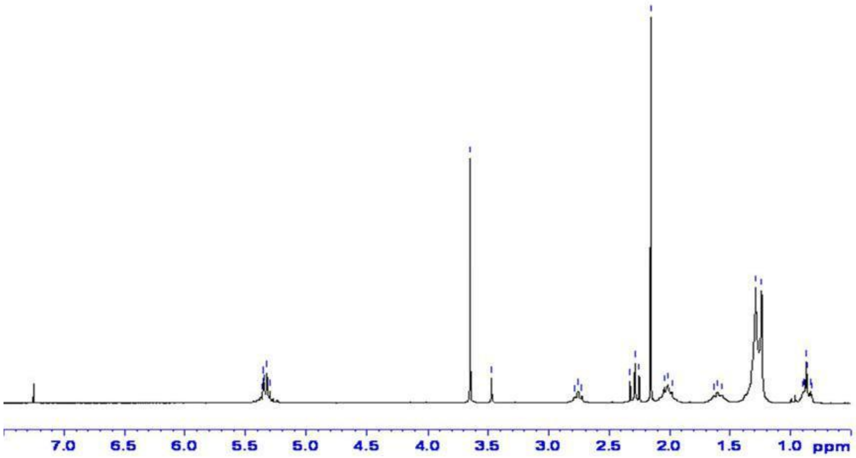


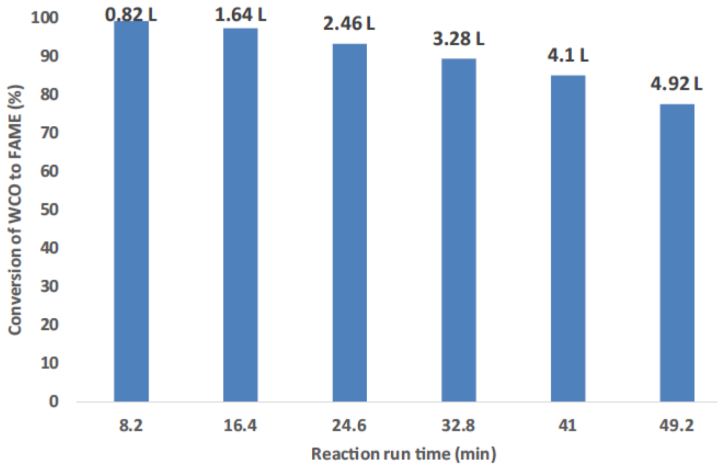
Figure S7. A typical ^{1}H NMR of FAME obtained from transesterification of cooked oil with $SrO@SiO_2$ yielding 99.4 wt. % conversion

7.2. Article 2

Continuous flow through a microwave oven for the large-scale production of biodiesel from waste cooking oil

Alex Tangy, Indra Neel Pulidindi, Nina Perkas, Aharon Gedanken

Bioresource Technology, 2016, DOI: 10.1016/j.biortech.2016.10.068



Sustainable catalytic activity of SrO/SiO_2 in fixed bed continuous flow MW irradiation process is observed for 24.6 min of irradiation.

Electronic Supplementary Material

Continuous flow through a microwave oven for the large-scale production of biodiesel from waste cooking oil

Alex Tangy, Indra Neel Pulidindi, Nina Perkas and Aharon Gedanken*

Department of Chemistry, Bar-Ilan University, Ramat Gan 5290002, Israel

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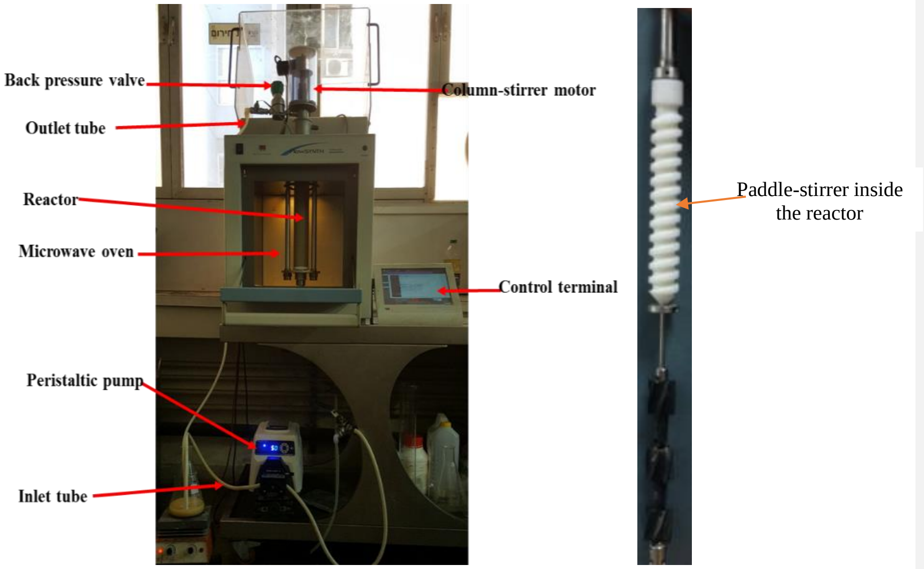


Fig. S1. Experimental setup for the continuous-flow biodiesel production based on microwave irradiation. Stirring shaft with three Weflon15 blades for the tubular reactor of the FlowSYNTH (the outlet and inlet marked are for the experiments using commercial SrO as the catalyst; however, the inlet and outlet are reverted when the biodiesel production is carried out using a fixed-bed reactor packed with the SrO/SiO_2 catalyst).

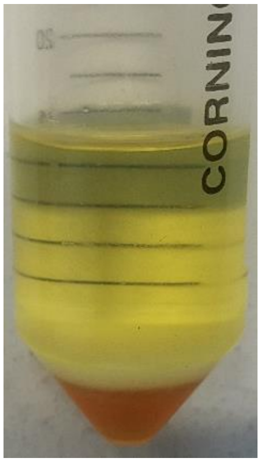


Fig. S2. Product obtained from the transesterification reaction.

Table S1. Experimental conditions adopted for GC-MS analysis of the biodiesel samples for the identification of various components in the FAME

Instrument		**GC-MS conditions**	
GC			
Injection mode		Splitless	
Injector temperature		250 °C	
Split ratio		20	
Constant column flow mode		1 mL/min	
Carrier gas		Helium	
Column oven temperature progress			
Temperature (°C)	Rate (°C/min)	Hold (min)	Total (min)
70	-	1	1
180	35	1	5.14
220	3	0.67	19.15
280	45	0.5	20.98
Column: VF-5 ms			
Length		30 m	
Diameter		0.25 mm	
Film thickness		0.25 μm	
MS			
Ionization mode EI auto		EI auto	
Start m/z 50		m/z 50	
End m/z 350		m/z 350	

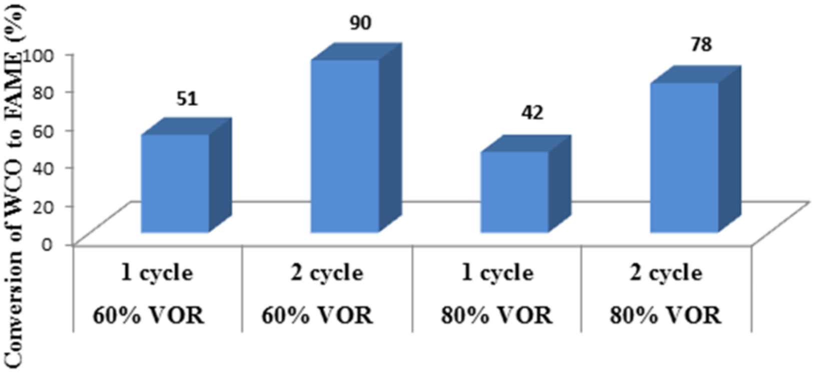


Fig. S3. Effect of cycle number and velocity of rotation (VOR) of the stirring shaft on the conversion of WCO.

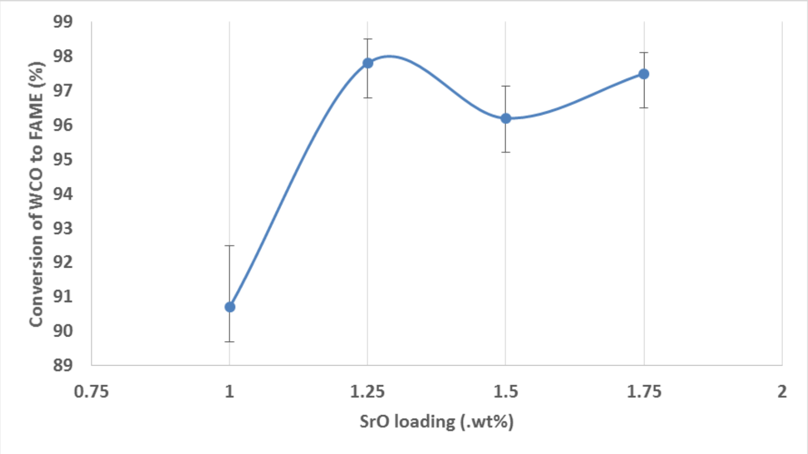


Fig. S4. Effect of amount of SrO catalyst on the conversion of WCO to biodiesel.

Table S2. FAME components – GC-MS analysis of the FAME produced from WCO under optimized reaction conditions.

FAME components	Biodiesel composition (%)
Hexadecanoic acid methyl ester (Z)	11.7
Octadecanoic acid methyl ester	7.2
9-Octadecenoic acid methyl ester (Z)	30.1
11-Octadecenoic acid methyl ethyl ester (E)	9.2
8,11 - Octadecadienoic acid methyl ester	6.2
9,12 - Octadecadienoic acid methyl ester	34.6
Eicosanoic acid methyl ester	1.0
∑Saturated Fas	19.9
∑Monounsaturated Fas	39.3
∑Polyunsaturated Fas	40.8

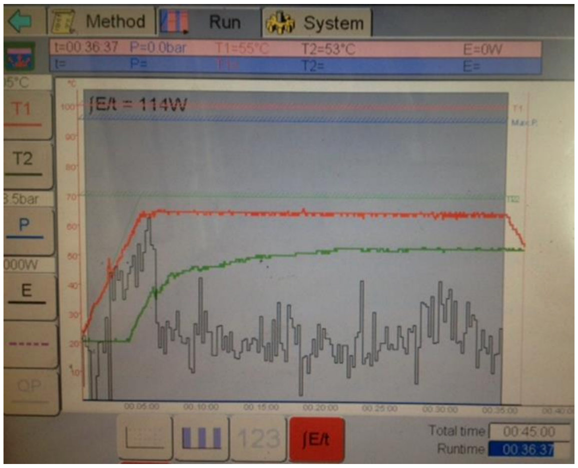


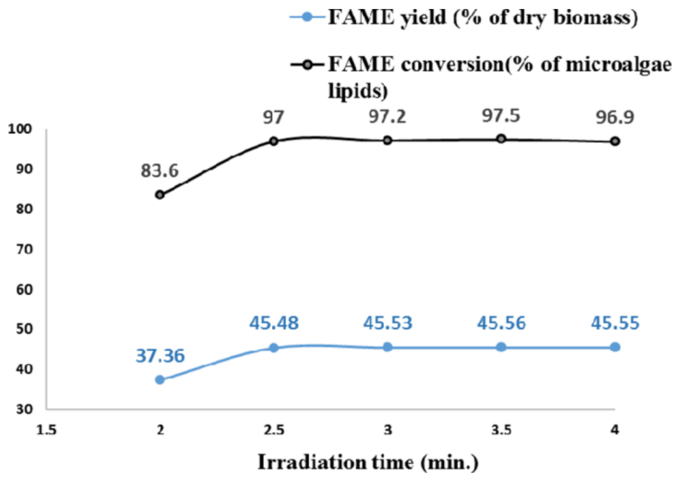
Fig. S5. Energy consumption profile for the biodiesel production process (reaction conditions: 1:12 mole ratio of waste cooking oil to methanol; 5 g SrO; 65 °C; after 30 min irradiation).

7.3. Article 3

In-Situ Transesterification of *Chlorella vulgaris* Using Carbon-Dot Functionalized Strontium Oxide as a Heterogeneous Catalyst under Microwave Irradiation

Alex Tangy, Vijay Bhooshan Kumar, Indra Neel Pulidindi, Yael Kinel-Tahan, Yaron Yehoshua, and Aharon Gedanken

Energy & Fuels, 2016, DOI: 10.1021/acs.energyfuels.6b02519



A lipid conversion value of 97 wt. % and a corresponding FAME yield of 45.5 wt % are achieved in reaction time of 2.5 min.

Electronic supplementary material

In-situ transesterification of *Chlorella Vulgaris* using carbon-dot functionalized strontium oxide as heterogeneous catalyst under microwave irradiation

Alex Tangy[#†], Vijay Bhooshan Kumar[#†], Indra Neel Pulidindi[†], Yael Kinel-Tahan[‡], Yaron Yehoshua[‡] and Aharon Gedanken[†]*

Note: [#] Alex Tangy and Vijay Bhooshan Kumar have contributed equally for this work

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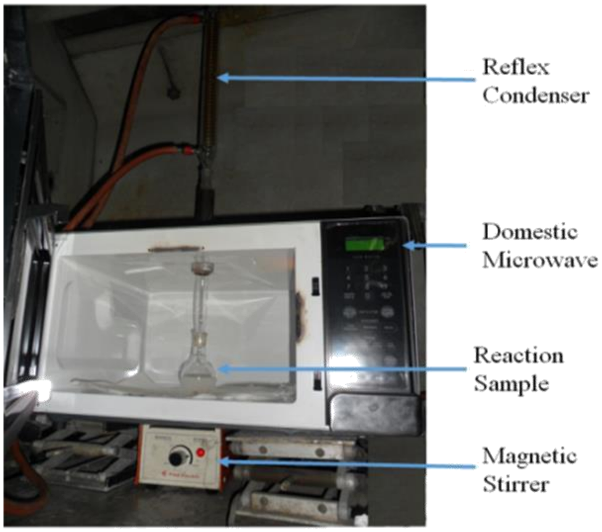

Figure S1. Modified domestic microwave oven

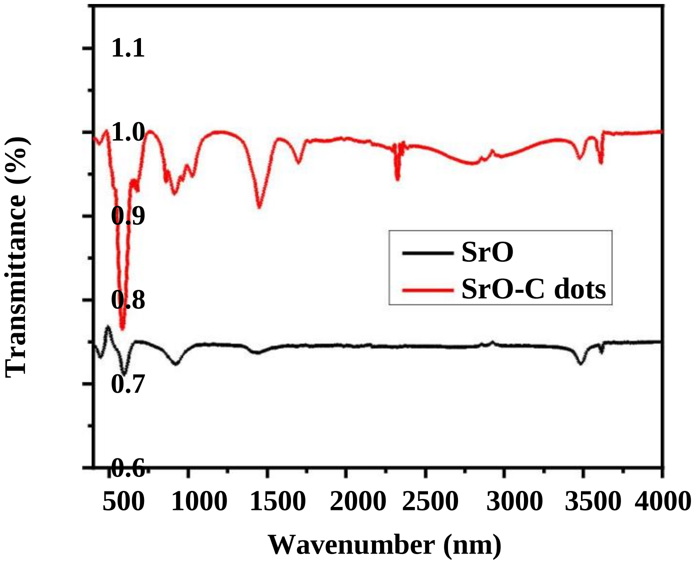

Figure S2. FT-IR spectra of SrO-C-dots and commercial SrO

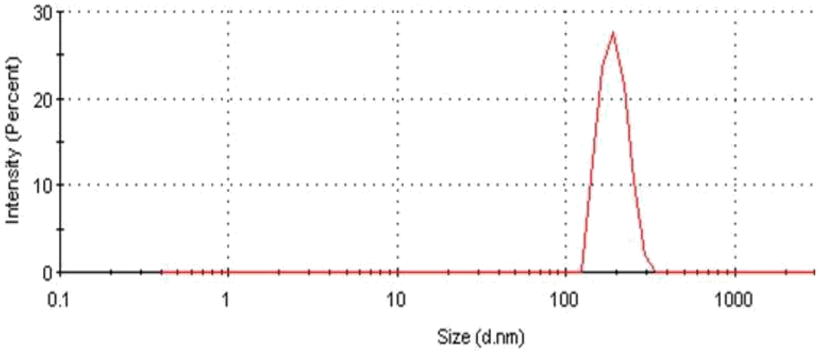

Figure S3. Dynamic light scattering (DLS) of SrO-C dot composite

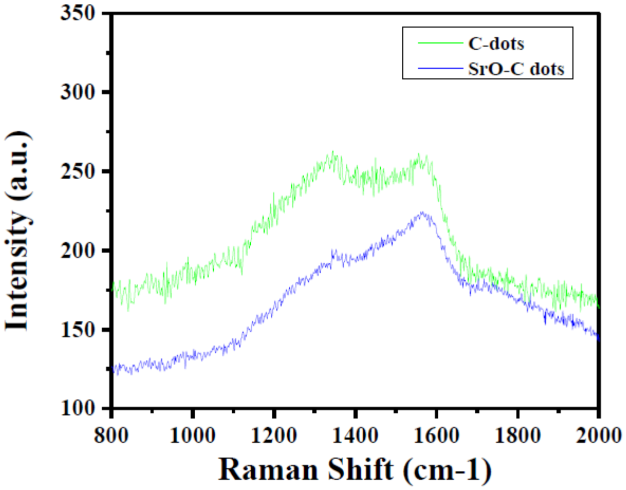

Figure S4. Raman spectra of C-dots and SrO-C-dot composite (PEG-400 is the precursor for C-dots).

8. Conclusion & future perspective

The potential of microwave irradiation for the acceleration of the transesterification reaction of waste cooked oil was exploited in a continuous flow process. Heterogeneous solid base catalysts, that could be a substitute to the commercial SrO catalyst, were developed. SrO/SiO_2 was synthesized by fabrication and deposition of SrO NPS on millimetric silica beads. The catalyst showed activity for the conversion of WCO to FAME close to 100% in just 10 s irradiation. Moreover, the catalyst could be easily separated and reused for 10 consecutive reaction runs with only less than 5 wt. % decrease of its activity. Such improvement was attributed to the unique morphology of SrO particles on the silica bead surface at the nanometric level, resulting in well dispersed active sites for the transesterification reaction even at a modest loading of 41.3 wt. % of SrO. SrO/SiO_2 is particularly important owing to the millimetric size, which could function as a potential catalyst in a continuous flow system without mass flow constrains. Therefore, this low cost, effective, and reusable catalyst was further adopted as fixed-bed catalyst in a continuous-flow MW reactor for the conversion of WCO to FAME. The catalyst exhibited a lifetime of 24.6 min with sustainable activity converting 2.46 L of feed to biodiesel without almost any loss in activity.

Conversion of microalgae (*Chlorella vulgaris*) to FAME under MW irradiation in a batch process was also performed in a single step by synthesizing carbon dots on SrO (SrO-C-dots), enhancing functionalization, increasing the surface area of the catalyst and then, increasing the number of accessible active reactant sites. A lipid conversion value of 45.5 wt. % and a FAME yield of 97 wt. % were achieved using the SrO−C-dot composite catalyst in a short reaction time of 2.5 min. The SrO−C-dot catalyst shows improved performance for the transesterification of lipids compared to the conventional SrO catalyst. The enhanced catalytic activity (2.4-fold) of the SrO−C-dot composite is attributed to the unique structural features of carbon-dots with a variety of oxygen, carboxylic, and phenolic functionalities that promote the esterification of FFAs in the algal biomass along with its advantageous properties attributed to its nanometric dimension. Thus, a SrO−C-dot composite catalyst is designed in an innovative way with very high potential for the fast and enhanced production of FAME from microalgae.

Therefore, the obvious deduction from all these reactions conducted using strontium based catalyst is that the combination of SrO and MW irradiation allow an almost complete conversion of WCO and microalgae, to biodiesel in short time, from hours to seconds, and in moderate conditions, reducing drastically the energy consumption required when using conventional heating. Moreover, most of the literature based on comparison with other catalysts proved both the superior catalytic activity of SrO and its reusability several times.

However, some challenges need to be solved for the adoptability of SrO based catalyst in an industrial process. Converting WCO in large scale using such catalyst remains problematic due to the short lifetime of the catalyst, because of the leaching of SrO and its partial dissolution in both biodiesel and methanol. A cheap and efficient technique need to be optimized also for the removal or conversion of FFA containing in WCO in esters. Therefore, great efforts should be made to improve the process efficiency and economically viable. Moreover, large-scale production of biodiesel from microalgae remains a dream due to the high production cost even in the early stage of the growth and harvest of microalgae.

Nevertheless, all of these goals are aimed at an industrial scale biodiesel production in an economically viable and environmentally friendly way, replacing, hopefully, in near future, the homogeneous base catalyst used nowadays in large-scale production for industry. This could be a possible solution to the current twin problems being faced by humankind namely, the energy crisis, and the environmental decay.

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תקציר:

תוכן עניינים

עבודה זו נעשתה בהדרכתו של פרופ׳ אהרן גדנקן
מן המחלקה לכימיה של אוניברסיטת בר-אילן

שיטות קטליטיות חדשות מבוססות SrO להפקת ביו-דיזל מחומרי מוצא בלתי אכיל בעזרת מיקרוגל: יישום והתאמה למערכות גדולות

חיבור לשם קבלת התואר "דוקטור לפילוסופיה"
מאת:
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רמת גן **כסלו תשע"ז**