



Catalyst derived from wastes for biofuel production: a critical review and patent landscape analysis

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Abstract

The global scenario turned towards converging their focus on sustainability owing to its adverse response in the climatic conditions, else unlike other planets earth may go unbecoming to live. The major contributor in for this worsening scenario of the climatic condition is polluting the atmosphere by various ways. In addition to this, the major polluting factor around the globe is vehicle and industrial waste which is contaminating the environment on hourly basis. The derived outcome of this issue is to cut the pollutants of the fuel mixing with atmospheric air and when this is either stopped or reduced, it saves the mother earth from pollution. The biofuel derived from wastes based catalysts is considered to be a better alternative and such biofuels have lesser environmental hazards when compared with conventional fossil fuels. So, the review in this article narrows down to waste catalyst derived biofuel along with their performance which contributes in the self-sustenance of biodiesel production. The article flow through the path of progress of biofuel and about the destination of its progress in near future which is discussed along with the patent landscape analysis. Scope of the article can be clearly understood from the facts revealed from the patent analysis. So, the first segment discusses about the ways to derive the biofuel from the agriculture waste, biomasses, gasification as well as from the microalgae. Focus of this review has also been given for the description of various natural sources used to derive catalysts, performance of the catalysts used for biodiesel production in terms of its efficiency and the challenges associated with the use of natural sources as catalysts for biodiesel production.

Keywords Catalyst from waste · Landscape analysis · Biodiesel production · Efficiency

Introduction

The decline in easily available oil reserves forced the researchers to carry out rigorous researches on possible substitutes for every petroleum-based products during the past few decades. Many researchers stated that biodiesel, which were produced by the transesterification of lipids, could be

taken as a potential alternative on which researches were carried out on a full swing from the beginning of nineteenth century (Senthil et al. 2016). Biodiesel is the major source of renewable energy and finds its applications in distinct fields like transport, power and heat. Commercial mass production and economic production of biodiesel could be carried out by most efficient catalytic transesterification process. Usually for transesterification acid catalysts, homogenous base and heterogeneous base catalysts were used. But, destructive issues arise while using acid catalysts and their usage was also accompanied by few more undesirable facts such as larger reaction time, requirement of higher quantities of acid and high molar ratio of the mixture (Subramaniam et al. 2013). Utilization of homogenous catalysts was limited by their higher manufacturing cost and non-reusable nature while the utilization of heterogeneous catalysts were hindered by undesirable phenomenon such as leaching, poisoning and deactivation of the reactants. Additionally, these synthetic catalysts were not suitable for a long run biodiesel production and economy in process. Hence, various researchers

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focused on developing solid-based catalysts from agricultural, food and industrial wastes (Alagumalai et al. 2021). These biowaste render maximum possible utilization of wastes to produce useful energy which aids in developing a sustainable process. Managing and disposal of biowaste is currently a persisting problem, as the generation of biowaste witnessed a staggering increase from various sources such as municipal waste, agricultural, forest residue and food waste. The constituents of biowastes such as lipids, protein, starch, hemicellulose and cellulose act as the cheapest raw materials for the biological production of energy from those wastes. By using this biowaste as a renewable feedstock they could be easily converted to bioenergy with the aid of appropriate technologies and are used as catalysts in biodiesel production (Alrobaian et al. 2020).

Need for waste derived catalyst

In order to analyse the trends in usage of catalysts derived from natural resources or wastes, understanding the growth rate of the biofuel in the near future is highly important. So, the requirement to forecast the future as well as by understanding the present efficiency rates of the biofuel seems eminent. The journal articles, web articles, patent landscapes are all required to provide the assurance for the growth of waste-derived catalyst used biodiesel production. Specifically, the patent landscape analysis contains the geography, applicant and number of patents filed in a year provide a clear vision about the growth rate. Further, it provides data to do research in this biofuel domain. Figure 1 denotes the

global bio-based oil yield predicted by various authors in which the average yield was noted to be 20 cu m/ha year and 1500 gallons of oil per acre year. One forecasting was observed in the graph that reaches a 15,000 gallons per acre year and this signifies the utilization of biodiesel in the forthcoming days in a stronger way. Figure 2 denotes the prediction of biodiesel production by three major players in the field. It clearly portrays that by 2024 the production may raise approximately by twofold with USA as major producer.

Figure 3 depicts the revenue generated out of sustainable aviation fuel (SAF) production over the current decade. It clearly states that even the most complex aviation fuel will be turned sustainable in next 10 years. From all these

Renewable diesel production capacity, million gal/y

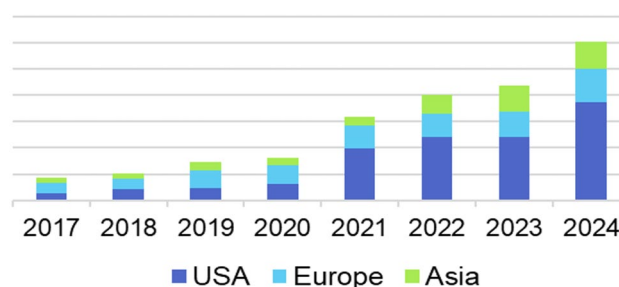


Fig. 2 Production forecasting of bio-diesel (<https://www.idtechex.com>)

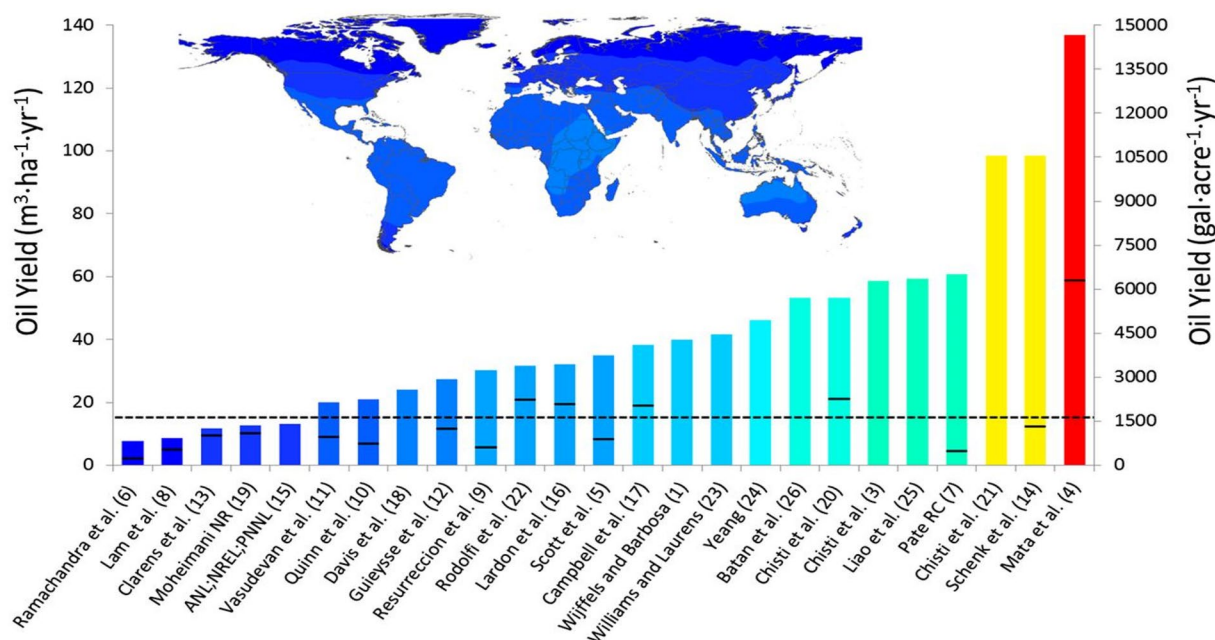


Fig. 1 Review of global oil yield (<https://www.pnas.org>)

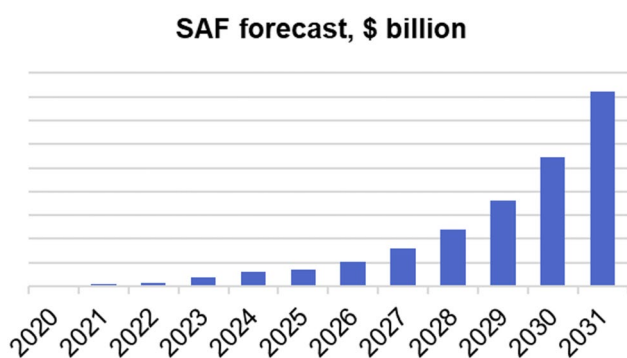


Fig. 3 Prediction of SAF production (<https://www.idtechex.com>)

forecasts and predictions, the demand and necessity of bio-diesel production can be well noted.

Patent landscape analysis

Cost of processing and technology used for processing the biomass into waste-based catalysts for biodiesel production are some of the important aspects to be considered. Mainly, waste materials were used for the catalyst synthesis that could effectively replace the uneconomical metal catalysts which incurs more cost for its synthesis and were not environmental friendly. Synthesis of waste materials uses various technologies that vary from one geographical location to the other. But the trend of utilizing waste biomass as feedstock for catalyst is booming and widespread. In order to substantiate the need for analysis of waste-based catalysts used for bio-diesel production, a patent landscape analysis has been carried out. Upon performing this analysis, it was understood that the technology is reorienting itself towards nature for the derivation of catalysts rather than using synthetic methods. The landscape analysis is carried out for the catalyst-based biofuel production shown in the following

table. Table 1 denotes the number of patents filed based on the catalysts used for biodiesel production. Counts are given for various countries, major patent applicants, and year-wise counts of patents. The total count is 8667 as per the record for the catalysts for production of biofuel.

Similarly, the number of patents published based on the catalysts prepared from waste and utilized for bio-diesel production is listed in Table 2. As in the previous case, the count is given country-wise, applicant wise and year-wise. The total count is 5245 as per the record for the waste-based catalysts used for bio-diesel production.

More like the former cases, next landscape analysis shows the number of patents filed with respect to the waste-based catalysts derived from agricultural wastes and utilized for the bio-diesel production. Country wise, applicant-wise and year-wise count is given in Table 3. Since this technology is in the growth phase, the total number of filed-based agricultural waste-derived catalysts is only 90 in number.

The landscape analysis is carried out for the micro catalyst for biofuel shown in the Table 4 and for nano catalyst as shown in Table 5. The analysis was more alike the previous ones with respect to country, applicants and years. It was noted from the analysis that a total of 2043 patents and 883 patents were filed on micro and nano catalysts so far depicting its steady growth over the previous decade. Figure 4 denotes the patents filed on catalysts, waste-derived catalysts, agricultural waste-derived catalysts, micro and nano catalyst-based biodiesel production by various countries and during the past decade.

Trend in commercialization of catalyst production could be clearly witnessed from the patent landscape analysis. Hence, the importance of reviewing about the waste-derived catalyst for sustainable biodiesel production could be clearly seen. This article clearly focusses on bringing out various aspects of waste-derived catalysts such as its production, nature, efficiency and utilization in

Table 1 Catalyst-based biofuel production (<https://patentscope.wipo.int/search>)

S. no	Country	No. of patents	Major applicants	No. of patents	Year wise count	No. of patents
1	USA	3,884	Shell Oil Company	270	2012	755
2	PCT	2,168	Shell Internationale Research Maatschappij B.V	219	2013	817
3	European patent office	969	The regents of the University of California	139	2014	857
4	Australia	685	Uop LL	132	2015	741
5	Canada	621	Strong force IoT portfolio 2016 LLC	131	2016	673
6	China	70	Afton Chemical Co	128	2017	543
7	United Kingdom	70	Exxonmobil Research and Engineering Company	128	2018	461
8	Japan	34	Exxonmobil Upstream Research Company	120	2019	531
9	Republic of Korea	28	Bp Co North America Inc	101	2020	439
10	New Zealand	22	Innospec Limited	100	2021	85

Table 2 Waste-based catalyst biofuel production (<https://patentscope.wipo.int/search>)

S. no.	Country	No. of patents	Major applicants	No. of patents	Year wise count	No. of patents
1	USA	2,457	Shell Oil Company	223	2012	495
2	PCT	1,365	Shell Internationale Research Maatschappij BV	175	2013	509
3	European patent office	497	Strong force IOT portfolio 2016 LLC	131	2014	541
4	Australia	470	UOP LLC	113	2015	465
5	Canada	362	Exxonmobil Research and Engineering Company	100	2016	414
6	UK	30	BP CO North America Inc	96	2017	331
7	Israel	16	Xyleco Inc.	69	2018	282
8	New Zealand	16	Anellotech Inc.	65	2019	347
9	China	10	Verenium CO	64	2020	274
10	Sweden	6	Danisco US INC	58	2021	51

Table 3 Waste-based catalyst biofuel production (<https://patentscope.wipo.int/search>)

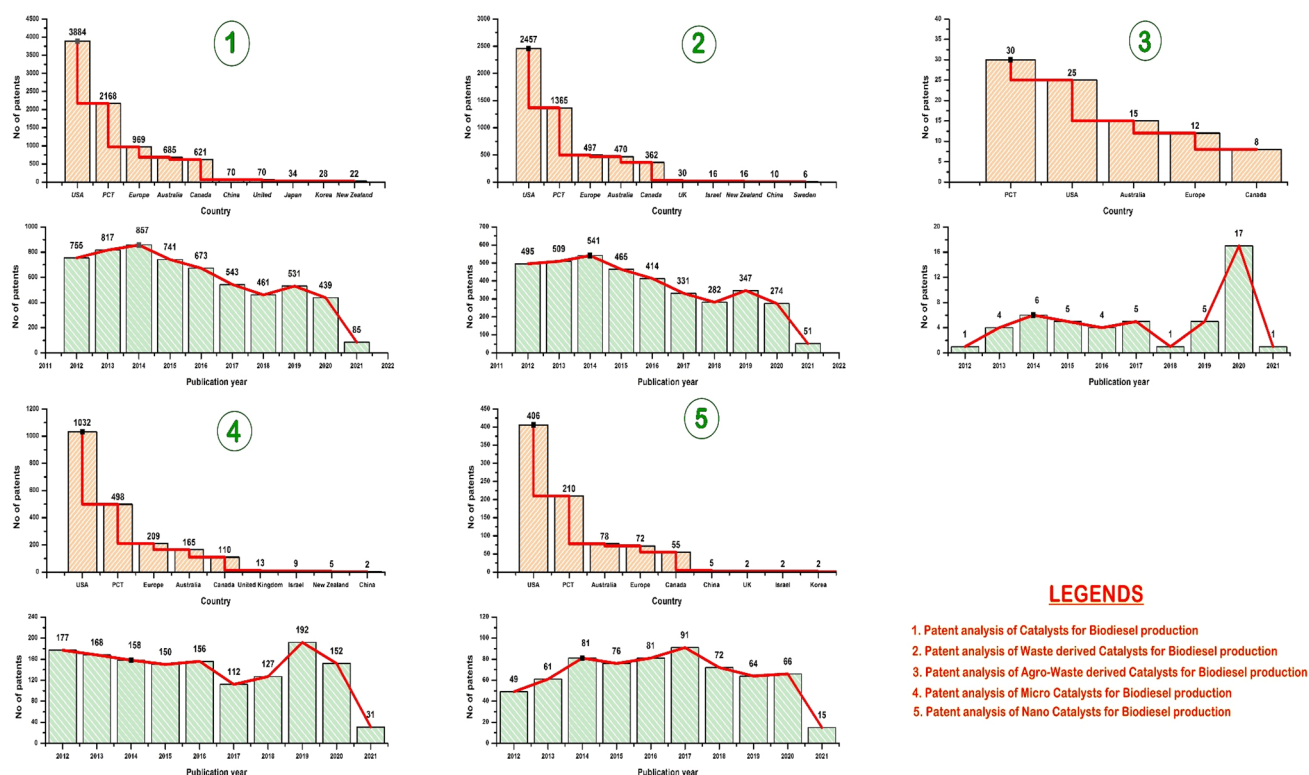
S. no.	Country	No. of patents	Major applicants	No. of patents	Year wise count	No. of patents
	PCT	30	Pivot bio Inc.	10	2012	1
2	USAa	25	Metanomics GMBH	8	2013	4
3	Australia	15	ENI SPA	6	2014	6
4	European patent office	12	Biocheminsights Inc	5	2015	5
5	Canada	8	BP CO north America INC	5	2016	4
6			BASF SE	4	2017	5
7			Endicott Biofuels II LLC	4	2018	1
8			Green Tech Research Co Ltd	4	2019	5
9			National University of Ireland Galway	4	2020	17
10			Winwick Business Solutions Pty Ltd	4	2021	1

Table 4 Micro catalyst for biofuel production (<https://patentscope.wipo.int/search>)

S. no.	Country	No. of patents	Major applicants	No. of patents	Year wise count	No. of patents
1	United States of America	1,032	Strong force IOT portfolio 2016 LLC	130	2012	177
2	PCT	498	Verenium co	49	2013	168
3	European Patent Office	209	Basf enzymes LLC	42	2014	158
4	Australia	165	Shell oil company	41	2015	150
5	Canada	110	Gevo Inc	34	2016	156
6	United Kingdom	13	Shell internationale research maatschappij BV	32	2017	112
7	Israel	9	Microchips Inc	30	2018	127
8	New Zealand	5	Solazyme Inc	28	2019	192
9	China	2	The regents of the university of California	27	2020	152
10			Ceres Inc	25	2021	31

Table 5 Nano catalyst for biofuel production (<https://patentscope.wipo.int/search>)

S. no.	Country	No. of patents	Major applicants	No. of patents	Year wise count	No. of patents
1	United States of America	406	Afton chemical co	113	2012	49
2	PCT	210	BP co North America Inc	23	2013	61
3	Australia	78	Twist bioscience co	21	2014	81
4	European Patent Office	72	The regents of the university of California	18	2015	76
5	Canada	55	Raindance tech Inc	16	2016	81
6	China	5	Tegreene clarencet	15	2017	91
7	United Kingdom	2	Microvi biotech Inc	14	2018	72
8	Israel	2	Ferren bran	13	2019	64
9	Republic of Korea	2	Hillis w daniel	13	2020	66
10	Sweden	1	Ishikawa muriel y	13	2021	15


Fig. 4 Patent analysis graphs for catalysts used for biodiesel production

manufacturing of biodiesel. Subsequent sections deal with various class of waste-derived catalysts that are widely used for biodiesel production.

Agri waste as biofuel catalyst

Straw to biofuel

The technique reveals a way of formulating biofuel with the aid of graded catalytic liquefaction process over the

straw. Straw was used as a major raw material in this process and the solid straw material is converted into biomass feedstock using the liquefaction process. By using this feedstock, biofuel is derived from graded alcoholysis in presence of magnetic $\text{CaO-Al}_2\text{O}_3\text{-Fe}_3\text{O}_4$ as catalysts. Under the catalysis of simple lower alcohols and the mentioned catalysts, the straw reacts during predefined temperature for certain time period to obtain biofuel and residue (Zhao et al. 2015; Quanyuan et al. 2019). Therein, residue is dried, weighed, put in an autoclave with lower

alcohols, and heated to a next temperature point for reactions for the same period of time. The above operations are repeated successively. The method achieves recycling of the catalysts on the one hand, and improves the utilization rate and the biofuel yield rate of biomass on the other hand (Lee et al. 2013).

Lignocellulose to biofuel

The invention relates to the field of biofuel preparation and discloses a preparation method of biofuel. The method included degrading a lignocellulosic raw material in the presence of catalysts is to obtain an aldehyde group-containing compound and reacting the aldehyde group-containing compound with low-degrade aliphatic alcohols to obtain the biofuel. The method helps prepare the biofuel by a one-pot method, which reduces the production cost and solves the problem of tedious operation in the process of preparing the biofuel (Ramesh et al. 2018; Mukhopadhyay 2015; Beer et al. 2009).

Biofuel from waste biomasses and algal biomasses

Microalgae biomass

Microalgae come under the classification of one-cell variant of plant biomasses along with assorted nature, unveiling the numerous potentials aimed at developing the liquid fuel for locomotion. Microalgal variant is capable of cultivating in freshwater as well as saturated salty water (or both) with proficient utilization of carbon dioxide from the vicinity with supplementary contribution in world-wide carbon level fixation which is up to 40% (Ho et al. 2013a; Brosowski et al. 2016a; Papilo et al. 2017a). These kinds of algal biomasses can be manufactured from microalgae based species since they possess a natural capability to generate rich energy content oils from completely dried algal cell biomass. *Botryococcus* spp. has hoarded up to fifty percentage long chain oil with hydrocarbons derived from the dried cell mass (Zhai et al. 2015a; Kojima and Zhang 1999). Figure 5 denotes the production method of micro algal-based catalyst based on a recent filed patent. The potential diversity of algal species which is in millions might have supplied researchers with numerous options for identifying biosynthetic pathway-based potential microalgae strains using their genetic data.

Fig. 5 Production method (Quanyuan et al. 2019)



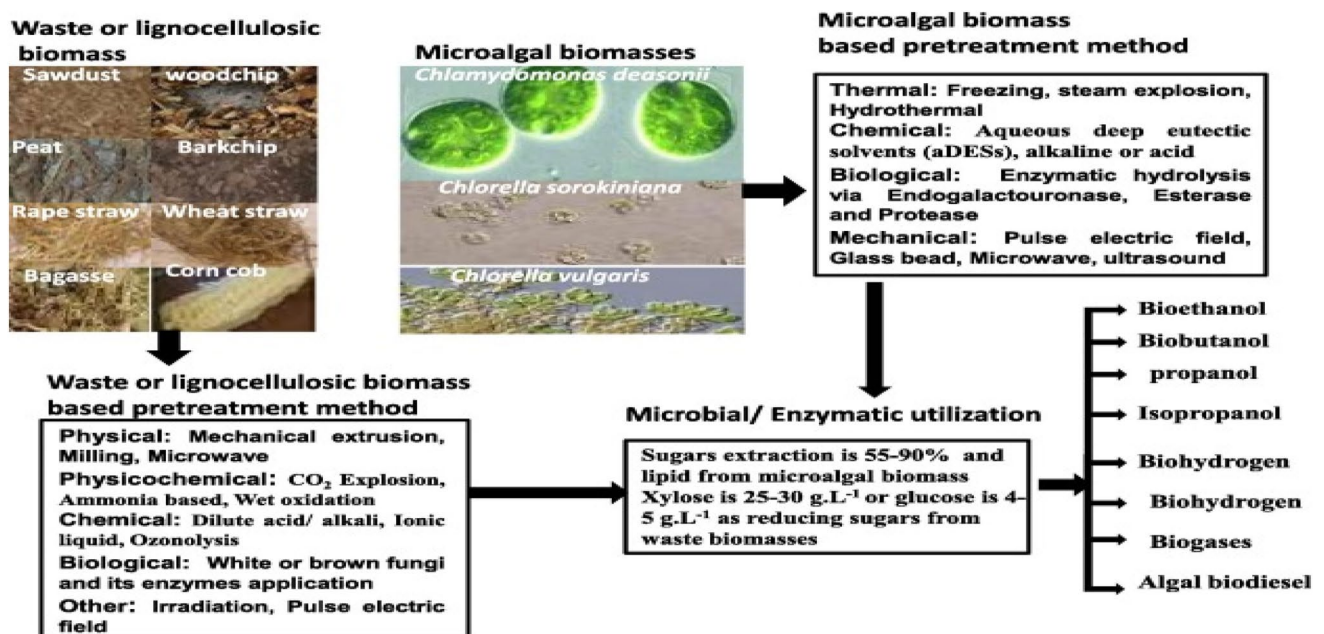


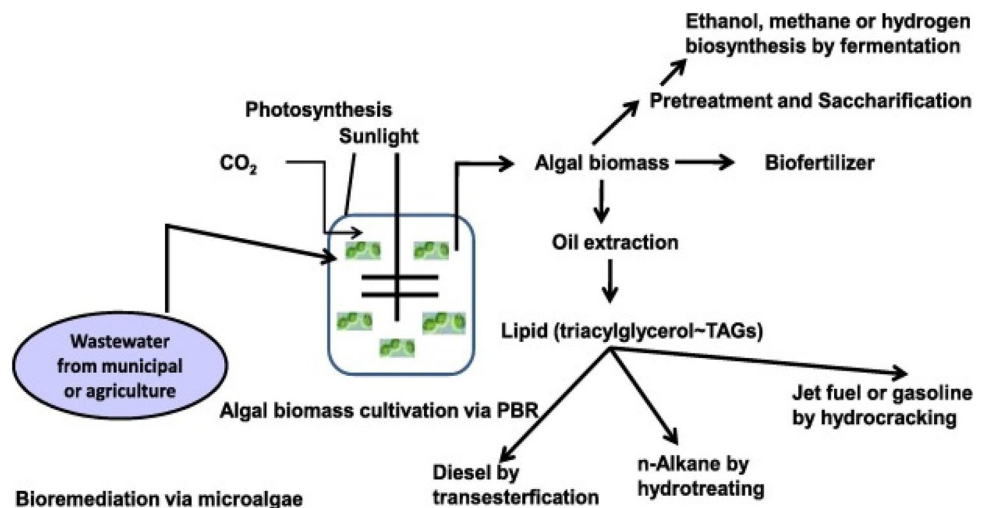
Fig. 6 Bioenergy sources from different types of waste and algal biomasses (Srivastava 2019)

Microalgal species have the potential to be removed from waste streams during treating wastewater, where they are used to remove nitrates as well as phosphates before being disposed of as effluents. Figure 6 denotes the different types of algal biomass and various biodeisel variants prepared out of it.

The procedure of farming of microalgae biomass along the unwanted water creeks is found to be the remedy for wastewater with algal based biofuels manufacture through competing monetary scale. These possessions held by the microalgae is being provided as an appropriate forum through additional prospective for the growth of economical biofuels production (Parker et al. 2008; Ramesh et al.

2020). Enhanced engineering practise is being contributed an imperative role over the augmentation in blending of algal based biofuel that must be additionally influenced through the effective methods protocols for the nutrient ingredients flow as well as the irradiation energy from light. The construction of photo-bioreactors (PBRs) is used by professionals (in engineering as well as biology) to combine the abilities of organisms to nurture effectively in accessible mechanisms with low cost for processing while maintaining axenic as well as quite good controlled development ecosystems besides productivity increases and significantly reduced the contamination through the improvements in the latest progression in the technologies for cell production,

Fig. 7 Resources for biofuel (Srivastava 2019)



harvesting as well as extracting oil with the aid of algae based biomass (Douskova et al. 2009; Hannon et al. 2010) and it is shown in Fig. 7.

Since ancient times, high requirement for supplementary existence with increased energy usage is being met by producing algae biomass in more expensive plant designs with even more costly production. However, recent advancements in bioreactor project development (i.e., toward more affordable constructions) may resolve the above issues. Through the usages of large exogenous uncovering surfaces and the interior side layer with light absorption structures, as well as gas mobilisation mostly through structural components, numerous designs with particular pilot level plants still have potential besides efficacious blending as well as increased light radiation dissipation. These initiatives may bring the formulation of microalgal-derived biofuels nearer to being a financially feasible procedure in certain pilot plants. It also can operate on such a limited scale because within a specified period of time by conducting the monetary evaluation process (Wen et al. 2009).

Utilization of eukaryotic algae organisms is already demonstrated for the manufacturing process of clean energy biofuels as well as bioenergy carrier. Different microalgae organisms have been found to biosynthesize starch additives besides alcoholic biofuel, lipid compounds for diesel fuel producers or originators, as well as hydrogen for clean fuel cells. Microalgal organisms have a greater capacity for converting radiation energy into other biofuels substances than terrestrial source biofuel feedstocks such as higher plants (agricultural crops) due to their ability to thrive in salt water systems as well. Recent times, a great deal of beneficial research has been conducted with the goal of identifying a few really bioenergy-contributing genes as well as metabolic processes in various species of microalgal species through the implementation of efficacious genetic components. Rapid advancements in research capability enable the enhancement of genetic components for the manufacturing of target-based biofuels in microalgal species (Srivastava 2019).

Microbes with high efficiency it has demonstrated their capacity to generate electricity when used in the design of microbial fuel cells (MFCs). Efficient MFCs have demonstrated direct implementation in the creation of additional microbial energy extracting facilities. MFCs are commercially available polymer electrolyte membranes (PEMs) that include fuel or a machine and do not require fuel exfoliation. MFCs are composed of biocompatible materials; they function at room temperature as a biological catalyst for self-generation of electricity all through treating wastewater via anaerobic treatment but rather energy extracting techniques. Numerous MFC designs are developed on a large scale, starting with low power densities or compactness and progressing to the highest densities possible with the best

MFC systems. The increased wide range of designs for MFC apparatus has accelerated in recent years as MFC progresses in terms of power concentrations (Ramesh et al. 2020; Lehr and Posten 2009).

Scenedesmus abundans microalgal biomass revealed its competence for additional lipid combinations, decent resource of fatty acids and greatest biodiesel properties due to the presence of several phosphate compounds intensities. Phosphate intensities (60 milligrams per litre) are being developed from the biomass (of 0.77 grams per litre) through lipid titration (of 0.18 grams per litre) although intensity of light is also used to produce a biomass of 0.74 grams per litre in presence of same amount of lipid titration. On the pH six or eight, biomass (of 0.77 g per litre) as well as the lipid intensities (of 0.18 g per litre) are being stated as the best biomass stage or lipid intensity state. All the actions of growing are being shown as an effective impact over the fatty acid bio-synthesis technique as well as biodiesel nature of the harvesting oil combinations (Beer et al. 2009; Biffinger and Ringeisen 2008; Ho et al. 2013b). (FAMEs—Fatty Acid Methyl Esters) based biodiesel nature are being checked to ensure the fuel quality with the aid of renowned standards for biodiesel including Indian, European as well as American to evaluate the bearable conditions of raw material as algal oils as biodiesel resources as well as little extra cases is revealed in the following Table 6.

For biodiesel manufacturing, beneficial applications of fresh water-based green microalgal organisms *Scenedesmus abundans* (employ as a considerable material resource) is being grown in various cultivation conditions including such as BBM, B-11 as well as modified H-13 for the cell production along with the lipid constituent production. Reformed constituent of H-13 based medium is being shown the uppermost biomass of 1.1 g per litre along with the lipid production of 0.49 g per litre and KNO_3 of 0.32 g per litre. Numerous techniques for exacting the lipids and the biodiesel trans-esterification process were analyzed since they possess fatty acids constituting sixteen to eighteen carbon chain length and due to the diverse nature of biodiesel. These were stated with respect to the Brazilian National Petroleum Agency along with the biodiesel standards of Europe as a prospective feedstock to produce the biodiesel (Papilo et al. 2017b; Ramesh et al. 2021a).

Agricultural crop biomass residue

Agricultural undertakings are being carried out by farmers all through their plant cultivation as well as these are being generated massive amount of non-wet biomass discarded remainders. Crop grownup remainders or wastes have been left over in the agriculture land and it is being reduced the soil erosion along with the nutrients recycling process back into the soil itself. Crop-based biomasses waste are being

Table 6 Bioenergy by natural sources and biodiesel yield

S. no	Floral biomass	Derived oil from natural source/oil feedstock	Comments on reaction or by-products	Total yield	References
1	<i>Scenedesmus obliquus</i>	Bioethanol and Algal biodiesel	489 mg/l of lipid yield obtained	99.7% of ethanol	Lehr and Posten (2009)
2	<i>Scenedesmus abundans</i>	Algae biodiesel	1.14 g/l of biomass and 0.51 g/l of lipid yield obtained	Biodiesel with carbon chain length of C16 and C18	Beer et al. (2009)
3	<i>Chlorella vulgaris</i>	Bioethanol and Algal biodiesel	50.51% of Carbohydrates and lipids were obtained	92.3% of ethanol	Biffinger and Ringeisen (2008)
4	<i>Chlamydomonas reinhardtii</i>	Biodeisel lipid/Ethanol or Hydrogen	60.2% of carbohydrates obtained	0.24 g/DCW ethanol	Ho et al. (2013a)
5	Green algae	Ethanol	44.2% sugar yield obtained	29.2% of ethanol	Ho et al. (2013b)
6	<i>Chlorella vulgaris</i> JSC-6 biomass	Biohydrogen and Biobutanol	91.25 mol/mol of sugar obtained	99.2% of ethanol and 105.3 g/Lh of hydrogen	Blinová et al. (2015)
7	<i>Rhodococcus opacus</i> PD 630	Lipid	Corn stover hydrosylate was alkali treated and used	1.32 g /l of lipid	Harun and Danquah (2011)
8	<i>Rhodospiridium toruloides</i> Y2	Lipid	Production catalysed by food waste along with detoxification	7.29 g/l of lipid	Dubini (2011)
9	<i>Rhodospiridium kratochvilovae</i> HIMPA	Lipid	Aqueous treatment of fruit pulp was made	4.78 g/l	Choi et al. (2010)
10	<i>Yarrowia lipolytica</i> QU21	Lipid	Industrial waste along with glycerol was used	1.29 g/l of lipid	Nguyen et al. (2009)
11	<i>R. opacus</i> PD630. Xsp8	Lipid	Xylose was used along with two different genes for yielding	11.2 g/l of lipid	Wang et al. (2016)
12	<i>Cryptococcus curvatus</i>	Lipid	Sulphuric acid waste treatment	2.81 g/l of lipid	Hannon et al. (2010)
13	<i>Cryptococcus curvatus</i>	Lipid	Non-detoxified hydrolysate and acid pretreated wheat straw was used for yielding	5.85 g/l of lipid	Wen et al. (2009)
14	<i>Escherichia coli</i>	Fatty acid Methyl ester (FAME)	Ionic liquid pretreatment	1.32 g/l of FAME	Srivastava (2019)
15	<i>Pseudomonas fluorescens</i> and <i>Candida rugosa</i>	Palm oil biodiesel	Lipase AK and AY combination	91% of biodiesel	Biffinger and Ringeisen (2008)
16	<i>Chlorella vulgaris</i> ESP-31	Lipid	Lipase immobilized using Iron oxide and silica nanoparticles	More than 90.5% of lipids	Blinová et al. (2015)
17	Novozym 435	Acid oil based biodiesel	Methyl esterification reaction with 10% glycerol	91.5% of biodiesel	Harun and Danquah (2011)
18	<i>Penicillium expansum</i>	FAME	Full fatty acid conversion with blue coloured silica gel adsorbent	92.8% of FAME	Dubini (2011)
19	<i>Fusarium heterosporum</i>	Phospholipids	Reverse micelle formation reaction with water rich content	94% of phospholipids	Kakucs and Kun-Szabó (2009)
20	<i>Enterobacter aerogenes</i>	Methanol	Deactivation and conversion of tetrabutanol	70% of methanol	Brosowski et al. (2016b)
21	Meretrix venus shell	Palm olein oil biodiesel	Calcination of shells at elevated temperatures	93.1% of olein oil	Papilo et al. (2017)
22	Dolomite rock	Palm kernel oil biodiesel	Calcination of rock at 800 °C	98.2% of biodiesel	Mandotra et al. (2014)

Table 6 (continued)

S. no	Floral biomass	Derived oil from natural source/oil feedstock	Comments on reaction or by-products	Total yield	References
23	Labeo rohita	Soybean oil based biodiesel	Calcination of Labeo fish scales	98% of soybean oil biodiesel	Brosowski et al. (2016b)
24	Sheep bones	Canola oil-based biodiesel	Calcination at elevated temperature to get HAP and calcium nitride further	95.5% of canola oil biodiesel	Brosowski et al. (2016b)
25	Mussel shell from fresh-water	Chinese tallow oil based biodiesel	Deionization and activation after calcination	90.2% of tallow oil biodiesel	Ramesh et al. (2021)
26	Oyster shell	Soybean oil biodiesel	Calcium oxide synthesis through calcination of shells	98.6% soybean oil-based biodiesel	Ramesh et al. (2021a)
27	Lime mud	Peanut oil biodiesel	Calcium oxide synthesis through calcination of mud	94.6% of peanut oil biodiesel	Nguyen et al. (2009)
28	Chicken eggshell	Palm olein oil biodiesel	Calcination of shells at elevated temperatures	94.3% of olein oil biodiesel	Ramesh et al. (2021)
29	Golden apple snail shell	Palm olein oil biodiesel	Calcination of shells at elevated temperatures	93.5% of olein oil biodiesel	Ramesh et al. (2021)
30	Quail eggshell	Palm oil biodiesel	Treatment of shells with 0.05 M hydrochloric acid and synthesis for calcium oxide	98.2% biodiesel	Ramesh et al. (2021)
31	Pig bones	Refined palm oil biodiesel	Calcination to obtain HAP and further reaction catalysed by potassium carbonate along with bones	90.6% biodiesel	Brosowski et al. (2016b)

utilized towards synthesizing the energy combinations without affecting the fertility of the soil. Other resources for the sustainable unwanted residue from milk whey sugar which is the left over from cheese manufacturing companies as well as compost organic amalgams (manufactured from livestock operating zones) is being provided the extra profits through its consumption for manufacturing of bio-energy through reduction of discarding costs along with effluence speediness. Consumption prospective of biomass from solid plant (forest) is being reported for the purposes of combustion (of around 455 TJ per acre) in a sub region of Hungary as well it is feasibly accessible there for the thermal energy generation with assimilation structured profile. It might employ to substitute natural substance in gases state or diminish fossil fuel usage for thermal generation in the common—housing sector including such Ajka Power-Plant. Beginning from the solid biomass, the supreme prospective of 1020 TJ per acre of bio-energy might be utilised for industrial as well as agricultural division through mitigation of firewood disputes (Knápek et al. 2015).

Numerous applications of biogenic by-products, ingredients, leftover parts, as well as waste material have provided substitute carbon resources besides renewable resources. The authors present a 4—stage categorization

of appropriate biomass volume as well as a structured comparative analyse of the established form. Theoretical as well as technical analyses of dry biomass prospects have been presented in conjunction with its prevailing use as a precursor material as well as principal energy resource in Germany (currently 6.9%, with even an objective of 12.8%). There seems to be data on a total of 93 distinct biomass variants with a technological biomass prospects ranging from 93.1 to 122.8 million Mg (DM) and a per capita consumption of 1,500 kg. There are reports of 63.1–72.2 million Mg (DM) in existing use, but only 26.9–46.9 million Mg (DM) in underutilised situations. Required to manage the integrated and reliable essence of biomass feedstock can indeed be completed in a prospective way besides bioenergy manufacturing (Baum et al. 2013).

Consumption of biomass for electricity generation can indeed be accomplished by continuing to increase the electrification ratio in order to accomplish nationwide energy security Untapped potential for biomass-based supply exists in agricultural as well as plantation contaminants (cassava stalks, dried rice straws, straw along with rice husk, rice chaff, corn cobs, corn stalks, shell residues, fiber, liquid waste residues of palm oil processing factories, empty

bunches fruits as well as kernels. Imaginative research efforts can indeed be conducted by calculating the conceptual energy potential value of 7.69×10^7 GJ/year) using statistical modelling methods established by BEE—Biomass Energy Europe. This value is approximately equal to generating electricity of 2.14×10^7 MW/h per year that could also be utilised as an alternative source of energy (Zhai et al. 2015b).

Sophisticated ways of investigation of energy along with the economic analysis of capable practises for diverse variants of biomass is being reported through giving their method of handling along with method of usage aiming at the energy expansion. Liquid nature biofuels compounds, bio-methane, electric power as well as heat energy production is being reported to harvest from transformation methods through production of finally used of energy based bio-products. Recognising of the complete biofuel production pathway is being searched for the each as well as separate methods of manufactured biomass along with analysis technique of energy efficacy evaluation that is based on net-energy worth assessing from 1 hectare of plant growing area. The modifications in fuel—biomass production path is found owing to variations in biomass production transformation capability methodologies as well as final used energy bio-chemical products. Efficacy of bio-mass use is being analysed with actual ways of use of biomass planting techniques with transforming tactics along with economical efficacy parameters of the distinct constituents of the biofuel path in the situations in Czech Republic (Gan and Smith 2012; Melis 2009).

Production volume of Polish agriculture with regard to biomass are being utilized for energy generation. Prospective of agricultural biomass in Poland by 2020 is reported in 3 key zones;

1. Probable ingestion of renewable energy dependent on energy type
2. The energy prospective from agriculture remainders
3. Obstacles to the usage of biomass.

In upcoming (2020) for Poland, the total energy consumed will suggestively intensification (over 10%) that will be resilient mandate for transport bio-fuels as well as electricity expectant to derived from renewable energy resources (80%). For this tenacity, 1.0 to 4.3 million hectare of crops is being used for energy generation along with the accelerating share of biomass for heat, electricity and biofuels generation (KarimiAlavijeh and Yaghmaei 2016).

Progress of novel energy sources along with optimization of the energy supply organisation might be prevented the energy deficiency issue by the energy saving as well as emission lessening in the GHGs. Concept of agriculture based energy synthesis as well as building of an agricultural

depend energy design along with technical skill oriented procedures is being designed to supply the energy resources as well as its mandate to several remote regions. In countries like China, for numerous energy sources they depend on other countries are being reported by blend of several accomplishments of agriculture field in the energy producing sector. Know-how equipment besides the manufacture method with agriculture as well as forest sectors for energy sources are being used over this system. Marginal fields of under developed plants based biomass in China, along with its energy plants germplasm sources as well as forest and agriculture depend unwanted energy—encompassing feed-stock sources are being reported as biomasses sources. Economic, social, as well as environment depend viable growth in China might be fulfilled the energy holding method with reduction emission includes CO₂ (Ibrahim 2012).

Numerous types of biomass resources are being potentially utilised for the production of biofuel. Economic standard for the allocation of biomass might be assessed by the profit of woody biomass process depends on the case study of 2-bio-products. Implementation of mixed-integer programming model might aid in distribution of several methods of biomass feedstock in practise of production of diverse biofuels ingredients as well as several methods of by-products in the optimization method of chemicals supply chain as well as limited cases is presented in the Table 7. This method tactic is originate to assist in forest grown biomasses implementation through aiding in distribution issue in the US—East Texas. Biofuel synthesizing scale, carbon dioxide reduction strategy, as well as absolute price, is being found to be considerably important which is affecting the distribution of biomass implementation with beneficial effects on improving the remarkable way for forest origin biomass (Najafi et al. 2009).

Table 7 Quantity of oil extracted from agro based material sources

S. no	Natural catalyst source	Quantity of biodiesel (gal./acre year)
1	Algae	5000–20,000
2	Oil palm	635
3	Coconut	287
4	Jatropha	207
5	Rapseed	127
6	Peanut	113
7	Sunflower	102
8	Safflower	83
9	Soybeans	48
10	Hemp	39
11	Corn	18

Biogasification

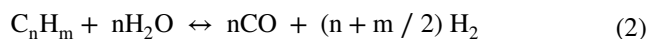
Many researches are being currently carried on the development of biomass gasification plants during the previous decades to install and operate these plants at industrial and commercial scale. Few authors experimentally stated that the major hindrances in installing and operating biomass gasification plants were due to the rendering of undesirable products like alkali metals, tar, carbon deposition, PM and nitrogenous complex deposition over the produced catalysts (Balaji et al. 2021). Tar is the major constituent of those undesirable products and it comprises of hydrocarbons with oxygen and condensable aromatic compounds. These compounds resulted in corrosion and blockage of the process path when developed during the reaction, thus deteriorating the quality of syngas produced (Ballesteros et al. 2002; Gelfand et al. 2013; Nitsos et al. 2017; Nitsos et al. 2016; Achinas and Euverink 2016; Ferm 1993). Though, tar degrades at higher temperatures, increasing the process temperature above certain limits increases the overall system temperature resulting in agglomeration of ash and fall of system efficiency (Matsakas et al. 2018). Defluidisation and bed sintering of fluidized bed gasifier plants were caused by alkaline materials while ash is responsible for the corrosion of system components (Jang and Choi 2018; Raganati et al. 2012; Bhuvaneswari et al. 2021). Many researchers emphasized on the disintegration of catalytic tar at higher temperatures through an optimized and cost effective process (Achinas and Euverink 2016; Ferm 1993; Banowetz et al. 2009; Milne et al. 1998; Asadullah et al. 2001; Dhepe and Fukuoka 2008; Dietenberger and Anderson 2007; Digman et al. 2009; Baker and Mudge 1984; Devi et al. 2003). Cleaner and enhanced calorific value gas in large quantity could be obtained from tar through enhancement of char gasification by incorporating appropriate catalysts such as dopants into it (Dietenberger and Anderson 2007; Digman et al. 2009; Baker and Mudge 1984; Devi et al. 2003; Mudge et al. 1985; Ramesh et al. 2021b). Current research experiments are giving prime importance to develop highly active and more stable gasification catalysts by using mineral like dolomite, olivine, noble metals and other nickel-based formulations (Asadullah et al. 2001; Sutton et al. 2001; Nishikawa et al. 2008; Aznar et al. 1998).

Usage of catalysts for gasification reaction could be done directly or could be placed in a secondary reactor that precedes the first one. Direct application of catalyst was termed as primary catalysis and for this process some of the major catalytic materials used include dolomite and olivine, alumina-supported nickel which were primarily used for steam reform improvements and in reactions involving water gas shift (Aznar et al. 2006; Hu et al. 2006; Lv et al. 2010; Anbuezhian et al. 2020; Arauzo et al. 1994).

These catalysts normally enhance the yield of carbon monoxide and hydrogen gas while they render lesser tar yields. Alongside, they minimize the agglomeration thus avoiding the gasification reactor bed chocking. But in some cases, experimenters observed that nickel-based catalysts got deactivated because of deposition of carbon on them (Banowetz et al. 2009; Arauzo et al. 1997; Ramesh et al. 2021c; Florin and Harris 2008). The catalysts placed on the preceding reactor were termed as secondary catalysts and these were used to process even gaseous products with catalytic materials like dolomite (Dhepe and Fukuoka 2008). Tar was disintegrated by dolomite at higher temperatures in the order of 750–900 °C and was widely used for hot gas cleaning applications (Digman et al. 2009; Garcia et al. 2002; Garcia et al. 1999; Garcia et al. 1998). When compared with secondary catalysts, primary catalysts were determined to be cost effective since the secondary catalysts increase the cost of production of syngas by a considerable amount. Hence for research experiments, primary catalysts were the first choice of the researchers due to minimal complexity in process during the gas treatment in the downstream reactor (Olivares et al. 1997).

Ni-based catalysts in bio gasification process

Ni-based catalysts are widely used for the purpose of dry and steam reforming process at the commercial scale (Garcia et al. 2002). In fact, these were the first-choice catalysts used for the cracking of tar in gasification reactions due to their superior cracking characteristics and their ability to enhance the reaction of water gas shifting as given in Eq. 1. These catalysts minimize the amount of tar formed and increase the yield of product gas and its quality. Ni-based catalysts were stated to be tenfold more reactive than their counterparts like calcined dolomite (Caballero et al. 2000; Caballero et al. 1997). It was stated in many studies that during biomass catalytic gasification, these catalysts were proven to be highly active for heavy hydrocarbon molecule steam reforming and slightly docile for the lighter molecules as shown in Eqs. 2 and 3, respectively (Digman et al. 2009):



Biomasse Kraftwerk Gaussing & Co. was running a facility to perform biomass gasification with the aid of dual fluidized bed gasifier (DFB) in which tar reformation and syngas removal from specific molecules were carried out by Ni-based catalyst at higher temperatures (Garcia et al. 1999). It was proven by various experiment that Ni-based

catalysts were ideally better for biomass gasification but the performance of these catalysts were hindered by various undesirable phenomenon such as sintering, coking, sulphur and alkali metal poisoning and attrition (Garcia et al. 1998). It was stated in the experimental studies that Ni-based catalysts were poisoned by carbon materials which results in the formation of high-density nickel carbides and formation of inactive carbonaceous layers through the condensation of nickel crystallites (Ramesh et al. 2021b, d; Corella et al. 1998; Kinoshita et al. 1995; Rostrupnielsen and Hansen 1993; Foscolo 2012). Coking of Ni-based catalysts occurs due to the aromatic biomass feedstock which has high molecular weight. Such coking could be dodged in a gasification plant through auto-thermal gasification process in which the formation of coke upon catalyst would be equalized by removal of coke by combustion (Abu El-Rub et al. 2004; Bangala et al. 1998; Bartholomew et al. 1980; Bartholomew and Sorensen 1983). In order to avoid the formation of coke with lesser amount of excessive energy, the threshold limit of steam-to-carbon ratio is considered to be a salient parameter to be evaluated (Rostrup Nielsen 1997).

Another problem faced by the Ni-based catalysts is the attrition in fluidized bed environments which arises due to the process complications in biogasification systems. Complications are more in these systems when compared with fixed bed gasification systems. Mechanical deactivation of the catalysts as a result of attrition could not be completely eliminated but could be reduced by the usage suitable reactors. Support elements such as olivine could be added to the catalysts to improve the mechanical strength of the catalysts which also reduces the deactivation of catalysts during biogasification (Baker et al. 1987). Catalytic activity of Ni-based catalysts could be enhanced by the addition of promoting element or dopant in addition to the support phase. It was observed that dopant-added or -promoted Ni-based catalysts possessed better mechanical strength and had reduced tendency towards attrition and coking (Tomishige et al. 2003; Ramesh et al. 2021e; Dibbern et al. 1986). Reduction of dispersion of metal on the catalysts, coking and crystallite size could be achieved by supporting the catalysts with acidity–basicity supports, pore structure support and interaction of nickel with support (Pfeifer et al. 2011; Wang and Lu 1998a, b; Lasa et al. 2011).

Other organic metal-based catalysts for biogasification

Utilization of alkali-based catalytic materials like dolomite which is made of calcium magnesium carbonate and olivine which is made of magnesium iron silicate were the highly used catalysts for the gasification of biomass and has attracted many researchers in the past decade. Tar cracking was investigated majorly based on the usage of

these dolomite and olivine materials by many researchers. Few authors investigated the catalytic activities of dolomite and olivine after calcinating and applying them in a reactor with movable bed and they stated that the performance of calcinated catalysts were superior to the non-calcinated ones (Devi et al. 2003). Same working setup was devised by few other authors to demonstrate that tar cracking increased at a temperature range of 800 °C and 900 °C when non-calcinated olivine and calcinated dolomite were used as catalysts. It was also noticed by the authors that at 900 °C, conversion of heterocyclic species occurred. It was also observed that initially the tar yield was 4 g/cu.m without catalysts' use and it reduced to 1.5 g/cu.m and 2.2 g/cu.m when calcinated dolomite and olivine were, respectively, used (Devi et al. 2005).

Owing to the cost-effective nature and free availability, limestone and olivine were broadly used as catalysts for biomass gasification. Specifically, these materials were utilized in fluidized beds in which the catalysts were affected by attrition due to the complex process conditions. In various studies, it was stated that when compared with silica or olivine, limestones undergo much attrition at the time of gasification reaction (Quyn et al. 2002). Mohs's scale of hardness was used for the measurement of hardness factor which directly governs the attrition at the time of gasification reaction. Attrition in DFB was also governed by the gas velocity type of particle separator function used after the riser (Wu et al. 2002; Lee et al. 2000; Ramesh et al. 2021f; Voloshin et al. 2016).

Potassium and sodium are the main types of alkali metals which were usually present in all class of biomass feedstocks as inorganic material constituent and these metals were also present in the ash settled at the bottom of the gasifier plants. At the time of pyrolysis, these metals result in the formation of highly reactive char which have adverse effects on the bio-gasification plant functioning. Hence usage of ash itself as a catalyst might solve this issue by not only undertaking the problem of ash disposal under control but also resulting in producing cleaner gases during the gasification reaction (https://www.researchgate.net/figure/Comparison-of-algae-with-different-crops-for-biofuel_tbl4_233746441, 2021; Balaji Devarajan et al. 2021; Nigam 2011; Abdelaziz et al. 2013; Xu et al. 2006). Yet, particle agglomeration was the result when these metallic particles were used as a catalyst and hence the catalytic effectiveness of the metals eventually reduced. Direct application of alkali metal catalysts resulted in higher formation of char after gasification reaction, ash handling issues and expensive and complex catalysts' recovery along with many other issues (Scoma et al. 2012; Gronenberg et al. 2013; Eroglu and Melis 2016). In few studies, Ni-based catalysts were added to the gasification reaction along with sodium carbonate placed in rice straw.

Astonishingly, the results showcased that the permanent gas generation from the gasification significantly increased (Ramesh et al. 2021g; Hasunuma et al. 2013). It was stated by the authors that the amount of alkali metal carbonate catalysts directly governed the quantity of permanent gases generation. From all the above discussions, it could be stated that the usage of catalysts derived from wastes and natural sources had many positive impacts over the bio-gasification process.

Catalysts from microalgae

Bio-based fuels are currently considered to be the potential alternatives for the fossil fuels which are not eco-friendly and exhaustible in nature. In many of the recent studies, algal biomass has been considered as a special feedstock to produce catalysts in synthesis of biofuel. Cultivation of algae may not regressively require an agricultural land where food crops grow and this will affect the cultivation of such crops. Besides, the extraction of algae does not demand a complex pre-treatment process when compared with the treatment process of lignocellulosic-based biomass. Since many species of microalgae comes under mixotrophs, they can be readily employed in sewage purification and also in energy source feedstock at the same time (Atsumi et al. 2009; Lindberg et al. 2010; Carere et al. 2012). Cultivation of biomass is the most important process as far as the algal biofuel synthesis is concerned, while for this process open-air systems, which are cheap and simple, and photo-based bio reactors, which offer better cultivation control, are employed in recent times. Conversion of biomass into biofuels can be categorized into major steps such as biochemical, thermochemical and chemical methods and direct combustion. Transesterification process was used for the production of biodiesel from triglyceride rich biomass and fermentation process was used for the production of bioalcohol from the corresponding biomass. Microalgal cells were also used for the production of biohydrogen through three major methods such as fermentation, indirect biophotolysis and direct biophotolysis as stated in few literature (Cha et al. 2013; Ho et al. 2013c). Table 7 denotes the gallons per acre per year of biodiesel production by using natural wastes and plants as catalyst materials. From the table it could be noted that the biofuel output from algal biomass was very high when compared with all other natural materials.

Currently, research focus has been given for the development of biofuel from algal biomass with higher efficiency and enhanced effectiveness. Focus was also given towards a fact that the developed third-generation biofuel must overcome the drawbacks in the first two generation biofuels (Verbeke et al. 2013; Ilmen et al. 2011; Tai and

Stephanopoulos 2013). Many research works were carried out in developing and optimizing the open-air or photo bioreactor technique of algae cultivation and also keen in discovering the most highly productive species of microalgae and the methods of genetic modifications (Ramesh et al. 2021h; Buijs et al. 2013; Ganesan et al. 2020). Besides, research works carried out in using the co-culture of algae as biomass source was also carried out simultaneously (Biofuels 2014). Few researches in this perspective were carried out using *Saccharomyces cerevisiae* for the production of third-generation bioalcohol was carried out which was used as a model algal organism (Day et al. 2014; Ramesh et al. 2021i; Dewulf et al. 2005). It was stated in the research that the energy market was not experiencing the competitiveness of third-generation biofuels, as they were at the phase of initial development. In spite of the availability of numerous exhaustive bio reactors, algal material feedstock had not become a popular raw material for the production of third generation of biofuels for engines. This could be possibly due to the non-availability of the optimized algal cultivation methods which hinders them from being applied for the production of third generation biofuels (Sohel and Jack 2011; Chisti 2008). Algal organisms were used not only as the energy source for biofuel production but also for the production of cosmetic and pharmacology compounds. Current researches and experiments on algal biomass portray that the algal biomass is extensively utilized in various applications such as genetic engineering of crops, inventing advanced harvesting techniques, optimization of thermal and chemical method for biofuels synthesis of and improvement in algal biomass rate of growth. Such research growth is possible due to the growth of energy demand, need of energy from eco-friendly systems unlike fossil fuels and the demerits associated with the first two generation of biofuels (Huang and Percival Zhang 2011; Wang et al. 2013; Vliet et al. 2009; Ramesh et al. 2021j). Commercialization of algal biomass could be done by enhancement of cultivation of algae and optimizing their mechanism of processing which needs a considerable research and experimental works. Yet, in near future, algal biomass-derived biofuels serve the purposes better in terms of energy requirement in a cost effective and eco-friendly manner (Paster et al. 2011). Figure 8 denotes the method of extraction of microalgae from biomaterials that could be used as catalysts for biodiesel production.

Figure 9 denotes the efficiency of biodiesel extracted from various natural sources. From the figure, it could be observed that the knot reject (KR) based catalysts (0.15 inch dimensions) derived from ethanol based biodiesel resulted in higher efficiencies when compared with all other waste derived catalysts.

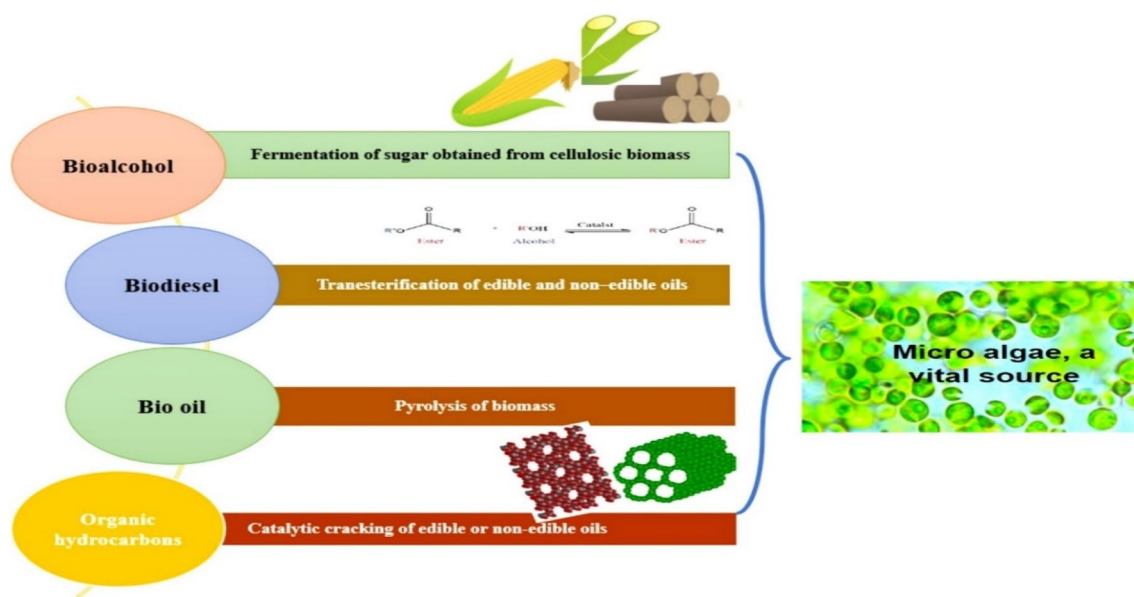
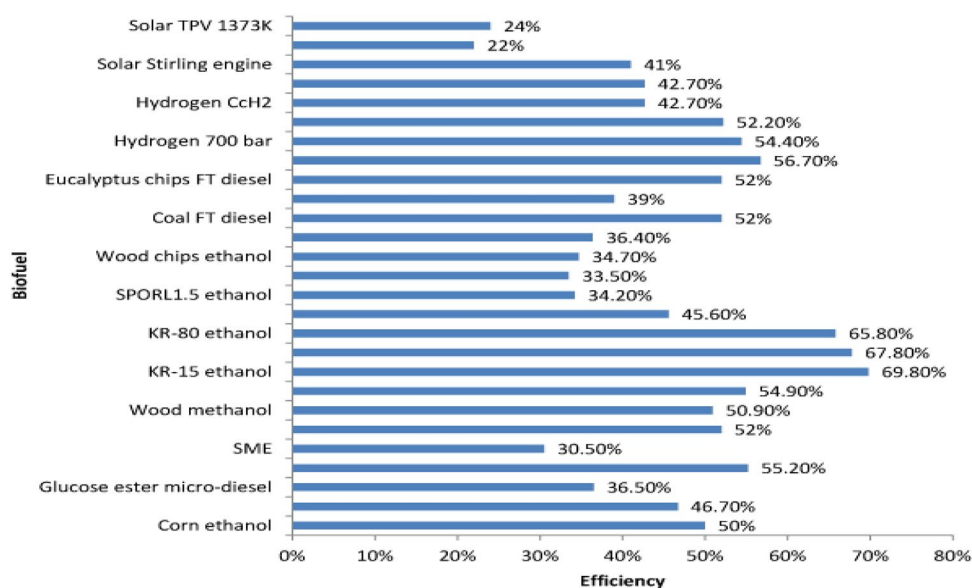


Fig. 8 Methods of extraction of biomaterials from Micro algae (Ganesan et al. 2020)

Fig. 9 Efficiency comparison (Day et al. 2014)



Catalysts for processing of pyrolysis oil

In order to generate biodiesel, pyrolytic thermal decomposition technique is commonly used without the presence of oxygen while the range of products rendered by this technique depends upon residence time, feedstock type and temperature of the reaction. It is a well-known fact that bio-oils consists of alcohols, sugars, acids, ketones, furan, esters, aldehyde, cellulose and hemicellulose derived multifunctional compounds and lignin derived compounds (Chen et al. 2012; Wernsman et al. 2005).

Figure 10 denotes the typical process of extraction of bio-oil from lignin and cellulose. The resulting pyrolysis oil was characterized by high viscosity and lower combustion characteristics owing to their degradation through condensation and polymerization reactions and these reactions result from the instability of nuptial biodiesel at ambient conditions due to its higher corrosive and acidic tendency. Besides, the stability of the biodiesel was further affected by its strong acidic nature due to the presence of organic acids within them and this also affects the catalysts' life-cycle which was used to transform the bio-oil to biodiesel through the process of hydrogenation (Wilson and Lee

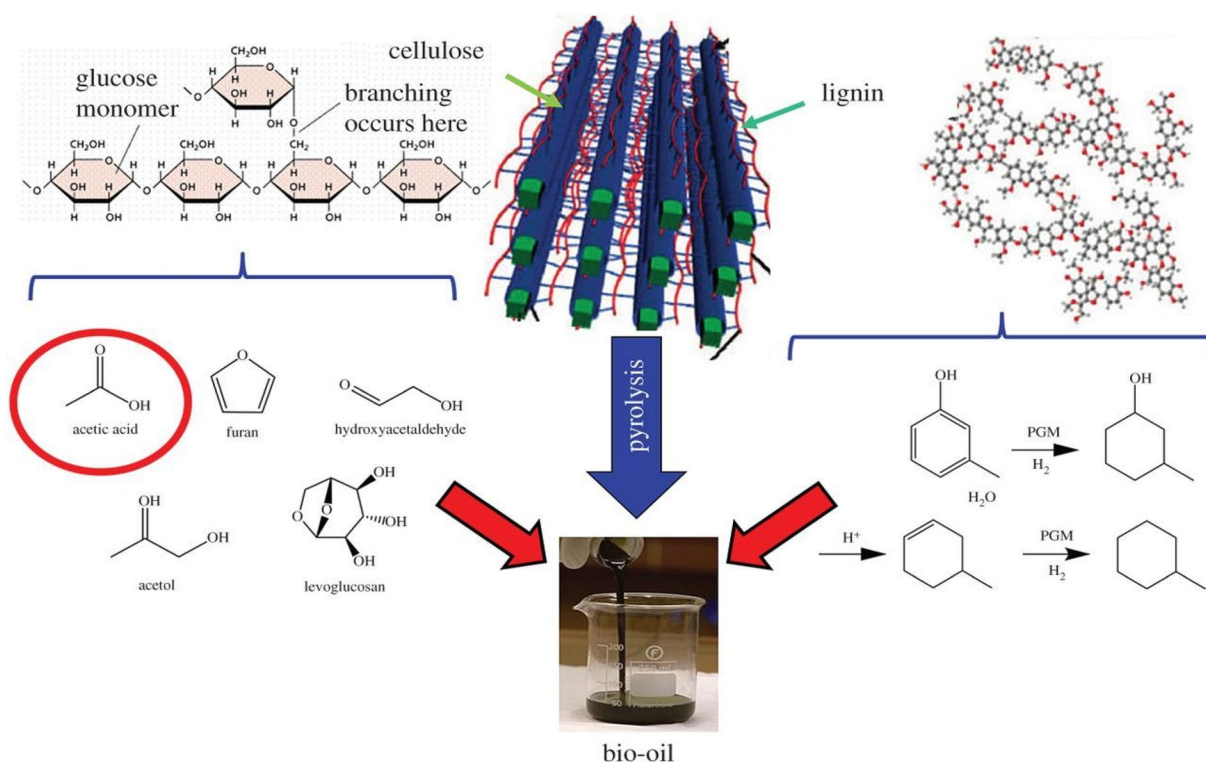


Fig. 10 Bio-oil products from lignin and cellulose (Wilson and Lee 2016)

2016; Wilson et al. 1999; Margolese et al. 2000). From few experimental studies, the stability of the biodiesel, before transporting and storing them, could be enhanced through the process of esterification of acidic components responsible for corrosive nature prior to upgradation of oil to fuel (Díaz et al. 2000; Dhainaut et al. 2010; Schumacher et al. 2005). Even though the usage of strong acids like sulphuric acid could effectively catalyse the esterification reaction, their usage was restricted due to their hazardous and corrosive nature.

In few other studies, it was proposed that sulfonic acids could be used as effective catalysts for esterification reactions but the silica surface's hydrophilicity remained as a constraint due to the cause of favourable situation for H₂O adsorption from hydroxyl groups. Introduction of organic functional groups during surface modification of polar surface oxides reduces the polarity of the molecules and the rate of transformation of liquid phase organic molecules were increased during acid catalysis (Ramesh et al. 2021k). Hydrophilic silica surfaces could be converted into hydrophobic by the incorporation of respective aryltrimethoxysilane or alkyl groups during the process of condensation or by co-grafting of organic groups like phenyl, propyl and methyl groups at the time of sol–gel synthesis reactions undergone by sulfonic acid silica atoms (Dacquin et al. 2010; Luque et al. 2008). In many other research works, some important

experimental facts like the influence of catalyst acidity over the hydrophobic nature of biodiesel, performance during the acetic acid esterification in presence of butanol and acid site density for the MCM-41 materials which were co-functionalized with sulfonic acid were evaluated (Lin 2013). Owing to the presence of more amount of pores and the inherent arrangement of structure of MCM-41, these materials were selected. As a result of their selection, models for accurate kinetic Monte Carlo simulations were given by them and also utilized for the modelling of MCM-41 pores for the dynamic simulation of octyl groups and sulfonic acid attached with them (Demirbas 2007). By conducting two simultaneous experiments, two catalysts were simultaneously used for the esterification of acetic acid along with butanol as shown in Fig. 11 a. In one set of experiments, the coverage of propyl sulfonic acid was varied between 0 and 100% of ML on the substrate of bare silica to form MCM-SO₃H and in the parallel set of experimentation, an octyl co-graft was developed containing both sulfonic acid and octyl groups on the silica substrate to form MCM-Oc-SO₃H. Figure 11b shows the existence of lateral atomic interactions between hydrogen bonding of sulfonic acid head groups along with the free silanols on the surface and these interactions were evaluated with the usage of octyl hydrophobic modifiers that alters the binding of sulfonic acid groups (Shah et al. 2004).

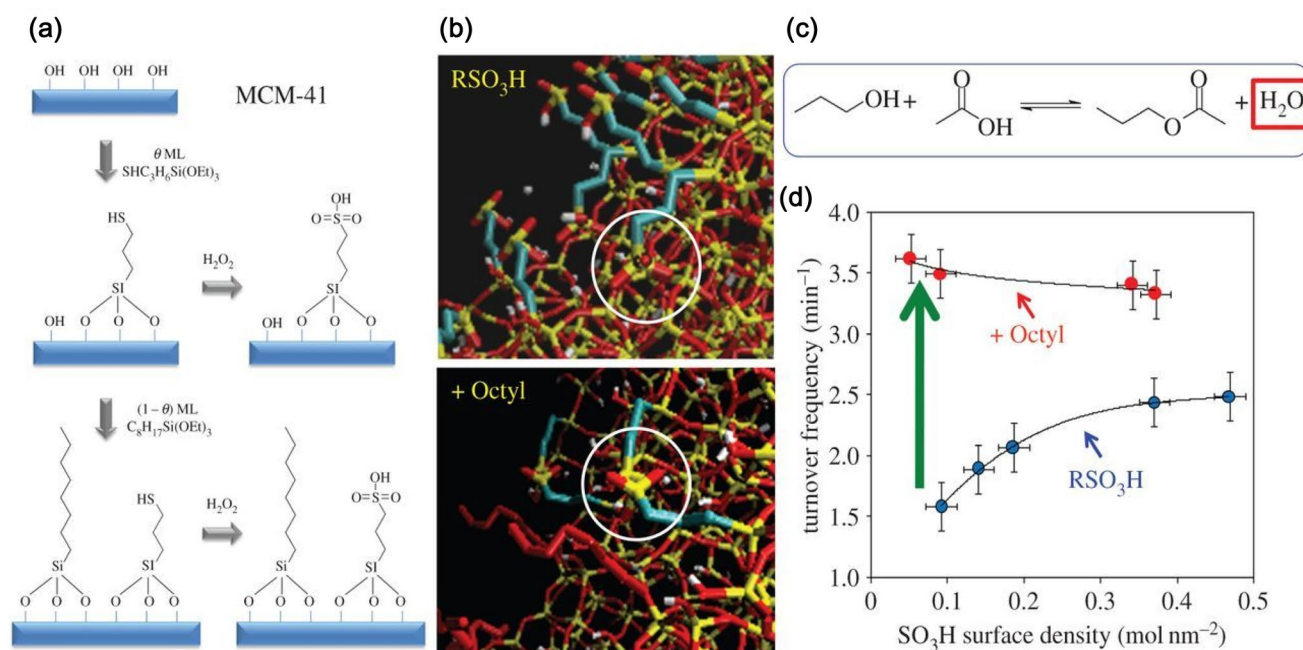
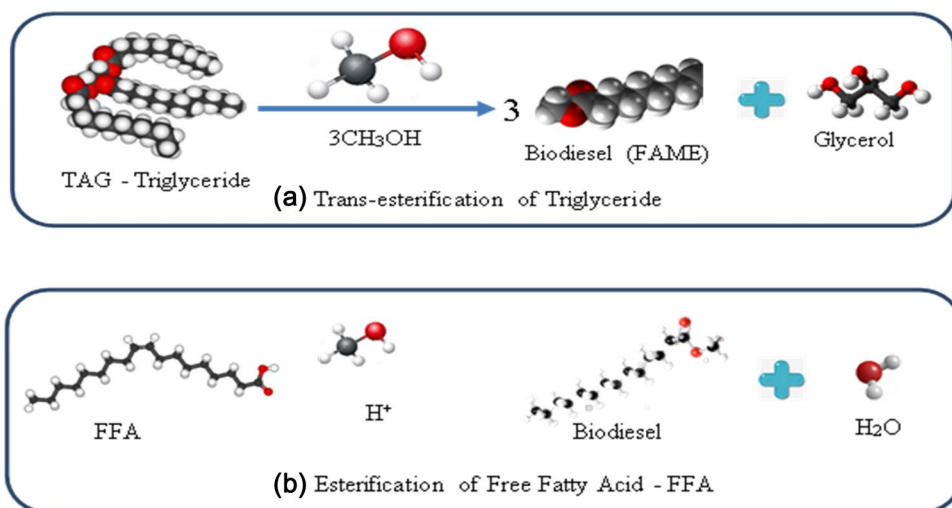


Fig. 11 **a** Sulfonic acid synthesis with octyl functionalization in presence of MCM-41 **b** pore model simulation of MCM-SO₃H with and without octyl functionalization **(c, d)** MCM-41v performance with butanol catalysed acetic acid esterification process (Wilson and Lee 2016).

Because of sulfonic acid loading, the acidic strength of polar grouped MCM-SO₃H materials increased to 118 kJ/mol from 87 kJ/mol and was measured using ammonia calorimeter. On the other hand, octyl co-grafting of MCM-Oc-SO₃H enhanced its acidic strength to 104 kJ/mol due to the coverage of SO₃H monolayer and with $\Delta H_{\text{ads}}(\text{NH}_3)$. As the content of SO₃H increased, the per site activity of MCM-SO₃H also increased during the esterification of butanol with the presence of acetic acid and this mirrored their acidity as shown in Fig. 11c. Turnover frequency of SO₃H monolayer was doubled even at lowest loads due to the esterification of MCM-Oc-SO₃H catalysts which were

promoted by octyl surface functionalization. Lower acidity and lower activity of MCM-SO₃H sub-monolayer materials were primarily due to the interactions of segregated sulfonic acid molecules with silanols surface group of molecules and these were witnessed by molecular dynamic simulations. It was also seen from the results that the acidic strength and the esterification activity was enhanced due to the reorientation of sulfonic acid head groups into interior of the pores and its interactions with octyl groups (Gaudino et al. 2005; Ying et al. 1999; Lu 2006; Mbaraka et al. 2003).

Fig. 12 Esterification of **a** Triglycerides **b** fatty acid



Biodiesel synthesis using tailored porous catalysts

Alternate fuels for blending with or to use in place of conventional fuels to accomplish a low cost renewable transportation fuel can be obtained from the biodiesel which were prepared as a result of esterification of algal-based or plant-based oil triglycerides that results in formation of fatty acid methyl ester as shown in Fig. 12a, b (Ramesh et al. 2020c; Melero et al. 2008; Garg et al. 2009). Commercial production of biodiesel through transformations was carried out through the usage of mineral acid or alkali as catalysts and this process renders a huge quantity of aqueous waste that is highly hazardous to the environment coupled with less economic feasibility. Solid acid catalysts have the ability to catalyse esterification and transesterification simultaneously under mild environments and these catalysts considerably reduce the process steps rendering the usage of even waste oils containing high free fatty acids.

Micropore networks of the active sites were meagrely accessed and the difficulty in mass diffusion and transportation constraints encumbers the performance of

micropores in biodiesel synthesis in traditional solid base and acidic systems. Utilization of solid catalysts with tailored porous structures having a high mesoporous area improves the diffusion of FFA and TAG in basic or acidic groups and this facilitates the improved catalytic activity and development (Chen 2006; Cao et al. 2009). Most widely, mesoporous solids with templated structure were accepted as catalyst supports while SBA15 silica was the highly opted catalyst support that was used consistently during biodiesel synthesis (Dacquin et al. 2012). The Santa Barbara amorphous (SBA) class of materials were manufactured from the copolymer block surfactants such as P123-PEO₂₀PPO₇₀PEO₂₀ (as shown in Fig. 13a, b) and pore diameters of these materials result were high when compared with the materials from HMS or MCM materials with ammonium or alkyl amine surfactants. Yet, the traditionally manufactured SBA15 silica functionalized with sulfonic acid had a lesser pore size in the order of 6 nm within a long and separate parallel channel like structures and these pores facilitate only slower pore diffusion, TAG transesterification and FFA esterification catalytic turnover.

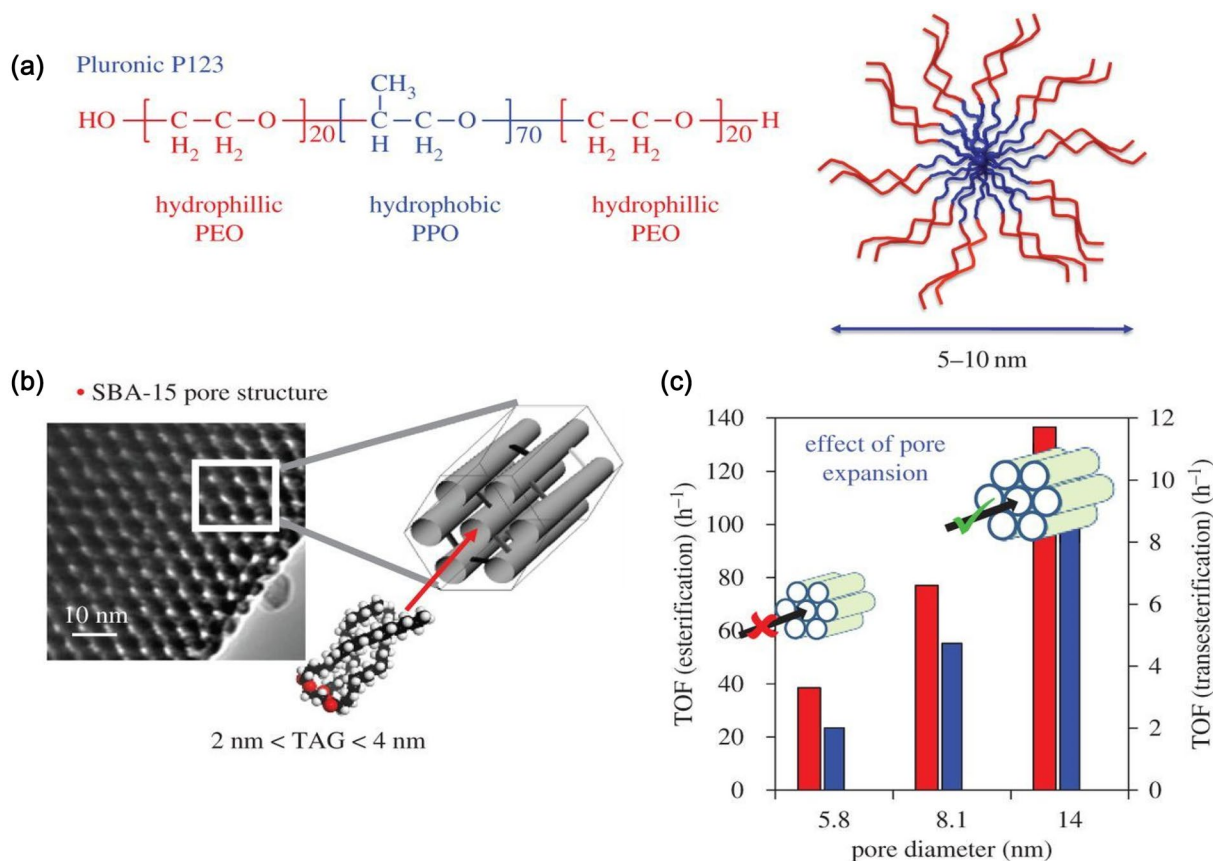


Fig. 13 **a** Structure of Pluronic P123, **b** hexagonal SBA-15 pore structure and **c** effect of pore expansion of RSO₃H/SBA-15 on TOFs (Wilson and Lee 2016)

It was ascertained from the experimental study that the pore diameters could be increased from 6 to 8 nm and 14 nm and a higher order mesoporous structures could be obtained by the use of poragens like triisopropylbenzene, triethylbenzene and trimethylbenzene which causes the increase in pore size by inducing swelling of pluronic P123 micelles (Pirez et al. 2012; Gheorghiu and Coppens 2004; Zhang et al. 2004). Expanded mesoporous SBA15 catalysts functionalized and oxidized with mercaptopropyl trimethoxysilane (MPTS) and hydrogen peroxide respectively renders an effective catalysts that could be used during the esterification of palmitic acid with methanol and tricaprylin and transesterification of triolein under mild environments. TOF was noticed to be higher in SBA15 catalysts which were obtained as a result of higher mass transportation of high density FFA and triglycerides as shown in Fig. 13c.

In order to enhance the mass transport phenomenon of SBA15 mesoporous structure with 6 nm pores, their two dimensional channel of micron length was converted into a three dimensional interconnected long channels with KIT-6 mesoporous silica material. Such transformation possibility offered by these materials renders the quantification of pore connectivity with organic acid esterification process by using various materials like PrSO_3H -KIT-6 and pore expanded propyl sulfonic KIT6 acids manufactured through MPTS grafting followed by oxidation (Ramesh et al. 2021k; Dacquin et al. 2010; Luque et al. 2008; Lin 2013; Demirbas 2007; Shah et al. 2004; Gaudino et al. 2005; Ying et al. 1999; Lu 2006; Mbaraka et al. 2003; Ramesh et al. 2020c; Melero et al. 2008; Garg et al. 2009; Chen 2006; Cao et al. 2009; Dacquin et al. 2012; Pirez et al. 2012; Gheorghiu and Coppens 2004; Zhang et al. 2004; Sun et al. 2003). Traditionally manufactured materials showcased 40% of propanic and 70% of hexanoic TOF improvements during acid esterification when compared with the PrSO_3H -SBA-15 catalyst

with a pore diameter of 5 nm purely due to the mesoporous diffusion within the material. Yet, for longer polymeric chained palmitic and lauric acids, the pore accessibility was limited when used for the esterification process.

Figure 14 denotes the significance of mesoporous catalysts reaction speed and the performance of KIT6 catalysts on biodiesel synthesis. From few of molecular level simulations, it was clearly understood by the researchers that in the region of Knudsen diffusion, hierarchically structured pores enhanced the activity of the catalysts due to the limited diffusion constraints faced by the reactants or products in the entry or exit level mesopores (Bhuvaneshwari et al. 2020). When rapid pore diffusion was needed in flow reactors and liquid phase channels, materials were manufactured using co-surfactant and micro emulsion processing methods that render a bi-modal and interpenetrating mesoporous structural network (Dacquin et al. 2009; Pinzi et al. 2009). In few of the experiments, attempts to combine a soft liquid crystalline nanospheres with hard polystyrene colloids were made to create a silica more alike SBA15 material with macro-mesoporous and an organized structure. In this material, the diameters of macro pores and mesopores could be individually obtained in the range of 200–500 nm and 5–20 nm respectively (Day et al. 2014; Azadi et al. 2013).

When the mesoporic network of SBA15 functionalized with propyl sulfonic acid was incorporated with macro pores, the tricaprylin transesterification rate and the methanol catalysed palmitic acid esterification rate highly improved since the PrSO_3H active sites in the mesopores were swiftly accessed by reactants through the transport path created by the macro pores. From the above studies, it could be stated that the tailoring of porous structures through biocatalysts greatly enhance the transfer rate of molecules through pores, thus facilitating the creation of biodiesel which could be an effective alternative to conventional fuel (Huber and Corma 2007; Vennestrøm et al. 2011).

In conventional bio refineries operation, pre-treatments carried out to segregate sugar from the biomass was considered to be a high waste generation process and this necessitated to be taken care of in newly developed atomic based and energy efficient lignocellulosic based catalyst processing. In this method, initial extraction or hydrolysis process to segregate sugar from the lignocellulosic biomass could be performed under mild environmental conditions resulting in minimal generation of wastes (Bozell and Petersen 2010). Yet, such process advancements were hindered by some basic problems like cellulosic stability and energy-efficient and eco-friendly disintegration of bio polymeric molecules which were the current day challenges. Even though traditional heterogeneous catalysts could not be directly employed in biomass processing

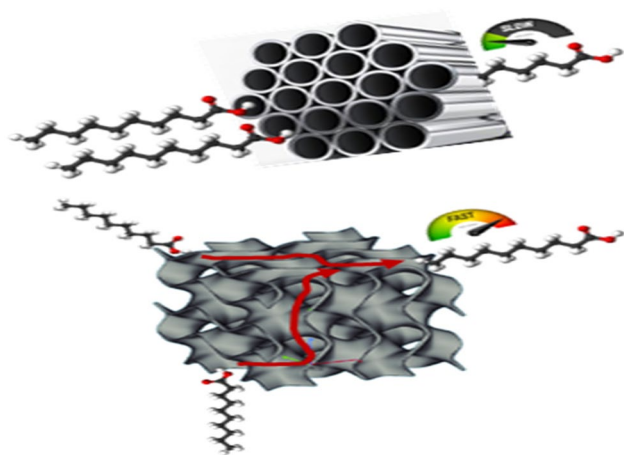


Fig. 14 Performance of KIT-6 catalysts for biodiesel synthesis

solid-phase reactions, few of the recent studies indicated that mechano-catalysis could be induced by ball milling of clay-based, carbon-based or cellulose-based catalysts which contains layered architecture. Innovations in reactor designs could be brought in by the simultaneous working of chemical engineers, catalytic chemists and molecular simulation experts by bringing in integrated process optimization along with development of new aforesaid heterogeneous catalysts. Such innovative reactors produce bio-based chemicals and biofuels from waste biomass and may aid in developing a sustainable process to utilize the renewable feedstock for catalyst production in the forthcoming years (Hick et al. 2010; Dornath et al. 2015).

Summary and conclusion

Various fields of materials science such as nanoscience, process engineering, materials chemistry and surface chemistry were completely explored to ascertain the effectiveness of lignocellulosic biomass from which the advanced fuel for transport use and renewable chemicals were manufactured. By doing so, the advantages rendered by then heterogeneous catalysts could be matched in some process like petroleum refining by some chemists and engineers and this demands the complete understanding of characteristics of the biomass and their influence over the deactivation of the catalysts for enhancing the speed of conversion of biomass into chemicals and production of biodiesel. Development and deployment of biomass and natural derived chemicals-derived next-generation fuels are in extreme necessity of rigorous government policies and appraisal schemes which promotes the use of biomass-derived fuels and chemicals as a potential alternate to widely used fossil fuel-based oils and chemicals. It was also stated in various studies that biomass-derived oils could act as substitutes to crude oil-based derivatives in short and medium term and the process of refining these biomass-based oils and chemicals in conventional refineries would be highly cost saving and this process dodges the high cost incurred by establishing new setups specifically for biomass-derived oils. The impacts created by a biomass-derived chemical could be easily enhanced by making it as a feedstock in place of fossil fuel-derived chemicals for the well-established infrastructure and technology and this acts as a potential raw materials for the oil processing markets. It could also be stated that the recently developed chemicals commence a novel value chain to the oil refining process by rendering improved process performance and new business ventures. Few experimental works in developing an economic model for biorefinery with pulp and paper operations and corn-based wet and dry mills were carried out and these models facilitated the

overcoming of few infrastructural problems faced during biomass processing by utilizing the underused infrastructural facilities.

Current day industrial and commercial demands deem the requirement of an alternative for the energy obtained from fossil fuel-based systems without compromising the supply volume, cost and the potential to provide energy which has to be at least on par with the current system. In the recent studies, experimenters and researchers are giving much emphasis to portray the recent trends in the utilization of waste biomass into potentially useful energy generating sources. Such biomasses extracted energy are considered to render second- and third-generation biofuels through advanced processing techniques. This study clearly explained the currently available technologies, in terms of their efficiency, to deliver bio-based fuels from sustainable and renewable catalyst feedstocks. With the increase in technological advancements, these efficiency values will continue to increase and reach a stage where biofuels are inevitable sources of energy in global industrial, commercial and transportation fields.

Declarations

Conflict of interest The authors have no conflicts of interest to declare that are relevant to the content of this article.

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