NEW AND INNOVATIVE SOURCES FOR BIODIESEL WITHIN THE LAST FIVE YEARS

Introduction

As air pollution concerns continue to grow from fossil fuel usage, so does the popularity and technological advances for biodiesel production. Biodiesel is a mixture of fatty acid methyl esters (FAME) or a bonded group of fatty acids, created through either esterification or transesterification. In esterification, fatty acids - the building blocks of lipid content (i.e. oils, fats, triglycerides) in animal or plant parts - are combined with alcohol and a catalyst to produce FAMEs and a water byproduct. Conversely, in transesterification, oils and triglycerides (esters themselves) react with alcohol and a catalyst to produce glycerol and less viscous esters that are more suitable as fuel. In the energy industry, biodiesel production is simply a chemical reaction with parameters like catalyst type, alcohol concentration, temperature, and time that impact its effectiveness during experimentation.

Vegetable oils from edible crops and fat from farm animals have been the conventional input of fatty acids, pronouncing them as the first-generation production of biodiesel. With biodiesel resources dwindling the amount of human food, second and third-generation productions have been instigated instead to scavenge high lipid content from renewable waste or perennial plants and algal biomass, respectively. Researchers across the globe are opening to a world of possibilities geared towards second and third-generation productions by utilizing their native resources and creatively transforming unconventional ingredients into biodiesel, targeting a greener and more sustainable future.

Brazil

A variety of almonds from the Syagrus cearensis plant native to northeastern Brazil (Figure 1) is rendered as a novice raw material for the creation of biodiesel due to its high concentration of fatty acids. In 2019, C. V. P. Pascoal et al. at the Federal University of Ceará designed an ultrasonic in situ transesterification experiment to assess the effects of different catalysts, the ratio of methanol, and reaction time on the Syagrus cearensis plant's biodiesel fuel generation[1].

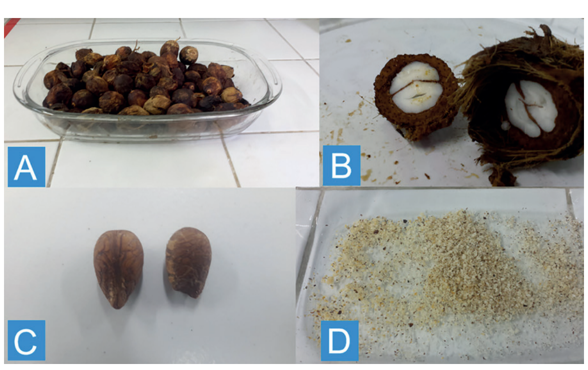


Figure 1. Syagrus cearensis almonds [1]

Ground almonds were deposited into a reactor linked to ultrasound equipment with a catalyst (either potassium hydroxide KOH or sulfuric acid H_2SO_4), methanol, and hexane before being filtered for gas chromatography of fatty acid methyl esters (FAME). As seen in Figure 2, an ultra-thermostatic bath was connected to the reactor to create around 49.4 Hz pulses to raise emulsification or the breaking apart of viscous liquids into droplets for better reactivity[1].

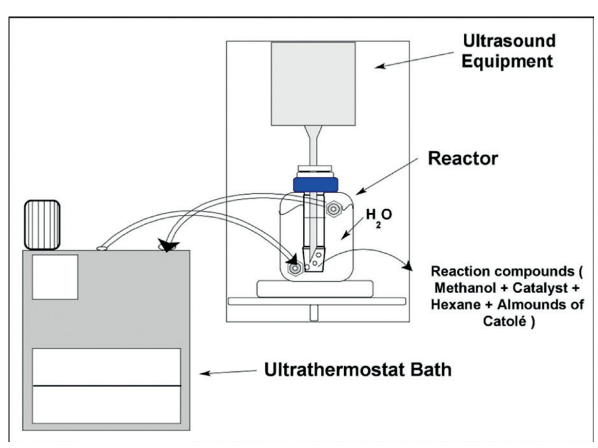


Figure 2. Reactor diagram showing the emulsification process [1]

Due to the novelty of the chosen plant, eighteen different experiments (each altering one of four variables) were conducted and triplicated to determine the highest percent yield of biodiesel. Pascoal's team's findings demonstrated that the optimal conditions for the conversion of almonds to biodiesel fuel through this method involved the use of a basic catalyst KOH, a 1:6 ratio of methanol and a 30-minute reaction time (Table 1). These conditions resulted in a 99.99% yield, which is highlighted and bolded in Table 1. The catalyst type and ratio most significantly contributed to the yield in FAME as seen in the Pareto graph (Figure 3). Despite the limited research on Syagrus cearensis, this study concerning in situ transesterification of Syagrus cearensis assisted with ultrasound successfully produced biodiesel and could be claimed as a potential new source[1].

Table 1. Experimental data using 18 different test conditions. Adapted from [1]

Catalyst Type	Catalyst Proportion (%)	Methanol Proportion (1:X)	Time (min)	FAME Yield (%)
KOH	1	60	10	10.75±1.02
H_2SO_4	1	60	10	10.38±2.55
KOH	1	60	30	20.24±0.97
H_2SO_4	1	60	30	11.87±2.19
KOH	1	6	10	11.87±1.53
H_2SO_4	1	6	10	11.33±1.39
KOH	1	6	30	12.89±2.38
H_2SO_4	1	6	30	11.07±1.34
KOH	3	33	20	59.55±0.52
H_2SO_4	3	33	20	12.29±0.53
KOH	5	60	10	80.98±3.94
H_2SO_4	5	60	10	11.02±1.33
KOH	5	60	30	81.54±5.48
H_2SO_4	5	60	30	10.76±0.55
KOH	5	6	10	65.14±2.60
H_2SO_4	5	6	10	13.84±1.32
KOH	5	6	30	99.99±6.57
H_2SO_4	5	6	30	10.95±0.67

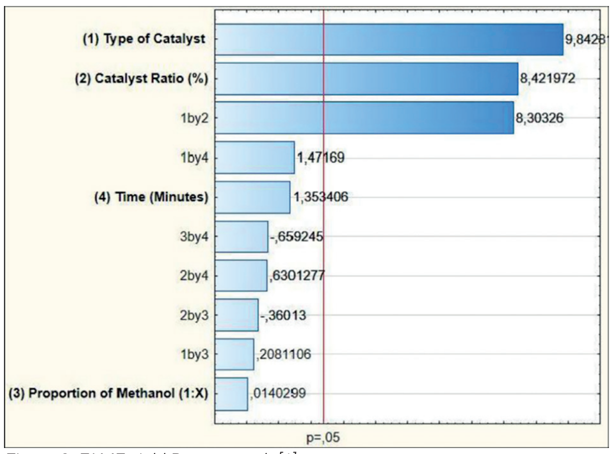


Figure 3. FAME yield Pareto graph [1]

China

Tobacco is an abundant, inexpensive oil plant with high seed lipid content that accounts for 36% to 41% of its weight[2]. Tobacco plants display the same characterization as other biodiesel plants, but increasing their lipid content would render them a more feasible source for larger-scale use. In 2020, Yinshuai Tian, et al. at Sichuan University and Hebei University of Engineering found out that lowering the level of proanthocyanidins (PAs), a compound responsible for the color of the seed, on the seed coat could increase its lipid content[2]. To obtain this goal, the CRISPR-Cas9 gene-mutating system was used to enhance two lines of NtAn1 genes (NtAn1a and NtAn1b) in wild-type tobacco plants (Nicotiana tabacum L., Figure 4) moderating PA biosynthesis to ensure a thinner seed coat, lower PA level, and consequently, an increased lipid content[2].

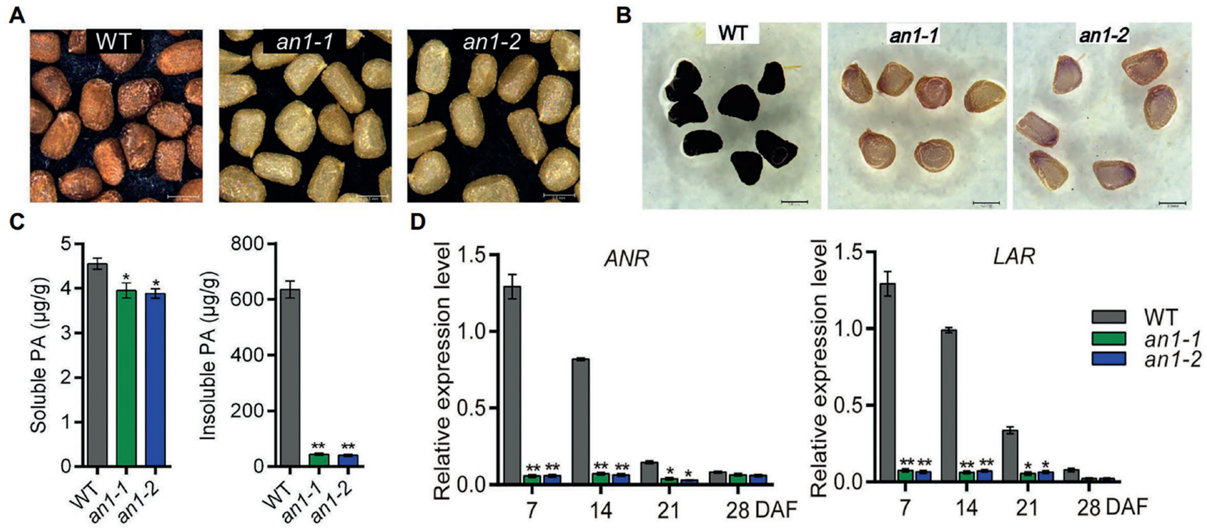

Figure 4. Nicotiana tabacum L. [3]

Resultantly, there was a noticeable change in the color of the seed coat from brown in the control wild-type tobacco plant (WT) to yellow in the mutated NtAn1a and NtAn1b genes seen in Figure 5A. For a better visual, the researchers used the reagent DMACA to stain detected PA content dark blue. Notice the lack of blue coloring in Figure 5B in the mutated seeds, indicating the successful lowering of PA content. Soluble and insoluble PA contents in the WT and mutated seeds were calculated through spectrophotometry; since mainly insoluble PAs were found in seed coatings, a significant decrease in insoluble PA content of the mutated seeds could be seen in Figure 5C. Lastly, Figure 5D displays the expression of the genes regulating ANR and LAR (enzymes that are a part of PA biosynthesis) days after flowering (DAF) of the tobacco plant[2].

Overall, Figure 5 illustrates the qualitative and quantitative measures to prove the desired change in PA content. Indeed, the targeted NtAn1a and NtAn1b genes successfully caused an 18% and 16% increase in lipid content, respectively, without changes to seed weight, size, or number per flower. The success of the CRISPR-Cas9 system on the tobacco plant implies its potential future implementation on other plants related to it (i.e. tomatoes, rice, grapes) to increase lipid content and cultivation time to meet the growing biodiesel demands[2].

Egypt

The use of vegetables and wild plants for biodiesel production is increasingly widespread. Nonetheless, in 2020, Nesma M. Helal et al. through Ain Shams University, King Abdulaziz University, and Tabuk University presented chief findings on the application of xerophytic plants native to the Western Desert of Egypt as the primary source of biodiesel production[4]. The plants Echinops spinosus (Figure 6) and Thymelaea hirsuta (Figure 7) were studied since they are most common and contain vast amounts of cellulose, oils, and fatty acids in their stems and leaves that are susceptible to energy production[4].



*The asterisks imply the drastic contrast in values between the mutated and WT seeds.

Figure 5. Effects on tobacco plants after CRISPR-Cas9 induced PA moderation [2]


Figure 6. Echinops spinosus [5]


Figure 7. Thymelaea hirsuta [6]

Plant material from both species was collected, extracted into air-dried powder with petroleum ether, underwent oil transesterification with methanol and KOH, analyzed with gas chromatography-mass spectrometry into FAME, and tested for diesel properties (summarized in Figure 8). Some of the diesel properties that were tested include the cetane number (CN), saponification value (SN), induction period (IP), and iodine value (IV)[4].

Based on the plants' FAMEs and oils evaluation found in Table 2, these species exhibited chains of fatty acids with high CN values that signify high fuel ignition speeds and delayed combustion time, high SN values that indicate high stability of the fuel, long IP times that represent the time it takes before undergoing oxidation, and low IV values from scorching desert temperatures that signify the high quality of the fuel. The plants' biodiesel properties were compared to the US (ASTM D 6751) and European (EN 14214:2008) standards with numbers that fairly surpass the recommended values, especially the CN, IV, and IP values, which are considered integral factors contributing to the overall quality of a fuel[4].

According to European standards, the recommended cetane number, iodine value (g I_2/100 g), and induction period (hours) are >47, <120, and >3, respectively. Meanwhile, according to USA standards, the recommended cetane number and induction period (hours) are >51 and >6, respectively. However, the corresponding values for Echinops spinosus were 229.99, 50.75, and 4.3 while that of Thymelaea hirsuta were 379.29, 29.16, and 19.8. In both cases, nearly all their properties score four times better than those recommended. In other words, both plant species satisfy the requirements for a biodiesel substitute and could be a promising primary source in the future[4].

Iran

The search for new sources continues into the sea as lipids extracted from the microalgae Nannochloropsis (Figure 9) are considered for biodiesel production. Nannochloropsis contains

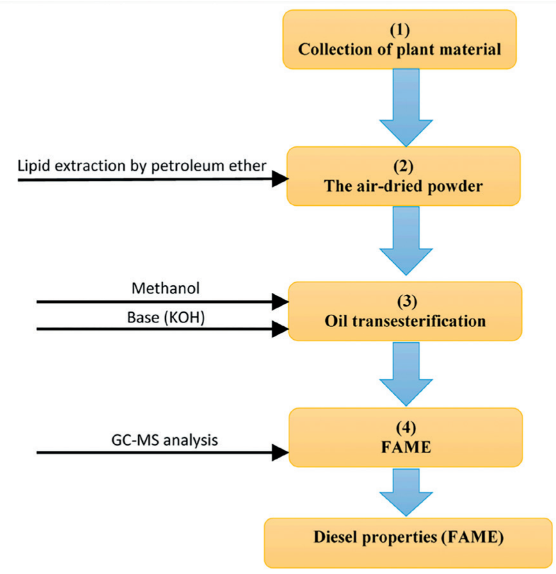


Figure 8. Stepwise process of FAME production [4]

50% of its lipid content in its dry biomass weight dominated by oleic acid (OA) and palmitic acid, crucial fatty acids for biodiesel production[7].

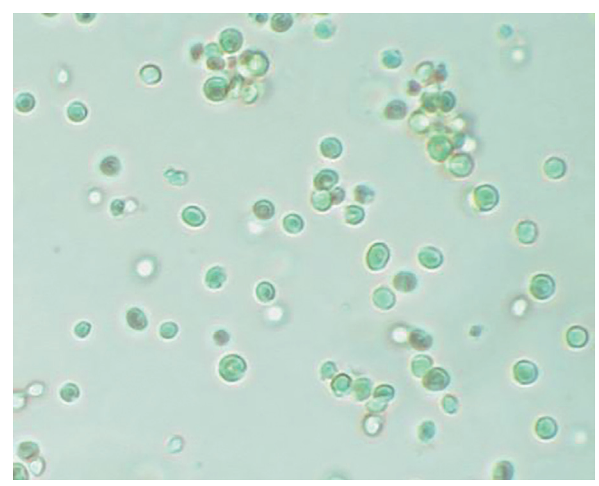


Figure 9. Nannochloropsis algae viewed under a light microscope [8]

In 2023, Kimia Karimi et al. at the University of Tehran studied the optimization of oleic acid's non-catalytic esterification with the response surface methodology (RSM) approach, assessing the reaction temperature, time, and molar ratio (methanol to oleic acid) [7]. Moreover, the optimization of the catalytic esterification of the synthetic oil (SO), consisting of 40% palmitic acid and 60% oleic acid, from Nannochloropsis was also tested, evaluating the same qualities as that of the oleic acid plus the weight percentage of the added catalyst[7].

It was discovered that: increased temperature aids in endothermic esterification processes by increasing oil and alcohol miscibility (Figure 10); longer reaction time assists the slow reaction rate of biodiesel production (Figure 11); excess methanol enhances the reaction (Figure 12); and percent yield reaches a 99% maximum with the desirable use of 0.13% catalyst sulfuric acid (H_2SO_4) at 67°C – 70°C and 7 – 9 methanol to SO ratio (Figures 13 and 14). As seen from the figures below, even a slight change in either temperature, reaction time, methanol to oil ratio, and catalyst weight can vastly improve the percent yield of biodiesel by as little as around 12% (Figure 10) or as much as 98% (Figure 11)[7].

Table 2. FAME diesel properties. Adapted from [4]

Properties	Echinops spinosus	Thymelaea hirsuta	European Standard (EN14214:2008)	USA Standard (ASTM D6751)
Oil Content (g/100 g)	76.1	30.2	-	-
Cetane Number	229.99	379.29	>47	>51
Saponification Number (mg/g)	27.97	16.07	-	-
Iodine Value (g I_2/100 g)	50.75	29.16	<120	-
Cold Filter Plugging Point (°C)	2.93	261.52	-	-
Degree of Unsaturation	142.12	16.23	-	-
Induction Period (hours)	4.3	19.8	>3	>6
Higher Heating Value (MJ/kg)*	47.52	48.33	-	-

**The EN14213 standard (for biodiesel intended for heatingpurposes) is >35.0*

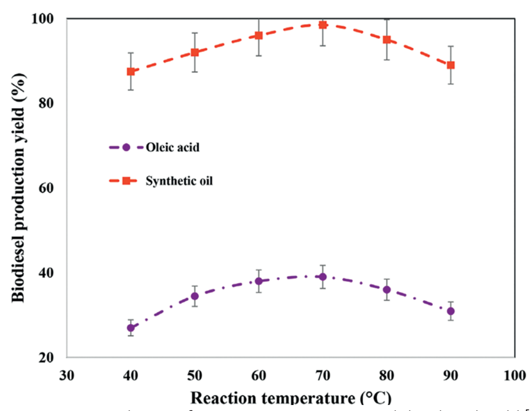


Figure 10. Correlation of reaction temperature with biodiesel yield [7]

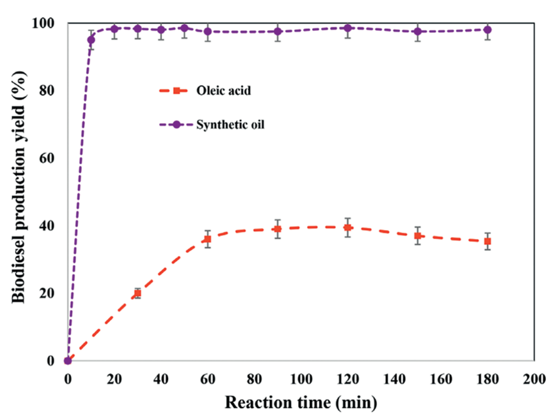


Figure 11. Correlation of reaction time with biodiesel yield [7]

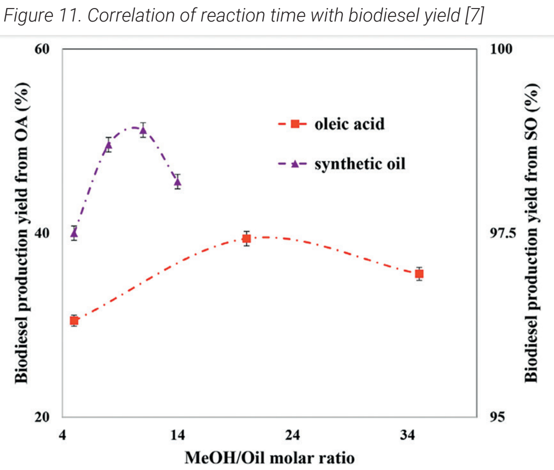


Figure 12. Correlation of methanol ratio with biodiesel yield [7]

In the end, oleic acid reached an optimal productivity of 40% at a temperature of 67°C, reaction time of 60 minutes, and molar ratio of 26.3:1. Meanwhile, maximum biodiesel production from oil extracted from Nannochloropsis was 99% at 69°C, a reaction time of 30 minutes, molar ratio of 9:1, and 0.13% weight of H_2SO_4. From this study, Nannochloropsis is concluded to be a viable biodiesel source with its fast-growing nature, abundance, carbon neutrality, and high, convertible lipid content[7].

Spain

With the increase of urbanization and expansion of wastewater treatment methods, the use of sewage sludge is considered a highly plausible, cheaper future direction for biodiesel production. In prior studies, sewage sludge was seen to pose unspoken financial liabilities in a thermal drying process before extraction that can account for up to 50% of its total operating cost[9]. Nonetheless, in 2023, Mostafa Zarandi et al. at Rovira i Virgili University and the Technology Centre of Catalonia compared three different biodiesel production methods from sewage sludge that could yield favorable financial and environmental results: dry extraction with lipids conversion, in situ transesterification (extraction and conversion in one step), and wet extraction (Figure 15)[9].

Both dry extraction routes involved a dewatering and thermal drying process with the first dry extraction route undergoing a hexane solvent recovery and acid-catalyzed transesterification procedure while the second dry extraction route went directly straight to in situ transesterification. Simultaneously, the wet extraction route trialed six different stages of hexane to sludge ratios, pH levels, and reaction rates before continuing onto the hexane recovery and acid-catalyzed transesterification procedure too. All three routes would end with a biodiesel product after a menthol recovery and purification process before being analyzed in a MATLAB program for financial and environmental evaluations[9].

The environmental evaluation of the routes was evaluated via the ReCiPe method of the Life Cycle Assessment which connects all activities from cradle to grave to its environmental damages per kilogram of wastewater in an index value over the interval [0,1]. Meanwhile, the financial evaluation considers direct manufacturing costs (i.e. labor fees, raw materials, utilities), fixed manufacturing costs (i.e. taxes, insurance), research and development expenses, the Break-Even Price or minimum market price of the product, and profitability. Conclusively, in situ transesterification proved to be the worst sludge-producing biodiesel pathway with ten times more environmental damage and five times more financial cost compared to the other two routes (dry extraction and stage 6 of wet extraction) as seen in the overwhelming red numbers in Figure 16. In situ transesterification had investment and manufacturing costs tallying up to $24.8 million and $19.4 million, respectively. On the other hand, dry extraction totaled $22.4 million and $9.7 million while wet extraction summed to as low as $10.2 million and $2.7 million[9].

Overall, wet extraction displayed better environmental and financial performance scores than those of dry extraction with the lowest normalized ReCiPe impact slope and the highest peak in profits seen in Figures 17 and 18, with stage 6 being the most favorable trial in the wet extraction process. Former studies have long worried about the expensive dry extraction method associated with wastewater, but with a newly discovered wet extraction process, the economic burden attached to it can be lifted. Thanks to this research, the outlook of processing wastewater with wet extraction presents itself as a more feasible biodiesel source[9].

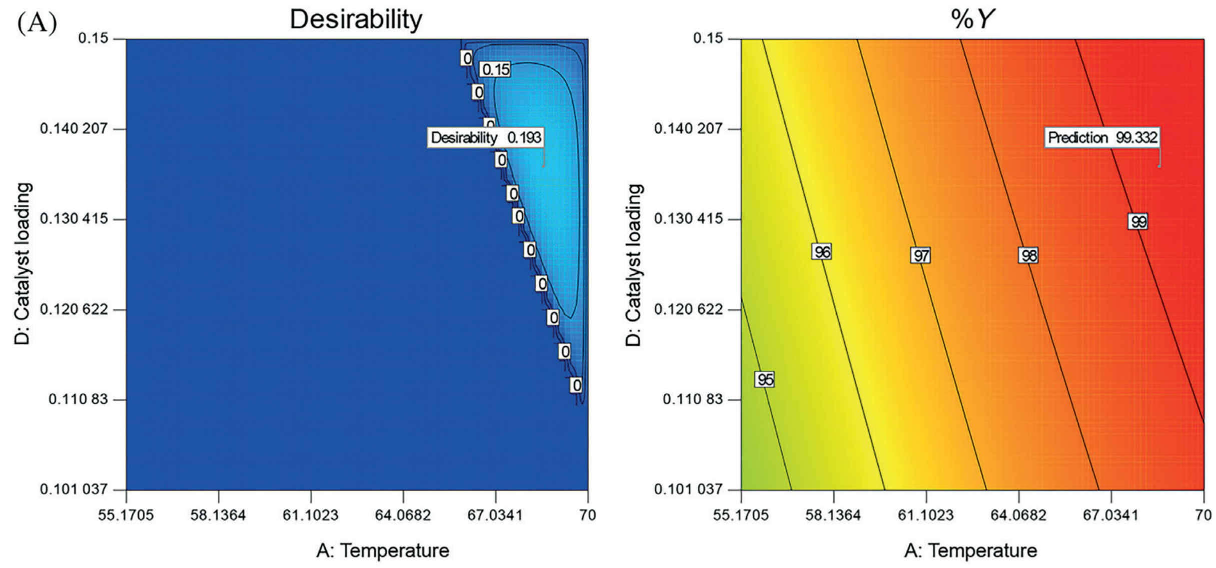


Figure 13. Desirability of catalyst loading with temperature and percent yield [7]

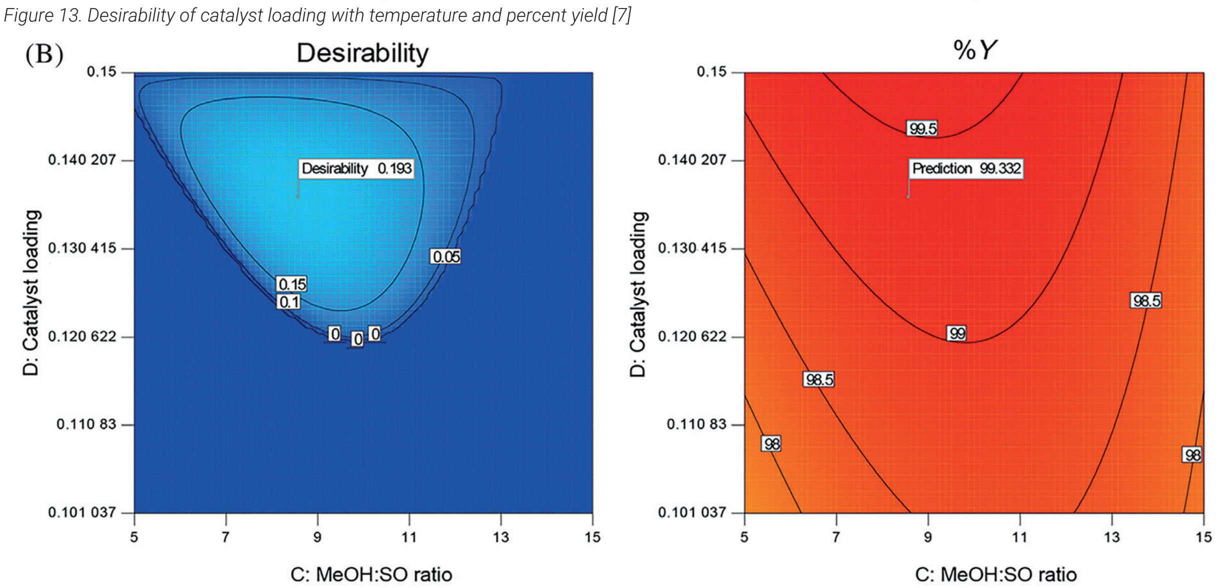


Figure 14. Desirability of catalyst loading with methanol to synthetic oil ratio and percent yield [7]

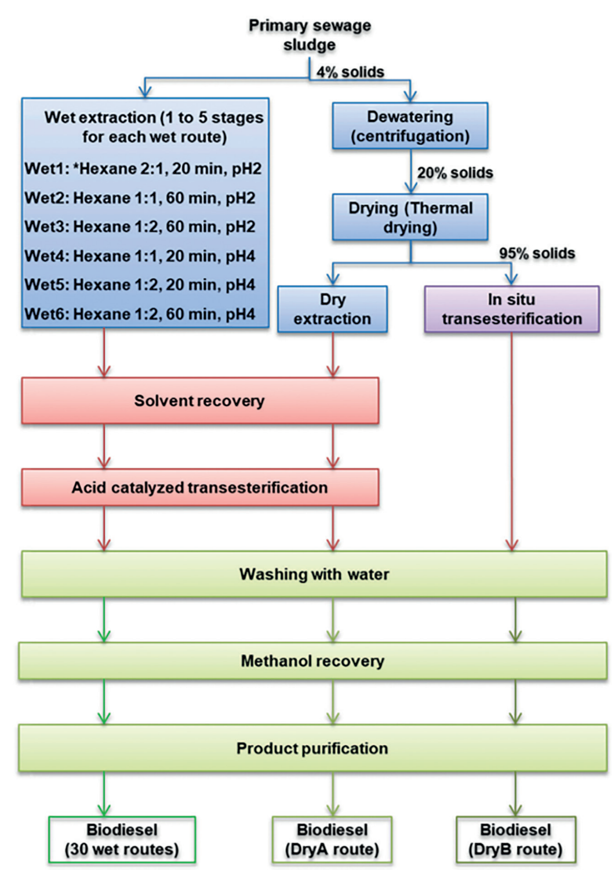


Figure 15. Flow chart showcasing various biodiesel production methods using sludge [9]

	DRY1(conventional)	DRY2(In situ)
Total investment costs ($)	22353477	24759597
Centrifugation and drying	6400000	6400000
Reactors	148789	933339
Distillation columns	688299	316706
Flush & other separation equipment	3274962	1968458
Mixing units	296604	1816410
Heat exchangers	420554	265841
Pumps	43513	56962
Storage	1398600	2277540
Total bare module	12671321	14035257
Fixed capital cost (bare + contingencies+auxiliary)	19437806	21530084
Working capital	2915671	3229513
Total manufacturing costs ($/t)	9653272	19367567
Raw materials	1227736	474545
Utilities:	1756157	10519467
Steam	1525064	8364674
Cooling	28423	156467
Electricity	202425	202604
Makeup water	245	21
Fuel (spray dryer)	0	1795700
Operation labor	717750	508500
Direct manufacturing cost	3701643	11502512
Overhead (fixed and general expenses costs)	5951629	7865055
BEP ($/t)	2031	4377

WET 100ml 60min pH4	1	2	3	4	5
Total investment costs ($)	10183422	11221484	12205787	13169487	14115793
Centrifugation and drying	0	0	0	0	0
Reactors	109547	127887	136293	141349	144290
Distillation columns	686733	687314	687580	687731	687826
Flush & other separation equipment	2338990	2488677	2625010	2757617	2885517
Mixing units	718089	1137060	1547590	1955125	2360089
Heat exchangers	467261	466835	468682	469262	469587
Pumps	53368	54652	55233	55589	55787
Storage	1398600	1398600	1398600	1398600	1398600
Total bare module	5772588	6361025	6918988	7465273	8001697
Fixed capital cost (bare + contingencies+auxiliary)	8855150	9757812	10613728	11451728	12274602
Working capital	1328272	1463672	1592059	1717759	1841190
Total manufacturing costs ($/t)	4695795	5481725	6171221	6735427	7459177
Raw materials	786021	909865	961325	923037	1022655
Utilities:	327923	436446	546819	648092	743717
Steam	238635	259561	282667	296782	305361
Cooling	1831	2437	2734	2933	3022
Electricity	87326	174274	261222	348170	435118
Makeup water	131	174	196	208	216
Fuel (spray dryer)	0	0	0	0	0
Operation labor	546750	661500	776250	891000	1005750
Direct manufacturing cost	1660694	2007811	2284394	2462129	2772122
Overhead (fixed and general expenses costs)	3035101	3473914	3886827	4273297	4687056
BEP ($/t)	1724	1524	1529	1555	1661

Figure 16. Sludge-derived biodiesel costs using dry vs. wet methods [9]

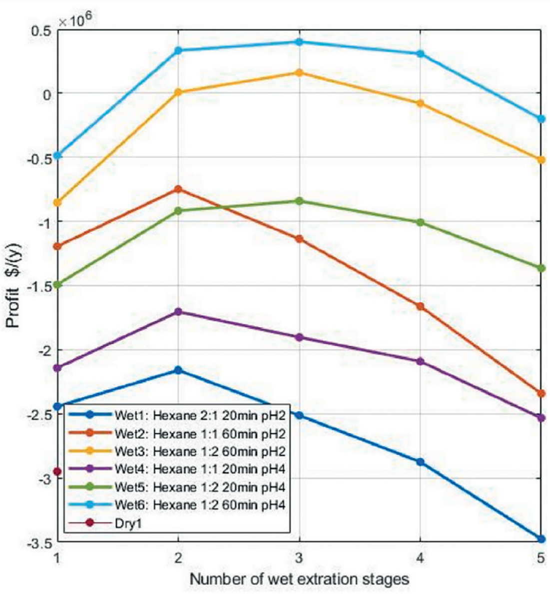


Figure 17. ReCiPe impact comparison for each wet extraction process type [9]

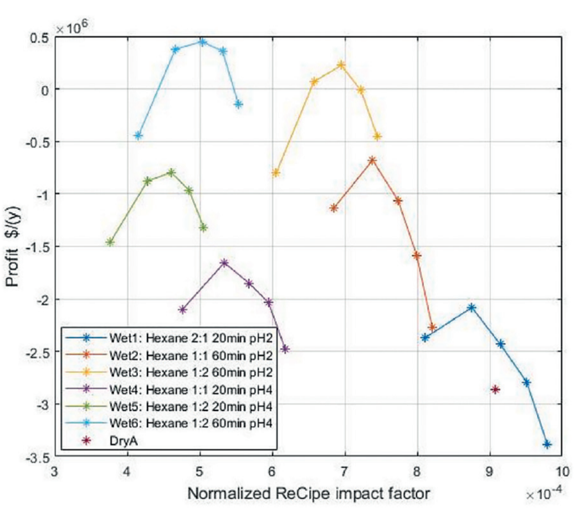


Figure 18. Profits of biodiesel made with each wet extraction process type [9]

Conclusion

Proposals for new biodiesel production take into consideration many aspects before they can be placed on an industrial scale: tedious research and experimentation, conformity to standards, financial liabilities, and eco-friendly deposition of waste. Despite the research successes with Brazilian almonds, mutated tobacco seeds, Egyptian desert plants, algae, and sewage sludge obtained in the last few years, these projects will still need to advance through many more arduous, evaluative stages before tangible changes can be made. Hence, the pathway towards a complete transition towards biodiesel from fossil fuels remains a continuous battle that researchers worldwide are collectively to surmount. Significant breakthroughs have been made within the last few years, and there is no doubt that this field of research will continue to blossom with even more fruitful innovations.

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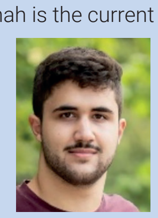
About the Authors

Dr. Raj Shah is a Director at Koehler Instrument Company in New York, where he has worked for the last 28 years. He is an elected Fellow by his peers at IChemE, CMI, STLE, AIC, NLGI, INSTMC, Institute of Physics, The Energy Institute and The Royal Society of Chemistry. An ASTM Eagle Award recipient, Dr. Shah recently coedited the bestseller, "Fuels and Lubricants Handbook," details of which are available at "ASTM's Long-Awaited Fuels and Lubricants Handbook 2nd Edition Now Available" (https://bit.ly/3u2e6GY). He earned his doctorate in Chemical Engineering from Pennsylvania State University and is a Fellow of The Chartered Management Institute, London. Dr. Shah is also a Chartered Scientist with the Science Council, a Chartered Petroleum Engineer with the Energy Institute and a Chartered Engineer with the Engineering Council, UK. Dr. Shah was recently granted the honorific of "Eminent Engineer" with Tau Beta Pi, the largest engineering society in the USA. He is on the Advisory Board of Directors at the State University of New York, Farmingdale (Mechanical Technology and Engineering Management); Auburn University (Tribology); and the State University of New York, Stony Brook (Chemical Engineering/Materials Science and Engineering). An Adjunct Professor at Stony Brook University, in the Department of Materials Science and Chemical Engineering, Raj also has over 575 publications and has been active in the energy industry for over 3 decades. More information on Raj can be found at https://bit.ly/3QvfaLX.

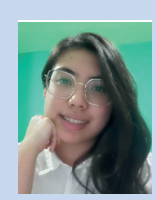
Contact: rshah@koehlerinstrument.com

Mr. Zachary Slade is part of a thriving internship program at Koehler Instrument Company in Holtsville and is a student of Chemical Engineering at Stony Brook University, Long Island, NY, where Dr. Shah is the current chair of the external advisory board of directors.



Zachary Slade

Ms. Rachel Ly is part of a thriving internship program at Koehler Instrument Company in Holtsville and is a student of Chemical Engineering at Stony Brook University, Long Island, NY, where Dr. Shah is the current chair of the external advisory board of directors.



Rachel Ly

Author Contact Details

Dr. Raj Shah, Koehler Instrument Company • Holtsvile, NY11742 USA

• Email: rshah@koehlerinstrument.com • Web: www.koehlerinstrument.com