RECENT ADVANCES IN RENEWABLE DIESEL: TECHNOLOGIES, PATHWAYS, AND PRODUCTION INNOVATIONS

Introduction

Although fossil fuels have been the primary source of power since the mid-20th century, growing concerns over their sustainability have prompted research and production of alternative biofuels. Renewable diesel (alternatively known as "RD", or "green diesel"), is currently the second-most consumed biofuel in the US, behind ethanol, due to the significant advantages it presents [1]. Passing the ASTM D975 specification—a standard ensuring the safety and reliability of a fuel as diesel— for petroleum diesel, RD can be more readily substituted into existing infrastructure compared to other biofuels like biodiesel [2]. Additionally, passing the ASTM D975 specification proves the sustainability of RD, as the standard only allows the fuel being tested to produce a certain amount of pollutants. RD does not only match traditional diesel in sustainability, however—it offers significantly lower lifetime carbon emissions than that produced from petroleum-sourced diesel since carbon in RD originates from pre-existing carbon in the atmosphere, as opposed to decomposed organic matter in the ground [3].

However, concerns remain regarding the sustainability of such fuels. Using plant oils and animal fat as biomass may be cost-effective, but their sourcing has caused significant environmental impacts. The massive demand for palm oil, a common feedstock for RD, has driven large-scale deforestation in Indonesia and irreversible harm to rainforest ecosystems from its expanding cultivation [4]. Meanwhile, farming livestock, like cows and pigs, produces 15% of all global greenhouse gas emissions, which simultaneously pollutes soil and fresh water with runoffs from waste and antibiotics [5]. Consequently, increasing demand for these products for use in renewable diesel may be counterproductive. Instead, driving research into other methods of producing RD via genetically-engineered microbes and the co-pyrolysis of waste might be a more feasible and environmentally responsible approach to sustainable biofuel developments

This paper will review advances made since 2022 in the conversion of waste oil and plastic to fuel through co-pyrolysis, catalytic optimizations to increase the efficiency of those processes, and an alternative, biological process converting lignocellulosic biomass to fuel using microbes.

Efficiency and Sustainability of Co-Pyrolysis of Waste Cooking Oil and Plastic

One approach to improving the sustainability of RD is by using existing waste streams to produce more efficient fuel. A 2024 study conducted by Divyansh Singh and Abhishek Paul investigated the effects different ratios of feedstock had on the resulting RD. The researchers procured waste cooking oil (WCO) and polyethylene bags from NIT Silchar hostels and produced nine different renewable diesels from varying feedstock ratios through co-pyrolysis. The resulting fuels were then tested, and their physical and chemical properties were compared.

It was found that as higher percentages of waste plastic (WP) were used, the presence of density, acidity, and fatty acid methyl ester (FAME) dwindled, while cetane number and energy content rose. The researchers suspected that the radicals produced from the pyrolysis of WP stabilized the ones produced from WCO, resulting in higher quality fuel [6]. It should be noted that some of the produced oils were considered too viscous, acidic, and light, which would cause increased wear and possibly damage to a standard compression ignition engine. As a general trend, higher waste plastic mixtures presented better fuel quality but lower yield. The most practical feedstock mixture, known as D70P30, consisted of 40% waste cooking oil and 60% waste—the optimal balance between quantity and quality. The D70P30 blend was produced with a 70.9% liquid yield; gas chromatography-mass spectroscopy and Fourier-transform infrared spectroscopy revealed "a strong presence of Alkanes and Alkenes, which closely resemble fossil fuels," like traditional petroleum diesel [6].

The same authors conducted research on the practical application of this fuel, aiming to assess the efficiency and sustainability of renewable diesel when blended with petroleum diesel in varying proportions. Singh and Paul created three blends of D70P30 and petroleum diesel at 10%, 20%, and 30% renewable diesel concentration. As seen in Figures 1a and 1b, mixing the RD with petroleum diesel allowed for mixtures with properties significantly more suited for use in existing engines compared to the pure RD. As the concentration of petroleum diesel increased, the acidity, viscosity, and FAME levels decreased, making the properties of the blend closer to traditional petroleum diesel, making direct substitution into existing infrastructure easier.

The different fuel blends were then tested in a single-cylinder, water-cooled diesel engine whose mechanical output and gas exhausts were monitored and recorded. Different fuel injection angles were tested to find the most efficient timings for these fuel blends. It was observed that the mixed fuels tended to be more energy efficient than the pure petroleum diesel, with the 10% RD being the most efficient, followed by the 20% [7]. The researchers attribute the increased performance of RD blends to the higher lower heating value (LHV) (energy produced per unit of fuel), oxygen content, and cetane numbers—the latter two of which contribute to more complete combustion. Additionally, they characterized the weak performance of higher RD blends on the increased viscosity seen in Figure 1b, which caused improper atomization and thus, lower-quality combustion. Injecting fuel later in the pistons' cycles presented an increase in efficiency due to the fuel being given more time to mix with the air, with the greatest increase being from 15°bTDC to 20°bTDC [7]. The most energy efficient conditions were with the 10% RD at 30°bTDC, which had an energy efficiency of 33.6% [7].

Nonetheless, efficiency is only a fraction of sustainability. Singh and Paul also measured the gas emissions of the fuels, where the 10% RD produced the least CO, hydrocarbon, and smoke emissions. The greater exhaust gas temperature exhibited by the 10% RD fuel compared to the other fuel mixes signified more complete, and therefore cleaner, combustion of its constituents

Fig. 1a Physiochemical properties of different fuel mixtures [7].

	0% Renewable	10% Renewable	20% Renewable	30% Renewable	100% Renewable
Density@12°C (kg/m^3)	830	813.6	811.8	808.1	782.9
Kinematic Viscosity@40°C(cSt)	2.1	2.19	2.31	2.57	3.9
Cetane Number	55	55.9	57	58.2	71.7
FAME(v%)	0	0.48	0.52	0.59	1.24
LHV(kJ/kg)	45512	45529	45655.7	45691	45794.5
Acid Value (mg KOH/g oil)	0	1.4	2.2	3.3	9.6

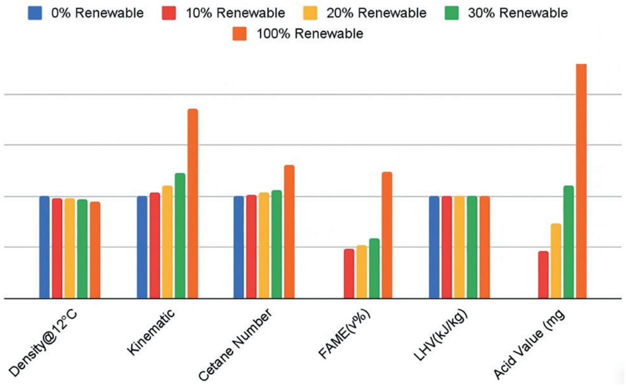

Fig. 1b Ratios of values between different fuel mixtures for comparison [7].

[7]. This increased temperature was seen in all three RD fuel mixtures but was less extreme as the concentration of RD increased, again, due to the increased viscosity. Unfortunately, the hotter exhaust temperature that reduces carbon emissions also increases NO$_x$ emissions, with the 10% RD at 30°bTDC producing 3.4 gNO$_x$/kWh [7]. The decreased NO$_x$ emissions seen in higher RD ratio fuels confirm that the nitrogen in the RD is not the driving cause of the NO$_x$ emissions, but rather, the greater exhaust gas temperature.

Effects of Catalysts in the Pyrolytic Production of Biofuels

Besides optimizations in the composition of feedstock, research has also been done on the usage of a catalyst in the co-pyrolytic production of renewable diesel. Sara Pourkarimi et al. observed that the addition of a Co/HZSM-5 zeolite catalyst in a 1:10 ratio with ulva (an edible algae) and azolla (an aquatic fern) feedstocks, resulting in a higher quality fuel in a lesser quantity. The catalyzed fuel's oxygen to carbon ratio was approximately a third of the original ratio and improved the fuel's energy yield by about 7% [8]. Additionally, the catalyst lowered the number of phenolic compounds, and consequently, reduced pollution generated by the combustion of this fuel. However, this improved fuel efficiency was offset by a reduction in the total fuel yield. Without a catalyst, bio-oil yields were 34.43% for ulva and 30.64% for azolla, but the addition of a catalyst reduced these to 26.1% and 23.5%, respectively.

Research was also conducted on the most effective method of incorporating a catalyst into the co-pyrolytic production of renewable diesel. While it was determined that the presence of a different beta-zeolite catalyst significantly reduced the amount of unavailable C$_{21+}$ hydrocarbons in the final product [9], additional research was done on a one vs. two-step catalytic pyrolysis [10]. By exposing only the vapors produced by the pyrolysis to the catalyst (two-step catalytic pyrolysis), heavier fractions were favored in the final product. While this resulted in a greater fraction of renewable diesel, it reduced the total amount of usable fuel produced due to an increase in gaseous product and unusable heavy hydrocarbons, as seen in Figure 2. Introducing the catalyst directly to the feedstock before beginning the reaction (one-step catalytic pyrolysis) allows for better yield in this specific reaction.

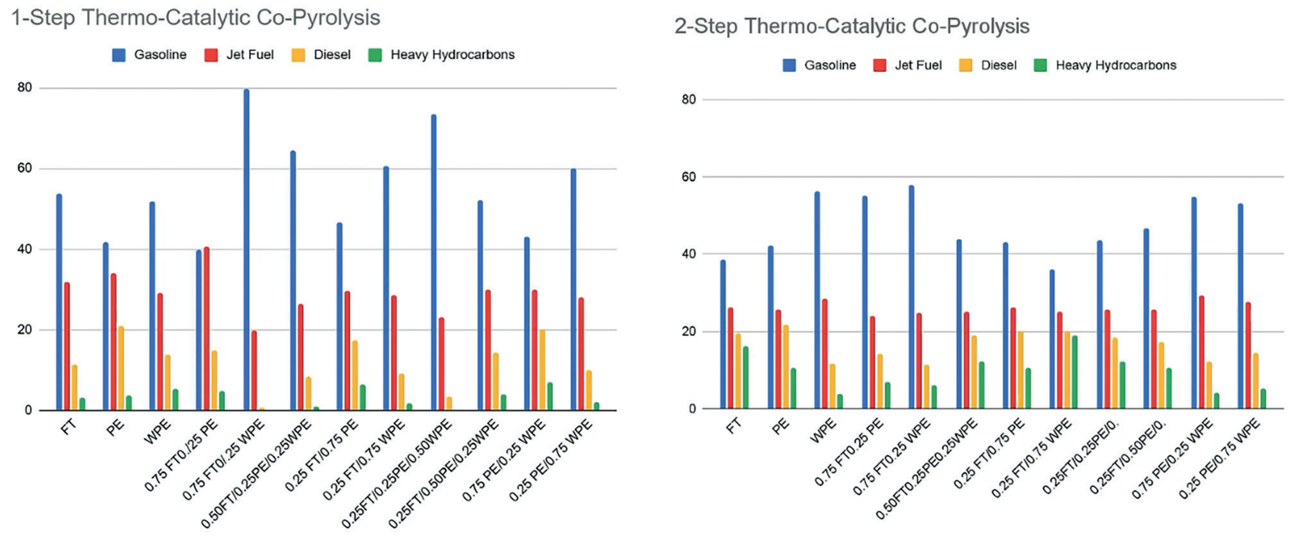

Fig. 2—Composition of liquid products from various ratios of feedstock [10].

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Microbes in the Production of Biofuels

Sustainability concerns surrounding traditional biofuel feedstock have prompted research into the use of bioengineered microbes to produce feedstock from greater varieties of biomass. Yeast and fungi can accumulate up to 70% lipid after feeding on simple carbon sources, like inedible plant waste, piquing research interest in their applications towards second-generation biofuels production [11].

> *One approach to improving the sustainability of RD is by using existing waste streams to produce more efficient fuel.*

Wujun Liu, Weifeng Mao, Cuili Zhang et al. conducted a study on yeast and fungi-derived biofuels, comparing one and two-phase processes in which Rhodosporidium toruloides yeast cells convert lignocellulosic biomass into lipids that can be efficiently transformed to renewable diesel lipids. Wujun Liu, Weifeng Mao, Cuili Zhang et al. prepared two types of media: a sanitized one-phase medium, consisting of sugar mixtures, yeast extract, and salts and a two-phase media with unsterilized solutions of varying amounts of lignocellulosic biomass-derived sugar mixtures. The one-phase mixture was given 5mL of yeast cell cultures, whilst the two-phase yeast was allowed to incubate in YEPD for 36 hours before being separated by centrifugation and portioned into 5*10^9 cell samples before finally being added to the two-phase media. After six days, the one-phase biosynthesis had produced a lipid content of 53.6%. However, the two-phase biosynthesis achieved a comparable 51.7% lipid content after only 48 hours, rendering it a much more favorable and efficient process. It should also be noted that despite the lack of sterilization in the two-process media, the pre-propagated yeast still thrived after being introduced. If scaled to an industrial level, this two-phase media technique could lower costs by omitting sterilization and increase profits through faster processing [12].

Although genetically engineering microbes would be a clear next step to enhance the efficiency of this biosynthesis, researchers at the Korea Institute of Science and Technology have pursued an alternative approach. Rather than editing the genes of yeast, the researchers have used CRISPR—a gene-editing—tool to cause a mutation in the HvCOMT1 gene of a barley plant, reducing the amount of lignin in its straw [13]. The modified barley straw produced 34% more ethanol than its wild counterpart. Although its production of RD has yet to be tested, more accessible sugars will most likely facilitate microbial conversion of lignocellulosic biomass in the straw into lipids, boosting overall RD yield.

Being the most abundant source of biomass worldwide, using lignocellulosic biomass to produce RD could be significantly more sustainable than waste oil or plastic. While used cooking oil is generally considered waste, as renewable diesel production scales, competition between consumer usage and large-scale renewable diesel production will likely cause increased plant oil prices and food prices [12]. Increased demand for plant oils may cause an increase in deforestation as farms grow to meet demands. Due to how abundant it is in industrial waste, lignocellulosic biomass is a promising, affordable feedstock for renewable diesel in comparison.

Conclusion

Renewable diesel has emerged as a promising alternative to petroleum-based fuel, and although concerns about its sustainability remain warranted, new research may offer solutions. The ecological damage caused by the production of plant oils for RD production cannot be ignored, but recent developments in the variety of available biomass sources like waste cooking oil, plastic bags, and grain straw via co-pyrolysis and microbial biosynthesis demonstrate possible paths towards sustainable RD production. Additionally, research into catalysts makes these processes more efficient, improving their sustainability and scalability. However, despite these innovations in sustainable bio-fuels, challenges regarding their implementation remain. Bio-fuels still remain significantly more expensive than petroleum-based fuels, making the switch impractical for most consumers. More research must be done on improving the cost-efficiency of current—or new—production processes for the sake of a greener future.

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