ADVANCES IN METHANE TO GASOLINE PROCESSES

Gasoline is one of the most important fuels used today, serving as the fuel to most light vehicles. A majority of the gasoline produced comes from the fractional distillation of crude oil; however, the drilling and refining of oil results in harmful pollutants and damages ecosystems. There is ongoing research in the production of biogasoline, a potential alternative to conventional gasoline. Rather than being based on oil, biogasoline derives from feedstock, which is replenishable and more carbon neutral. There are several different pathways that start with the use of biomass as a feedstock and result in gasoline as a product. Biomass can undergo processes such as pyrolysis, gasification, anaerobic digestion, and methane reforming to produce synthetic gas (syngas). Syngas can then be converted to various hydrocarbons, through the Fischer-Tropsch synthesis, which can be further processed into fuel gasoline as part of a larger process known as gas-to-liquids (GTL) [1].

This paper aims to highlight the recent advances in methane to gasoline processes initiated by the anaerobic digestion of a biomass feedstock. While other upstream processes such as pyrolysis and gasification, also produce syngas, they do not make methane as an intermediate product. Methane is not required for biogasoline synthesis, but this paper focuses only on processes that produce and utilize methane.

Anaerobic digestion

Anaerobic digestion (AD) is the process in which microorganisms break down biological matter in the absence of oxygen. The main product of this process is biogas which is primarily composed of methane (50 to 75 percent), carbon dioxide, hydrogen sulfide, and other components [3]. There are four primary steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. In the hydrolysis step, the feedstock is broken down into simple sugars by bacteria. Acidogenic bacteria then convert the simple sugars and proteins into intermediates such as carbon dioxide, hydrogen, and volatile organic acids. After this, acetogenic bacteria convert these organic acids into other intermediates, which include acetic acid. Finally, the organic intermediates undergo methanogenesis where they are converted into methane [4]. This is a versatile process with various feedstocks such as wastewater, crop residues, manure, and landfill waste.

Although anaerobic digestion is an established and widely used process, researchers are still finding ways to make it more efficient and economically viable. The most common type of AD is through single-stage batch reactors where all the steps happen in one tank. These reactors are often used because of their simplicity and low cost. However, they are subject to biogas loss when manually emptying the tank and are not efficient [5]. Regardless, over 97% of European countries use a single-stage system [6]. One idea proposed to improve AD is by using a two-stage reactor. Although it is more costly, separating the first two steps (hydrolysis and acidogenesis) from the last two (acetogenesis and methanogenesis) allows for more optimal conditions for the bacteria in each reactor, such as the pH levels they operate at [5]. Recent research has shown that methane yield increases by 10-30% via two-stage AD reactors [7]. Other alternatives for AD currently under examination include dry-digestion systems, co-digestion where multiple substrates are used to manipulate the carbon and nitrogen ratio, and the utilization of micronutrient boosters [7].

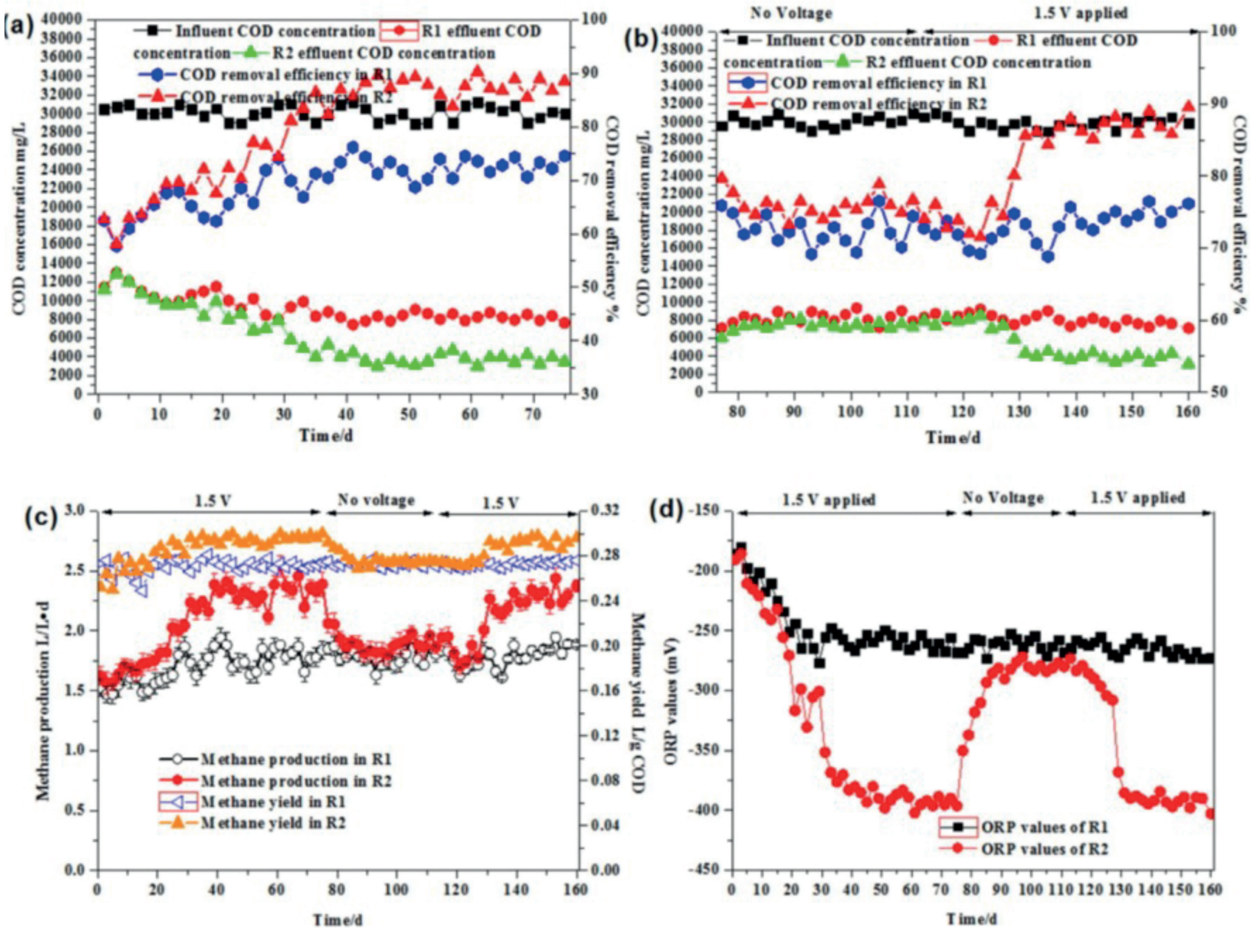

Figure 1: The operational performance of R1 and R2 during 160 days operation: COD removal (a and b), methane production (c) and ORP values (d) [9].

Anaerobic digestion has the potential to promote a circular economy by using the waste of the Fischer-Tropsch reaction as a feedstock. Fischer-Tropsch (F-T), a synthesis used downstream in the methane-to-gasoline process, notoriously produces large amounts of wastewater with a high dissolved hydrocarbon content, chemical oxygen demand (COD), and biological oxygen demand (BOD) [8]. AD is commonly used to treat this wastewater and is known to be a cost-effective strategy as it can handle high-strength organic waste [9]. However, a challenge in this treatment processis the incomplete mineralization of pollutants such as propionate and butyrate [8]. Because of this, the success of AD as a F-T wastewater treatment is dependent on how well it can control pollutant buildup [9]. The up-flow anaerobic sludge blanket (UASB) is the main type of reactor used in the methanogenesis stage of AD because it promotes good metabolic activity of the methanogens [10]. Recently, research has been conducted on the effects of using an electric field in conjunction with a traditional AD reactor to make the process more efficient. Castellano-Hinojosa et al.

Anaerobic digestion is not only a useful tool for treating F-T wastewater, but also a good feedstock for methane production and use. Approximately 76 percent of the COD in F-T wastewater is short-chain alcohols [11]. Short-chain alcohols like methanol are relatively simpler compounds to convert into methane which makes this wastewater an attractive feedstock [8]. In turn, this allows for a situation where unsafe waste is kept from polluting the environment, while also feeding a system where more gasoline can be produced downstream.

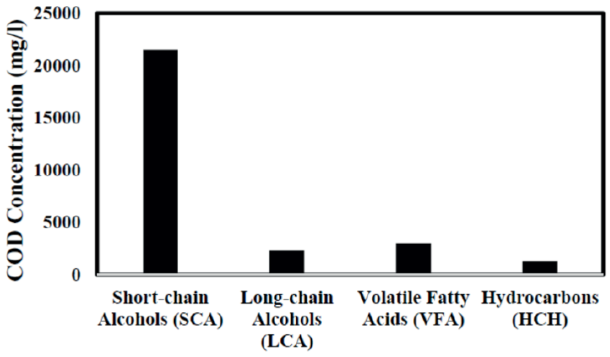

Figure 2. F–T wastewater composition with COD concentration [8].

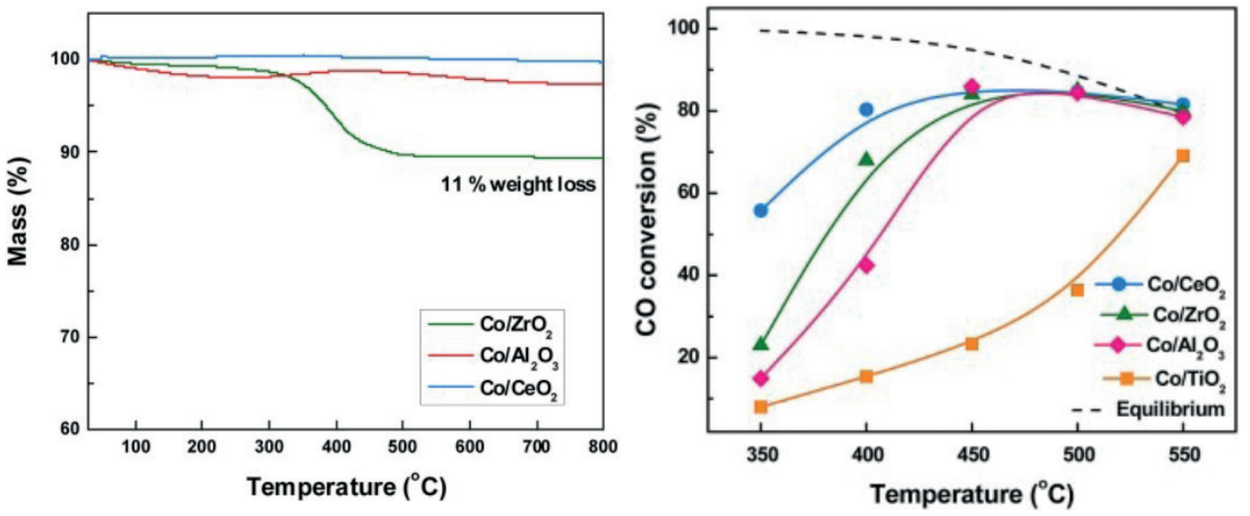

Figure 3: (Left) TGA results of supported cobalt catalysts after time-on-stream study. (Right) CO conversion with reaction temperature over supported cobalt catalysts. [15]

Methane Reforming

After the production of methane from AD, the methane needs to be converted to syngas in order to be usable for downstream processes. The two most common processes for the conversion are Steam Methane Reforming (SMR) and Dry Reforming of Methane (DRM). The benefit of DRM is its utilization of CO_2 as a feedstock giving it good greenhouse potential. However, this reaction typically does not produce a high enough percentage of hydrogen which is required for downstream processes, unlike SMR which allows for a higher hydrogen concentration. Another issue with DRM is the rapid deactivation of its catalysts, specifically nickel-based catalysts which are the industry standard. This is due to the high operating temperatures required and carbon formation [12]. Abdulrasheed et al. combines many of the developments and research on DRM catalysts and how their performance is affected by characteristics such as basicity, redox potential, and salient properties. Some of these features can be manipulated to produce a better catalyst however the DRM process still remains more immature than SMR [13]. In particular, Chein et al. [14] researched the effect of Ni/Al_2O_3 modified with CeO_2 as support on carbon deposition that causes deactivation. The researchers concluded that this modification may help with carbon deposition and that DRM performance can be enhanced, specifically the methane conversion and yield rates of syngas. Shen et al. [16] researched the Ni/$MgAl_2O_4$ catalyst for DRM at 500-700°C which is lower than the typical operating temperatures (above 700°C) for the process. Negligible deactivation was observed for the 100 hours on stream and the catalyst displayed stable performance. Research for optimal catalysts for the DRM process is still ongoing.

Since the DRM process typically does not produce enough hydrogen to be used in gasoline synthesis, a water-gas-shift reaction (WGS) follows. The WGS involves the reaction of carbon monoxide and water in order to produce a higher amount of hydrogen for a better downstream gasoline production . This process usually is done over a Fe-Cr catalyst for high-temperature shifts or a Cu-Zn-Al catalyst for low-temperature shifts. Environmental concerns over Cr have prompted research on finding alternative catalysts for the high-temperature shift. Jha et. al measured the catalytic activity of support oxides over a cobalt-base catalyst. The cobalt base was chosen because of the attention it has received in reactions such as the Fischer-Tropsch. It was found that the Co/CeO_2 catalyst demonstrated the highest catalytic activity and stability [15]. The experimental results are shown in Figure 3. From Figure 3 (left), results demonstrated that Co/CeO_2 mass percentage stayed nearly constant during the time of the process operation, demonstrating less catalyst degradation in comparison to the other catalysts. From Figure 3 (right), Co/CeO_2 also trumped the other catalysts in the conversion of carbon monoxide for nearly all temperatures.

Catalysts in Fischer-Tropsch and Methanol-to-Gasoline

The Fischer-Tropsch synthesis and Methanol-to-Gasoline are two methods used to produce gasoline from syngas. F-T is a part of a larger process called gas-to-liquids (GTL) which involves the conversion of carbon monoxide and hydrogen into larger-chain hydrocarbons [17,18]. One challenge in the use of this synthesis is the lack of selectivity, which makes it difficult to produce gasoline-range hydrocarbons at a high yield. According to the Schulz–Flory distribution ratio, a tool used to predict the lengths of hydrocarbon chains produced, the gasoline output does not exceed 48% with conventional reactor designs. For this reason, non-traditional catalysts in GTL must be researched so that selectivity for gasoline could be increased. Commercial F-T catalysts typically have transition metal bases such as iron, cobalt, nickel, and ruthenium which influence selectivity; nickel promotes methane formation, while cobalt and ruthenium assist with paraffin and olefin synthesis reactions [18].

Another approach to producing gasoline is called methanol-to-gasoline (MTG) which first converts the syngas into methanol. Methanol is then used as a feedstock to create gasoline. One of the leaders in this process is ExxonMobil which began researching this method in the 1970s and launched a demo plant in 2015 with fluidized bed MTG technology [2].

Unlike the F-T synthesis, the MTG process involves two major steps: syngas to methanol synthesis, and then hydrocarbon synthesis. Similar to F-T, this process must utilize the appropriate catalysts to increase gasoline selectivity. The ZSM-5 catalyst was originally developed for the MTG process by ExxonMobil with synthetic zeolites. With ZSM-5 and at optimal conditions (400 ºC and pressure 15–25 atm), the process can produce gasoline-range hydrocarbons with 80% selectivity. This is due to the catalyst's channel structure which allows for selective molecule penetration that produces gasoline hydrocarbons [19]. In addition, zeolites have high thermal stability and a high surface area which have also aided in their popularity [20]. A study conducted by Wan et al. [21] observed catalytic activity and methanol conversion under different operating conditions and it was concluded that reaction temperature had the greatest effect. Temperatures above 375°C allowed for complete methanol conversion and increased catalyst durability. However, at temperatures over 400°C, gasoline yield decreased and there was rapid catalyst deactivation. Respective values for methanol conversion, gasoline yield, and catalyst mass percentage from this study are shown in Figures 4.

Catalyst ZSM-5 was developed for MTG synthesis; however, current research for the incorporation of this catalyst into the Fischer-Tropsch synthesis is ongoing. The research primarily focuses on the combination of a traditional F-T catalyst with a zeolite shell which results in a hybrid catalyst [22,23,24]. Cobalt-zeolite catalysts, for instance, have been observed to significantly impact the composition of the F-T catalysts. In addition, pelletized zeolite-supported catalysts are relatively inexpensive and their combination with the F-T catalysts is commercially possible [22]. Zhu et al. used cobalt aluminun oxide (Co-Al_2O_3)/monolith catalyst with a ZSM-5 coating and measured the yield of gasoline-range hydrocarbons [23]. This catalyst was chosen because of prior research on the advantage of cobalt-based monolithic catalysts compared to traditional F-T catalysts often leading to unfavorable light hydrocarbons and low octane numbers which lower gasoline quality. Furthermore, past research has shown promising results of the ZSM-5 film on the selectivity of the process. This group hypothesized that the combination of the two could prove to be even more successful. Gasoline selectivity was found to be as high as 93.3% for the zeolite-coated monolithic catalyst, improving the gasoline quality as well. The yield percent of the catalysts is shown in Figure 5. Přech et al. [24] demonstrated a strategy for the preparation of a F-T-zeolite hybrid catalyst to maximize performance. They used various metal-zeolite composite catalysts which were all emulsioned with ruthenium (Ru) nanoparticles. The researchers found that the proximity between the active sites in the catalyst is an important parameter in designing efficient catalysts for gasoline synthesis. The Ru content and acidity of the catalyst shell also had an impact on the catalyst's efficiency.

Carbon Capture

Every process discussed in this paper produces carbon dioxide. The utilization of carbon capture technology can combat this by collecting and storing the carbon, although this process is costly. The three major types of carbon capture methods are through absorption-based, adsorption-based, and membrane-based capture [25]. The cost-effectiveness and efficiency of these methods are largely dependent on process parameters and goals. The transport and storage of the carbon also present additional expenses. Because of this, new methods and technologies are being researched to make it an economically viable option for corporations.

A new commercial method for carbon capture opened in China, which involves the valorization of carbon dioxide waste from a coke-oven facility. This plant, operated by Henan Schuncheng Group and commissioned by Carbon Recycling International, opened in 2022. It converts CO_2 into methanol and is based on the emissions-to-liquids technology (ETL) first demonstrated in Iceland. ETL uses flue gas emissions and hydrogen-rich emissions as the feedstock which then undergoes CO_2 purification and electrolysis prior to the clean conversion to methanol [26]. Currently, it can capture 160,000 tons of carbon dioxide each year and has a yearly capacity of 110,000 tons of methanol [27, 28]. The methanol can then be used as a feedstock for the MTG process to produce gasoline which is an environmentally friendlier alternative to releasing the CO_2 to the atmosphere.

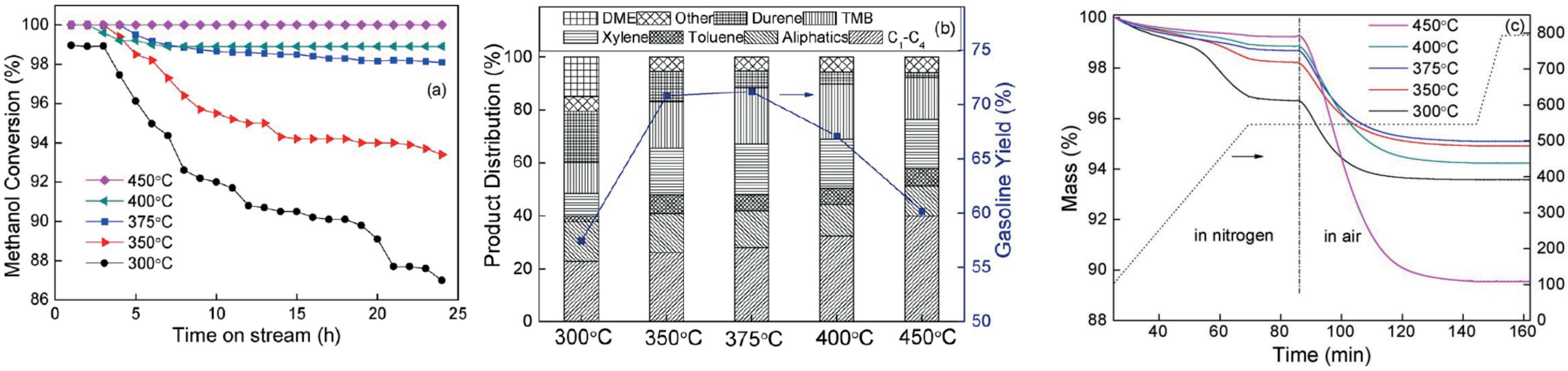

Figure 4: (Left) Effect of pressure on the performance of the nanocrystal ZSM-5 catalyst in MTG: methanol conversion. (Middle) Effect of pressure on the performance of the nanocrystal ZSM-5 catalyst in MTG: product distribution and gasoline yield . (Right) Effect of pressure on the performance of the nanocrystal ZSM-5 catalyst in MTG: TGA curves of the spent catalyst tested at different reaction pressures [21]

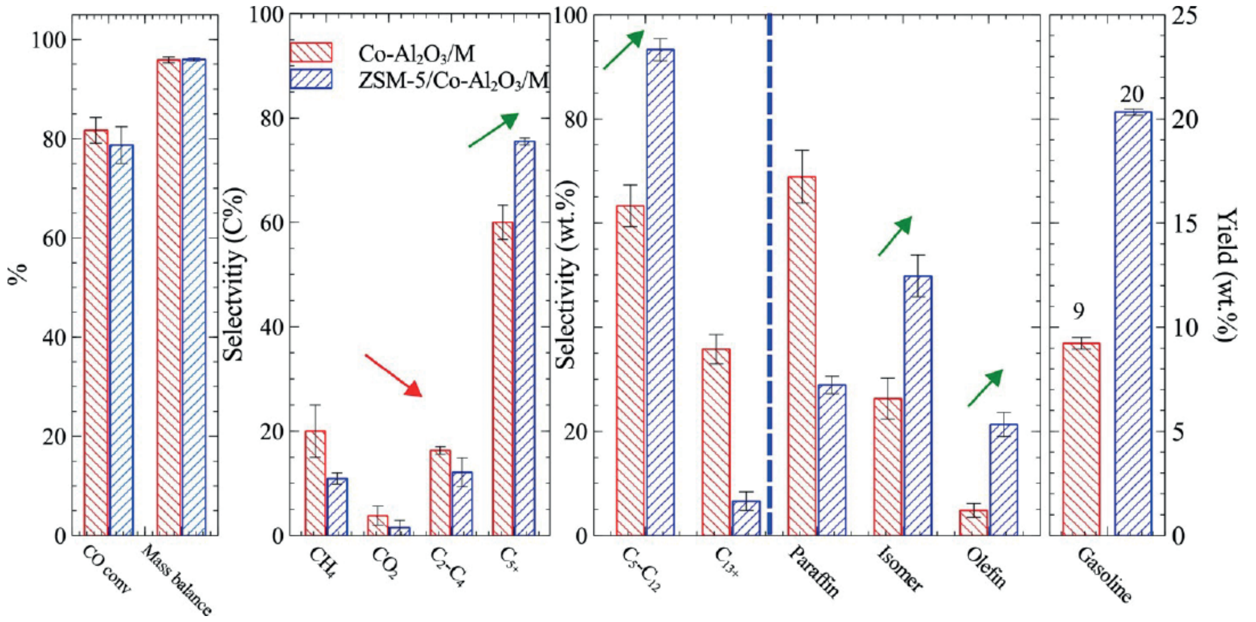

Figure 5: Overall performance summary for catalyst with and without ZSM-5 coating. [23]

Conclusion

There are many different methods and routes for producing biogasoline. There are not many commercial examples of this process since gasoline from crude oil is much more established and economical for companies. However, there is ongoing research worldwide to make the different stages of this process more efficient and viable. The conversion from biomass to gasoline, specifically involving anaerobic digestion, provides a potential alternative to conventional gasoline production with less harmful environmental implications. Ultimately, the types of reactors, catalysts, and syntheses chosen are dependent on the available technology and feedstocks of each country participating in this research.

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