RECENT ADVANCES IN THE PRODUCTION TECHNIQUES OF DENATURED ETHANOL

The fermentation of the sugar found in sugar cane and sugar beets and that of the starches of cereals like corn, sorghum, and barley comprise the majority of fuel ethanol produced worldwide. In the United States, nearly all fuel ethanol is produced from corn kernel starch and is considered a conventional biofuel under the US Renewable Fuel Standard Program[1]. Due to the almost record-high oil prices, the future of biofuel made from plant material is a topic of great interest worldwide. According to the Energy Independence and Security Act of 2007, conventional renewable fuels (corn starch ethanol) must reduce life-cycle greenhouse gas emissions compared to life-cycle emissions from fossil fuels by at least 20%, and biodiesel biofuels by 50%. [2] Cellulosic biofuels must reduce emissions by 60% to limit greenhouse gas emissions. In addition, EISA offers grants, loans, cash prizes, and R&D subsidies, as well as biorefineries that replace over 80% of the fossil fuels needed to run the refinery and for the commercial use of cellulosic biofuel [2].

There are potential sources of ethanol other than grain, starch, and sugar fermentation. Compared to using starch-based crops, producing ethanol from cellulosic feedstocks such as grass, wood, and crop residues requires more work. Cellulosic ethanol can be produced primarily by two methods: thermochemical and biochemical. The biochemical method entails hydrolyzing cellulose to extract sugars from it after a pretreatment that releases hemicellulose carbohydrates. Lignin is extracted from sugars and utilized to generate energy to power the fermentation process, which turns sugars into ethanol. Adding heat and chemicals to a biomass feedstock is the thermochemical conversion process that yields syngas, a hydrogen and carbon monoxide mixture. After being combined with a catalyst, syngas is transformed into liquid coproducts like ethanol.Grains require more fuel, fertilizer, and water than trees and grasses. Ethanol production from these sources is known as first-generation biofuel. Cellulosic ethanol, manufactured by converting vegetation unsuitable for human consumption, is classified as a second-generation fuel. Cellulosic ethanol has a lesser impact on the food chain than first-generation biofuels because it can be produced from agricultural waste products or energy crops grown on lands that are only marginally useful for food production.

As of 2020, Brazil is the second-largest consumer of gasoline-ethanol in the world, behind the US [1]. Dedicated pipelines for ethanol are being considered in Brazil and the United States and may become economical with expanded production. As part of the Renewable Fuel Standard (RFS) program, the U.S. Environmental Protection Agency (EPA) published a final rule on June 21, 2023, which set cellulosic biofuel volume requirements and criteria for 2023–2025 [3]. The cellulosic biofuel category primarily applies to Renewable Natural Gas (RNG), a form of natural gas made from biogas. The rule increases volume targets for cellulosic biofuel by 25% to 840 million gallons in 2023, by 29% to 1.09 billion gallons in 2024, and by 33% to 1.38 billion gallons in 2025 compared with the previous target [3]. Natural gas produced from biogas, known as Renewable Natural Gas (RNG), is the main product of the cellulosic biofuel category. The rule raises the volume targets for cellulosic biofuel by 25% to 840 million gallons in 2023, 29% to 1.09 billion gallons in 2024, and 33% to 1.38 billion gallons in 2025 [3]. Figure 1 shows the US's annual cellulosic biofuel production and new volume targets.

Denatured ethanol is commonly used in the biofuel industry for various purposes. In the context of biofuels, denatured ethanol refers to ethanol rendered unfit for human consumption by adding denaturants, such as methanol or bittering agents. The amount of ethanol in the fuel and whether an engine is designed to run on gasoline or ethanol will determine how much of an influence ethanol has on fuel economy [4]. This paper lists and discusses several advancements made in the production of denatured ethanol for the biodiesel industry and explores the sustainability journey.

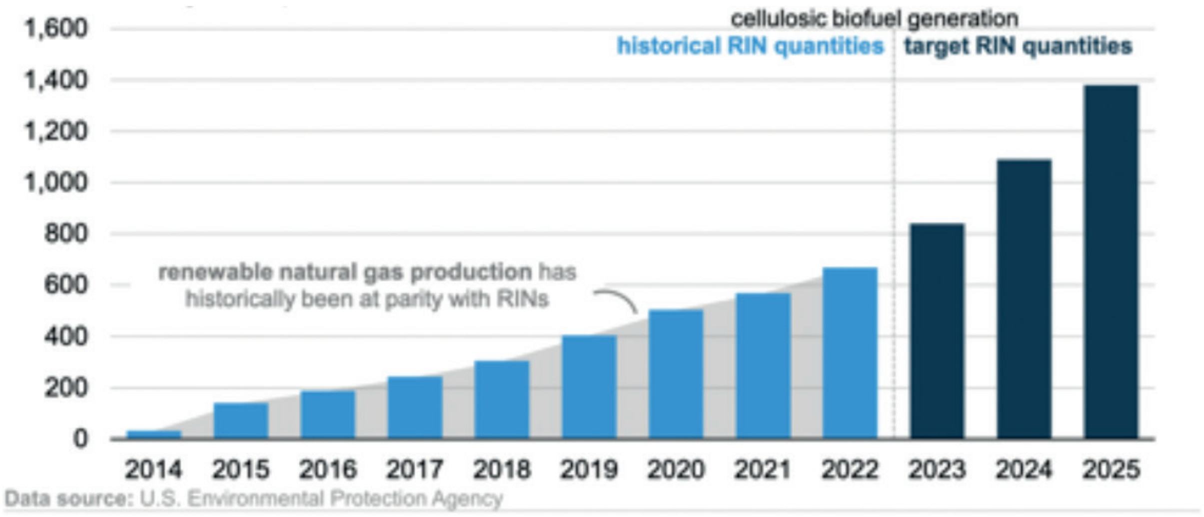


Figure 1: Annual cellulosic biofuel production and new volume targets under the RFS (2014-2025) [3].

Second-Generation Ethanol Production by Thermophilic Bacteria

The growing demand for sustainable biofuel is driven by the need for practical biorefineries that can use highly renewable and ecologically acceptable feedstocks to produce high-volume biofuels. Governments set targets in response to increased geopolitical instability, finite petroleum supply, and growing awareness of climate change. The necessity to meet an industrialized society's steadily rising energy needs is the primary cause of the spike in demand for biofuels. First-generation bioethanol, made from simple substrates like starch (from corn) and sucrose (from sugarcane and sugar beets), accounts for most bioethanol. Despite the success of the first generation of bioethanol production, there is rising worry over the feedstocks employed because they are frequently food crops - placing biofuel production in direct competition with food consumption and driving up food costs. Since second-generation biofuels are made from non-food (lignocellulosic) biomass, they allay these worries and show that biofuel production is moving toward sustainability by utilizing raw materials to supply the demand for bioethanol without interfering with food production. Lignocellulosic biomass is frequently derived from agricultural byproducts like straw made from corn or wheat [5].

Because thermophilic anaerobes can create ethanol from a wide variety of substrates and certain species can break down biopolymers like cellulose, starch, and hemicelluloses like xylan; there is growing interest in the biotechnological potential of these organisms. Microorganisms are classified based on the maximum and ideal temperatures for their growth. Extreme thermophiles thrive best between 65 and 79 degrees Celsius, moderate thermophiles between 50 and 64 degrees Celsius, and hyperthermophiles at temperatures above 80 degrees Celsius [5].

Optimizing ethanol yield during fermentation is important for efficiently producing fuel alcohol. When glucose is fermented, the greatest amount of ethanol produced is 2 mol ethanol/g glucose (0.51 g/L or 11.1 mM). Given the intricate structure of lignocellulosic biomass, yields from these substrates are often much lower, which is not surprising. Thermoanaerobacter ethanolicus and Clostridium thermocellum were the subjects of early studies on ethanol production from complex biomass, which used hemicellulose from birch and beechwood. 7.2 mM/g and 8.0 mM/g of ethanol were generated by Clostridium thermocellum [5].

When alkali was applied beforehand, similar yields were produced from corn stubs, sorghum stover, and paddy straw. Subsequent investigations using this Clostridium thermocellum revealed that these yields were significantly reduced by higher amounts of both grass and avicel hydrolysates. Wheat straw hydrolysates were used to create 6.3 mM of ethanol per gram of xylan by Thermoanaerobacterium saccharolyticum HG8. Thermoanaerobacter BG1L1 cultivated on corn stover and

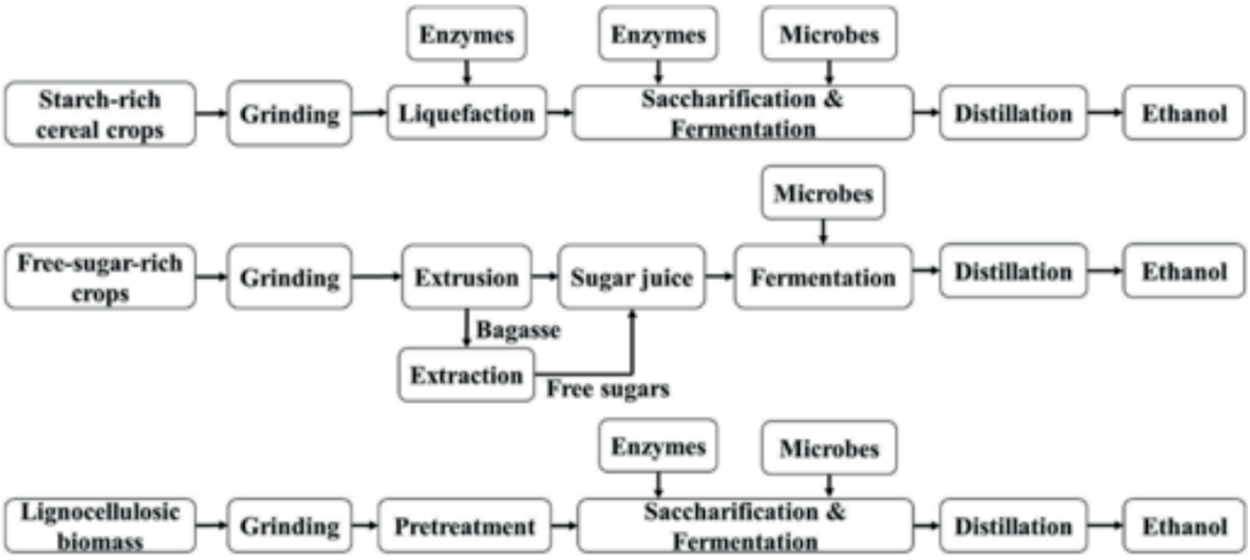


Figure 2: Major steps for fuel ethanol production from starch-rich crops, free-sugar-rich crops, and lignocellulosic biomass [6].

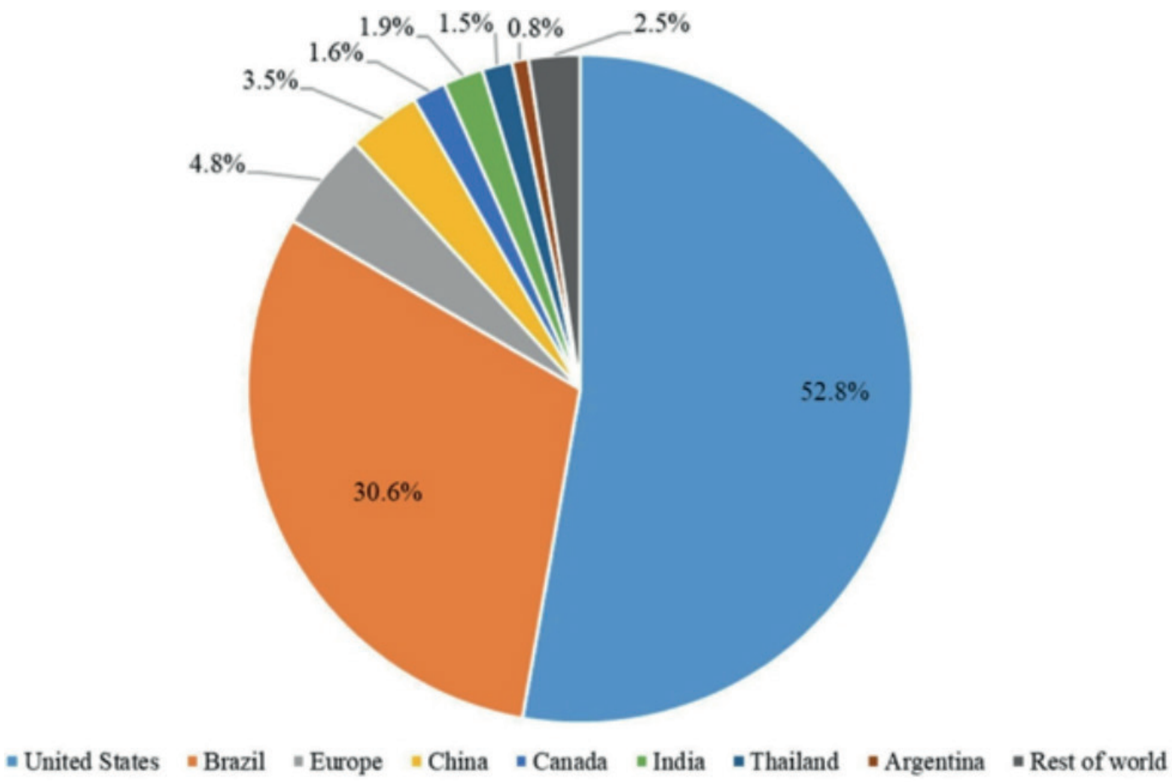


Figure 3: Fuel ethanol production worldwide in 2020 by country [6].

wheat straw has been shown to produce the highest known ethanol yields from complex biomass. Biomass hydrolysates produced ethanol yields of up to 9.2 mM/g when the biomass underwent acid or wet oxidation pretreatment [5].

Denatured Ethanol Production from Starchy Grain and Other Crops

Some productive types of starchy crops for the manufacture of ethanol are those with high waxy starch, low starch-lipid complex formation, and low protein cross-linking after cooking. It is technically and economically possible to produce 1.5 generations of ethanol by combining starch and fiber and separating them for first and second-generation ethanol production, respectively [5].

About 40% and 60% of the gasoline-ethanol produced worldwide is derived from free-sugar and starch bases, respectively. In 2020, 26,059 million gallons of ethanol were produced worldwide. With 54% of global ethanol production, the United States (US) leads the world in fuel ethanol production [6]. Other than Brazil, where sugarcane is the primary gasoline-ethanol source, starch-based crops fuel ethanol production in other nations.

Starchy crops' final ethanol output strongly correlates with their starch content. According to Srichuwong et al., corn with a maximum starch concentration of 75.2% produced the greatest ethanol yield of 0.38 g/g dry corn out of the five tested corn types with a starch content ranging from 68.9 to 75.2% [6]. According to reports, there is a 0.86–0.91 link between the amount of starch in sorghum and its ethanol yield. The wheat variety Dragana, which had a higher starch content (72.6%) than wheat types NS 40 S (70.5%), Rapsodija (66.1%), and Renesansa (67.6%), was also reported to have the greatest ethanol output of 0.41 g/g dry wheat [6]. Extractable or hydrolyzable starch content may better predict ethanol output than total starch content, as unextracted or unhydrolyzed starch cannot be converted into fermentable glucose, the precursor to ethanol. Corn, wheat, sorghum, barley, rye, cassava, rice, and triticale are the starch-rich crops that produce gasoline-ethanol. These crops' contributions to fuel ethanol manufacturing are mentioned in Table 1, and their production is shown in Table 2.

Utilization of Lignocellulose in the Production of Denatured Ethanol

Today, most of the fermentation-based ethanol generated is derived from sugars, grains, or cassava. Lignocellulose is being carefully considered as a potential substitute feedstock. However, fermentable sugars must be freed and separated

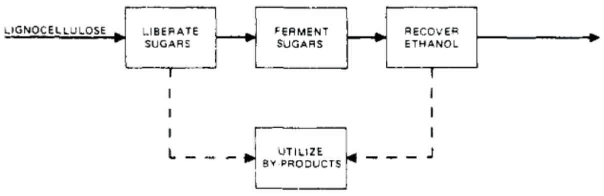


Figure 4: Ethanol from lignocellulose [7].

There are various methods for releasing sugars. Enzymatic hydrolysis and strong and weak acids are the three main process groups. The cellulose is broken down using weak acid hydrolysis methods, which use 0.5% sulfuric acid at a comparatively low temperature of 140–190 °C [7]. Higher temperatures and pretreatment methods have been used in experiments, which has led to a greater yield of glucose and less degradation of glucose. Approximately 70% of the predicted glucose output and 20% of the post-hydrolysis glucose concentration were reached at 500 °C.

Instead of requiring hours to get this final glucose concentration, residence periods in seconds are used to achieve it. However, certain byproduct materials that prevent ethanol generation are produced during hydrolysis in the presence of hemicellulose sugars due to the high temperature and short residence time. Catalysts are introduced before hydrolysis to counteract this issue [7].

Many lignin and hemicellulose byproducts are produced during the lignocellulose conversion to ethanol. For these byproducts to positively impact the overall process economics, they must either be marketed or utilized to produce energy.

Four conceptual process diagrams could serve as a foundation for additional development. Scheme 1 employs high temperature and short residence time for lignocellulose degradation; scheme 2 utilizes a pulping agent for lignocellulose digestion; the third scheme involves a cellulose

Table 1: Production of common starchy crops and food waste [5].

Starchy crops	Production (MMT)	Production percentage (%)														
		US	CN	BR	EU	IN	MX	RU	CA	NG	TH	CG	GH	ET	SD	UA
Corn	1111.58	31.3	23.5	9.1	5.8											
Wheat	763.95	6.8	17.5		20.2	13.4		9.6								
Sorghum	57.56	15.1	6.3			7.8	7.8			12.0				9.0	6.9	
Barley	156.12				40.2			12.8	6.7							6.1
Rye	11.53				68.9			12.4								
Cassava	252.02			6.4						21.4	11.4	10.8	7.5			
Rice	496.22		29.6			23.2										
Triticale	11.61		6.0		70.3											
Potato	334.00	5.6	24.5		8.2	13.2		6.1								6.1
Sweet potato	83.41		57.7													
Food waste	195.91	9.0	42.4		7.1	31.8		2.3								

Table 2: Fuel ethanol production percentage in the United States (year 2020), Brazil (year 2019), European Union (year 2019), China (year 2019), and Canada (year 2018) by feedstock [6].

Country	Fuel ethanol (%)										
	Sugarcane	Sugar beet	Wheat	Corn	Sorghum	Triticale	Barley	Rye	Cassava	Rice	Food waste
United States				93.5	2.2						0.2
Brazil	99.2			0.3							
Europe union		41.7	14.4	35.7		4.4	1.7	1.9			
China			4.1	80.2					11.6	4.1	
Canada			20.9	79.1							

solvent; and the last scheme employs strong acid hydrolysis to yield fermentable sugars. According to authors Jackson Yu and Steven F.Miller, out of the four schemes listed, applying scheme two is preferable since ethanol leaves the operation deactivated, greatly simplifying the enforcement of government tax regulations. Figure 5 demonstrates the method of high temperature and short residence time lignocellulose degradation [7]. This plan involves separating the undried wood particles and sending them, along with a catalyst, to an explosive defibrillator. Particle temperature is raised by the addition of high-pressure steam, and the addition of diluted acid matches vessel pressure. At 3000–4000 feet per second, the combined stream is sent through an extrusion dye, hydrolyzing the cellulose and breaking down the lignocellulosic structure. The surplus steam is extracted from the explosive defibrillator's discharge above a cyclone. The neutralization tank's effluent is steam-stripped to remove even more furfural [7].

The ethanol-rich overhead product is dehydrated. The relative volatility of water to ethanol is reversed, and water is recovered overhead from the second column. Ethanol is recovered from the extractive solvent in the third column, and the solvent is recycled. The ethanol will leave the plant as an ethanol/gasoline mixture. The energy requirements for dehydration and recovery of ethanol may be significantly reduced.

Conclusion

The market for ethanol was estimated to be worth USD 89.1 billion globally in 2019. From 2020 to 2027, it is projected to develop at a compound annual growth rate (CAGR) of 4.8% to reach USD 129.36 billion [8]. One of the main market drivers is using ethanol as a biofuel. Over the past few years, the automobile sector has experienced fast growth and numerous challenges in managing air pollution. To address the issue of increased air pollution from cars, ethanol is added to gasoline at percentages of 10% and 15% [9]. Major benefits from adding ethanol include better fuel economy, more thermal efficiency, and assistance with cold starts in the winter. The United States and Brazil are the global leaders when using ethanol as a biofuel. The process of producing denatured ethanol has advanced significantly, and one of the most widely used techniques is to ferment the sugar found in the starches of different grains.Most common processes include using thermophilic bacteria, starchy grain and crops, and lignocellulose to produce denatured ethanol. Further developmental work is yet to be done on producing denatured ethanol from lignocellulose so that the byproducts can be used to generate energy or be marketable [10].

References

1. U.S. Energy Information Administration. Ethanol explained - U.S. Energy Information Administration (EIA). Eia.gov. https://www.eia.gov/energyexplained/biofuels/ethanol.php.
2. US EPA, OP. "Economics of Biofuels." Www.epa.gov, 17 Apr. 2014, www.epa.gov/environmental-economics/economics-biofuels#:~:text=To%20limit%20GHG%20emissions%2C%20the.
3. Energy, US Department of. "New Renewable Fuel Standard Volume Targets Facilitate Renewable Natural Gas Production." CleanTechnica, 11 Dec. 2023, cleantechnica.com/2023/12/11/new-renewable-fuel-standard-volume-targets-facilitate-renewable-natural-gas-production/. Accessed 25 Jan. 2024.
4. Coyle, W. T. USDA ERS - The Future of Biofuels: A Global Perspective. www.ers.usda.gov. https://www.ers.usda.gov/amber-waves/2007/november/the-future-of-biofuels-a-global-perspective/.
5. U.S Department of Energy. Alternative Fuels Data Center: Ethanol Fuel Basics. Energy.gov. https://afdc.energy.gov/fuels/ethanol_fuel_basics.html.
6. Scully, S. M., & Orlygsson, J. (2015). Recent Advances in Second Generation Ethanol Production by Thermophilic Bacteria. Energies, 8(1), 1-30. https://doi.org/10.3390/en8010001
7. Li, Jun, et al. "Fuel Ethanol Production from Starchy Grain and Other Crops: An Overview on Feedstocks, Affecting Factors, and Technical Advances." Renewable Energy, vol. 188, Apr. 2022, pp. 223–239, https://doi.org/10.1016/j.renene.2022.02.038.
8. Utilization of Cellulosic Feedstock in the Production of Fuel Grade Ethanol Jackson Yu and Steven F. Miller Industrial & Engineering Chemistry Product Research and Development 1980 19 (2), 237-241 DOI: 10.1021/i360074a021
9. Ethanol Market Size, Share, Trends Global Industry Report, 2025. Grandviewresearch.com. https://www.grandviewresearch.com/industry-analysis/ethanol-market.
10. Beluhan, S., Mihajlovski, K., Šantek, B., & Ivančić Šantek, M. (2023). The Production of Bioethanol from Lignocellulosic Biomass: Pretreatment Methods, Fermentation, and Downstream Processing. Energies, 16(19), 7003. https://doi.org/10.3390/en16197003

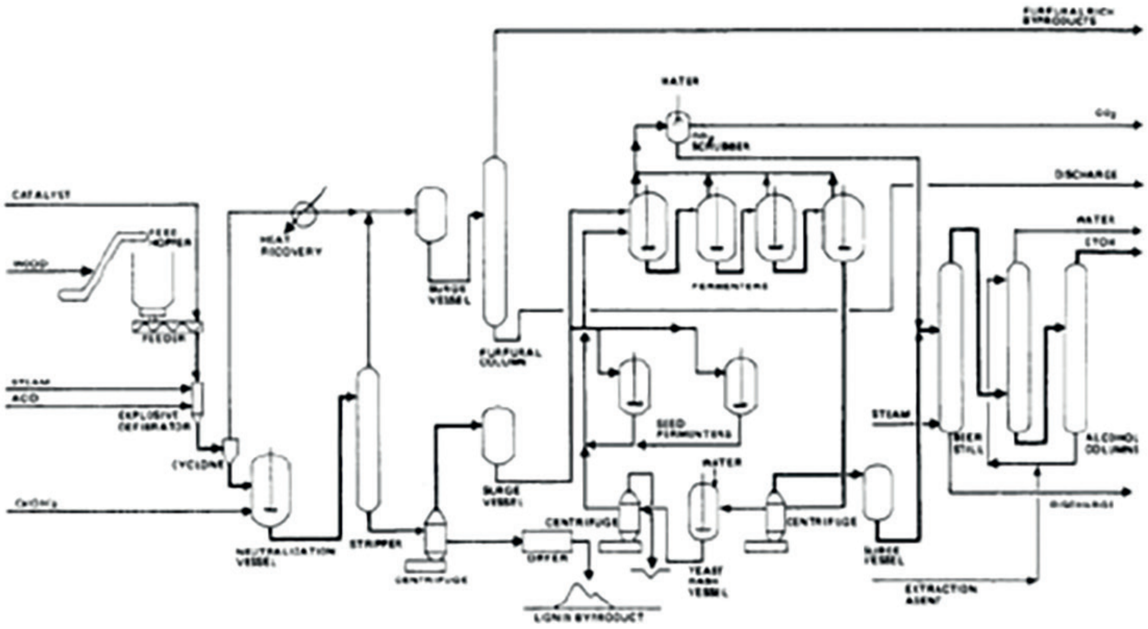
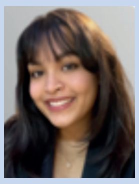


Figure 5: Weak acid hydrolysis of lignocellulose, scheme 2 [7].

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 The Pennsylvania State University and is a Fellow from 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 honourific of "Eminent engineer" with Tau beta Pi, the largest engineering society in the USA. He is on the Advisory board of directors at Farmingdale university (Mechanical Technology) , Auburn Univ (Tribology), SUNY, Farmingdale, (Engineering Management) and State university of NY, Stony Brook (Chemical engineering/ Material Science and engineering). An Adjunct Professor at the State University of New York, Stony Brook, in the Department of Material Science and Chemical engineering, Raj also has over 600 publications and has been active in the energyindustry for over 3 decades. More information on Raj can be found at https://bit.ly/3QvfaLX
Contact: rshah@koehlerinstrument.com

Ms. Salowa Siddique 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.



Salowa Siddique

Ms. Jacqueline Nowicki, QAQC Laboratory Manager at Valero Renewable Fuels in Minnesota. She has 20 years within the quality space, currently specializing in the ethanol field and bi-products. An active member of ASTM D02 and E48 committees.

Author Contact Details
Dr. Raj Shah, Koehler Instrument Company
• Holtsville, NY11742 USA
• Email: rshah@koehlerinstrument.com
• Web: www.koehlerinstrument.com

Ms. Jacqueline Nowicki, Valero Renewable Fuels
• 1444 120th St, Welcome, MN 56181, United States
• Email: jacque.nowicki@valero.com
• Web: www.valero.com