COAL BASED SYNTHETIC FUEL: INTERESTING POSSIBILITY?

In the 21st century, the world's relentless thirst for technological advancements and globalization has raised many questions about the sustainability of the energy supply system. For the past few centuries, to power, the steady rise of industrialization, the use of fossil fuels has skyrocketed. As such, one of the outcomes of using fossil fuels is an increase in carbon dioxide (CO_2) emissions, of which scientists predict that atmospheric carbon dioxide concentration has increased by 47% since the industrial revolution began [1].

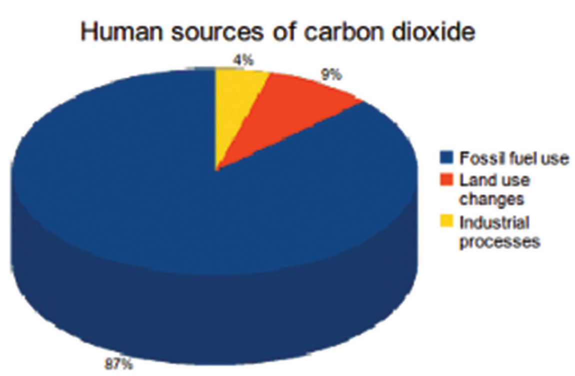

Figure 1: Reason behind carbon dioxide emission [2]

Amongst the three types of fossil fuels (coal, natural gas, and oil), coal is responsible for almost 47% of carbon dioxide emissions. Every ton of coal produces 2.5 tons of carbon dioxide, making it one of the main contributors to global warming [2]. Coal is used to generate large amounts of energy to be converted for use in electricity and the transportation sector.

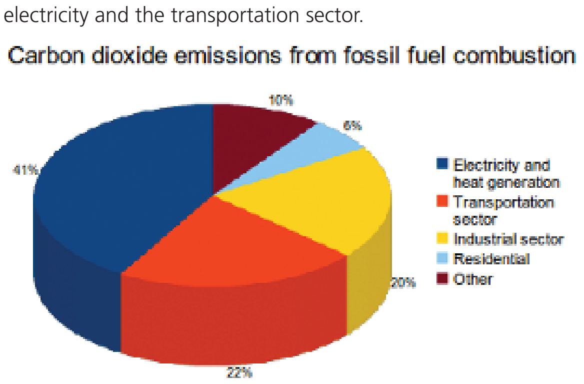

Figure 2: Uses of fossil fuels [2]

Due to its overwhelming impact on the planet's environment, many environmentalists suggest banning the use of fossil fuels and investing in renewable energy sources, but there are several obstacles to be faced during the transition. In the USA, renewable energy only sources supply 12% of the total energy demand, and if this trend continues, it will provide approximately 15% of the energy demand by 2050 [3]. Therefore, researchers are working on making the existing energy sources carbon-neutral and eco-friendly during the inevitable transition towards greater sustainability.

One of these carbon-neutral solutions is the creation of synthetic fuels or synfuel. Synfuel is derived from syngas, which is a mixture of carbon monoxide and hydrogen. During the production process, carbon dioxide is captured and used as a raw material to produce fuels equally efficient to existing fuels. This kind of approach can potentially reduce the production of 2.8 gigatons of carbon dioxide and is economically viable because existing gas stations do not have to be replaced, saving businesses a considerable amount of capital [4].

As researchers are looking for a substitute for crude oil, coal as a feedstock for syngas has gained interest because of its already established commercial and technological uses. Currently, scientists have divided the syngas production processes into pyrolysis, direct liquefaction, and indirect liquefaction [5], which is then utilized to create synfuels via the Fischer-Tropsch (FT) synthesis method developed by two German scientists in 1926, Franz Fischer and Hans Tropsch. Utilizing coal and steam to produce the necessary syngas, Fischer and Tropsch then used a collection of chemical reactions to convert the syngas into liquid hydrocarbon at 1 to 10 atm and 180 °C to 200 °C using cobalt as a catalyst [6]. Current studies have found that the Fischer-Tropsch process at a relatively high temperature (300-350°C) produces gasoline and linear olefins in the presence of iron-based catalysts. Whereas at a relatively low temperature (200-240°C) in the presence of iron or cobalt-based catalysts-high molecular mass linear waxes are produced [7]. For a low-temperature FT process, the ratio of H_2/CO is approximately 1.7, whereas, for a high-temperature FT process, to convert all the H_2, CO, CO_2 into their corresponding products, the ratio of $H_2/(2CO+3CO_2)$ must be 1.05 [8].

Indirect liquefaction of coal (ICL) has been found to be the most commercially viable process involving the gasification of coal. ICL includes two steps; in the first step, coal is converted into syngas (Coal+H_2O-CO+H_2), and during the last step, syngas is synthesized in the presence of a catalyst into liquid fuels. Syngas can be converted into liquid hydrocarbon through the Fischer-Tropsch process or by converting syngas into oxygenates such as methanol, dimethyl ether, etc. [7]. Both industries and researchers widely accept the Fischer-Tropsch process because of its high-quality products. During the gasification stage, the ratio of carbon monoxide and hydrogen should be approximately 2.2:1 or 2.5:1 to achieve the desired volume for when the hydrogen-water gas shift reaction (CO+H_2O-H_2+CO_2) takes place [9]. After that, the gaseous mixture can be converted into various liquid hydrocarbons. Shown below are the reaction mechanisms:

$$(2n + 1)\ H_2 + {}_nCO \rightarrow C_nH_{2n+2} + {}_nH2O\ \text{[paraffins]}$$
$${}_nCO + 2nH_2 \rightarrow {}_nH_2O + C_nH_{2n}\ \text{[olefins]}$$

Where n-is the number of carbon atoms present in a hydrocarbon chain, which ranges from 1-30. The chain growth probability (α) dictates the distribution of chain length, which is expressed in terms of their mass fraction (W_n) [10]. This relation can be expressed as, $W_n=n(1-\alpha)^2\alpha^{n-1}$

Synthetic diesel and waxes are made from paraffins, where n ranges from 12-19 at a relatively low temperature through the FT process, whereas synthetic gasoline is made from olefin products, where n ranges from 5-10 at a relatively high temperature [11]. In ideal conditions, the FT product consists of 40% straight gasoline and 20% propane and butane, and the remainder of the product cannot be converted into liquid hydrocarbons. However, the propane and butane can be oligomerized to gasoline because of their high octane value and branches, whereas gasoline has a low octane number due to its high linearity and low aromatic content [12].

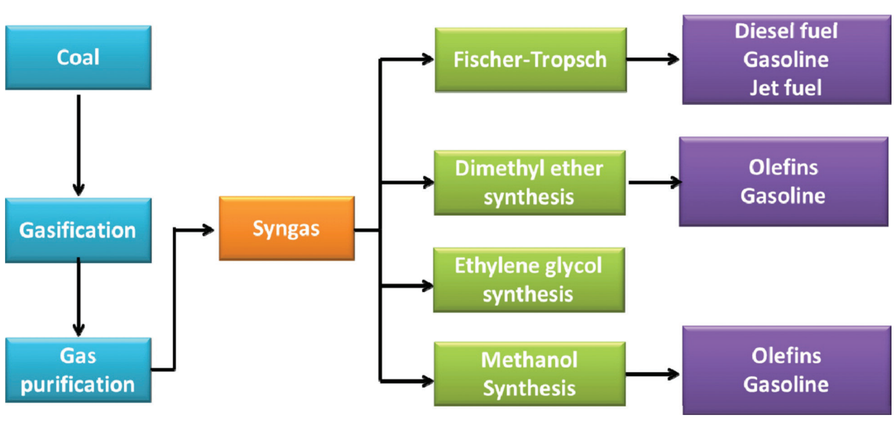

Figure 3: Simplified production process of synfuel [7]

Oxygenates such as methanol and dimethyl ether are gaining interest because of the widespread applications such as diesel fuel oil, cooking oil, chemical feedstock, etc. Currently, industries are trying to synthesize methanol in the presence of CuO-ZnO-Al_2O_3 catalysts because studies show that combinations of Cu/Zn-based catalysts promote methanol synthesis and the water gas shift reactions. To achieve the highest yield, maintaining the size of catalysts is very important because a study shows that smaller Co particles (<5 nm) decrease the turnover frequency[13]. But to maintain the nano-scale size of the catalyst particles, additional methods such as nitrate combustion, sol-gel, etc., techniques needed to be applied [7]. Researchers are trying to find a more stable and cost-effective way of converting syngas into methanol. Some researchers tried to convert methane to methanol directly, but this process had carbon and thermal efficiency of 35% and 28%, respectively, which is about half of the value achieved through ICL [13]. Therefore, it can be said that direct conversion of methanol and other oxygenates cannot serve the purposes.

Direct liquefaction of coal (DCL) involves dissolving coal at a high temperature (750-850 °F) and high pressure (1000-2500 psi) in the presence of hydrogen and a catalyst to break long carbon chains into shorter parts [14]. During this process, coal and solvents are used to prepare a slurry mixture while pressure is added using hydrogen, which is generated from coal or natural gases. The product contains gases, liquids, and a solid residue of coal minerals and carbon. To make the product usable as transportation fuels, it must first be refined, and the solid residue must be separated [15]. The resulting liquids have a thermal efficiency of 60-70% and can be used as a syncrude. After refining the syncrude, transportation fuels (gasoline, diesel) can be recovered alongside propane, butane, etc. [16]. Coal has a lower H/C ratio than that of petroleum, 0.7 to 1.2, respectively, and the addition of hydrogen during the liquefaction process enhances the properties of the resulting synfuel. Direct liquefaction of coal can be achieved using either a single-stage process or a two-stage process; however, due to the high H/C ratio yield of the two-stage process, it has had greater utilization compared to that of the one-stage process. After decades of research, the Bergius process, SRC-I, SRC-II, co-steam process, and H-coal process have proven to be efficient and cost-effective to produce synfuel from direct liquefaction [16]. The main difference between SRC-I, SRC-II, and H-coal is the addition of hydrogen and catalysts during the liquefaction phases. SRC-I, SRC-II use solvent and hydrogen pressure in the first stage, but catalytic hydrogenation is performed to upgrade it in the latter stages. SRC-I and SRC-II have a liquid yield of 20-40%, which is less than when catalysts are used in the first stage. Studies show that using acidic catalysts (Zinc chloride), the liquid yield goes up to 60%, liquid hydrocarbons are lighter, and nitrogen and sulfur concentrations decrease; however, research is still very elementary and yet to be used on a commercial scale[15].

	Direct coal liquefaction (DCL)	Indirect coal liquefaction (ICL)
Concentration of diesel	65% diesel	80% diesel
Diesel cetane number	42-47	70-75
Sulfur content	<5 ppm	<1 ppm
aromatics	4.8%	<4%
Diesel Specific Gravity	0.865	0.780

Table 1: Properties of the final product of ICL and DCL [11]

Finally, pyrolysis is the oldest method of extracting liquid hydrocarbons from the coal at a high temperature (950°C), but the liquid fuel yield is meager. Liquid output can be increased up to 20% by lowering the temperature to 450-650°C [17]; however, compared to ICL and DCL, there is little potential for this process to become mainstream because even it contains a higher H/C ratio than coal, it contains a significant amount of sulfur, nitrogen, and oxygen which lowers the efficiency of IC engines [13].

Another vital consideration of synfuel production is the reactors utilized during the process. Multi-tubular fixed bed, the slurry reactor, or the fluidized bed reactors, with either a fixed bed or a circulating bed, are the four most commonly used Fischer-Tropsch reactors [18]. The fixed bed reactors and the slurry reactors are both operated at relatively low temperatures (200-230°C), but in the fixed bed reactors, catalysts act as a surface-active agent in the tubes. In contrast, catalysts in slurry reactors have no specific position [18]. Among these two reactors, the slurry reactor is more convenient because it has a high conversion rate, and produced fuels demonstrate a high paraffinic nature with a low aromatic content (<3%) that is also nitrogen sulfur-free [15]. A study found that a slurry reactor operated at 250°C, using iron (Fe) as a catalyst, produces long hydrocarbon chains that can be refined to produce high-quality diesel, where the α value is approximately 0.9 [10]. In contrast, the fluidized bed reactors are operated at a higher temperature (300 to 330°C), mainly for alkene production [18].

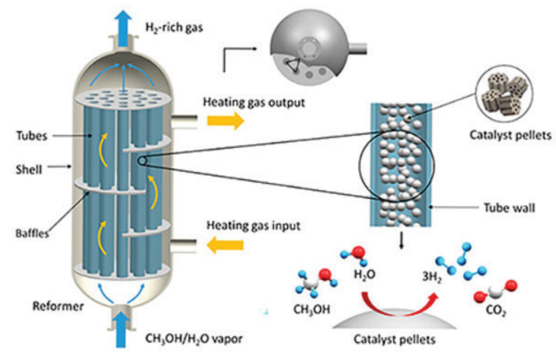

Figure 3: Multi-tubular fixed bed reactors [19]

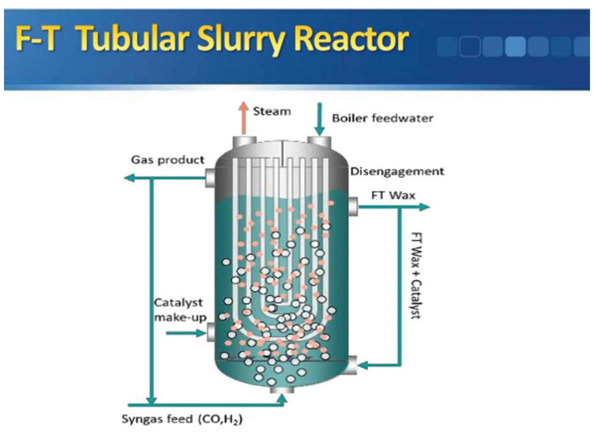

Figure 4: Slurry reactor[20]

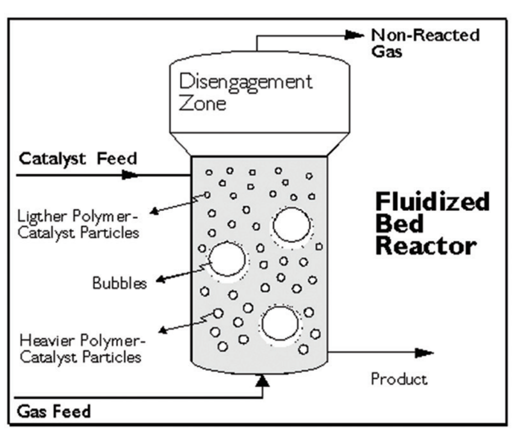

Figure 5: Fluidized bed reactor [21]

Many researchers believe that synfuel is a practical solution for the energy crisis. Although electric cars are gaining popularity due to batteries' shortcomings, such as increased vehicle weight and increased refueling time, electric vehicles are currently not the most optimal solution [22]. On the other hand, synfuels are proven to be equally efficient as existing diesel and gasoline fuels. As countries in Europe are shutting down coal-powered plants, it is time to think about the potential repurposed coal has for powering cars. Studies have found significant potential in this field. Although low energy density is still a problem for ICL fuels, blending can solve this issue. A recent study has found synthetic diesel can be used directly by internal combustion (IC) engines without distillation if it is blended with traditional diesel resulting in a 20 vol% synthetic diesel fuel, reducing emissions of nitrogen, carbon dioxide, etc. [23] and addressing the environmental concerns of the utilization of fossil fuels to power vehicles. Studies show that the optimum cetane number is 51-53 for fuels, and as it increases, engine efficiency increases, and greenhouse gas emissions decrease. By blending 20 vol% synthetic fuel with traditional #2 diesel, the cetane number rises from 45 to 51, lowering the sulfur, nitrogen, carbon, and other aromatic contents [23]. Another study tested the effectiveness of synthetic fuel in the four different diesel vehicles (category II-V), and the cetane number went up to 69 when 80 vol% synfuels were blended with conventional diesel reducing emissions by a similar rate [23].

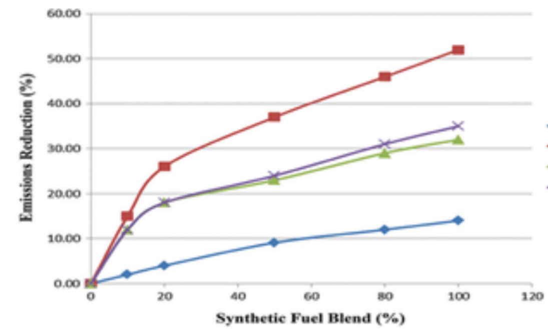

Figure 6: Synfuel blended in crude oil reduces emission [23]

Also, recently environmental legislators are limiting the aromatic contents in transportation fuels, opening the avenue for ICL-fuels due to their low aromatic content as well as inexpensive removal of toxic inorganic compounds such as mercury, cadmium, arsenic, and lead from the fuel, making it a better option than existing crude-oil based fuel [24].

Although synthetic fuel is carbon neutral and the current vehicles do not require any significant modifications to switch to synthetic fuel. Because fuels for typical internal combustion (IC) engines are a combination of carbon and hydrogen, each element has unique physical properties such as boiling point, heating value (HV), and density, and the gasoline, diesel produced from syngas have similar properties making it eligible fuel for current IC engines. The presence of nitrogen, oxygen, sulfur lowers the HV and produces gases like H_2O and CO_2, which causes a decrease in fuel efficiency and increases the cost of maintenance [25]. Although gasoline and diesel produced from syngas have a low concentration of nitrogen and sulfur, when it burns in the presence of oxygen, carbon dioxide is produced automatically, lowering the HV. Gasoline engines are capable of only using 15% of the fuel's total energy, whereas existing electric cars have an energy efficiency of 80% [26]. This shows that even if synfuels have the potential of replacing traditional transportation fuels, it is not going to be the best alternative, especially considering that money needs to be invested in developing the necessary infrastructure.

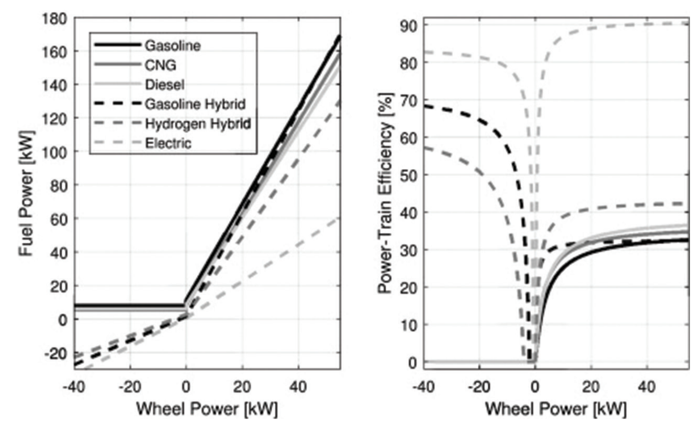

Figure 7: Efficiency of different fuels [22]

Synfuels can also be directly used in automobile engines because of the similar properties and chemical structure as the existing diesel and gasoline fuels, while currently available biofuels such as ethanol require vehicles to have specific engines. During synfuel production, most of the carbon dioxide and heavy metals are captured, making the process cleaner than existing crude oils [27]. A study goes even further to say that the lifetime cost of a vehicle running on synthetic fuels will be less than that of all the existing vehicles utilizing other fuel sources [28]. A recent car produced by McLaren Automotive runs on synthetic fuels showcasing that the internal combustion engine did not require any significant modification, showing its commercial appeal [29].

Table 2: Comparison of FT & crude oil [30]

Property	FT-crude oils	Crude oil
Paraffins	>10%	Major product
Naphthene	<1%	Major product
Olefins	Major product	none
Aromatics	5%	Major product
Oxygenates	5-15%	<1% O (heavy)
Sulfur	none	0.1-5%
Nitrogen	None	<1%

Despite having significant environmental benefits, synfuels have not gained popularity because of the production costs. A recent study shows that it will take approximately 30 to 40 years for the USA to adopt synthetic fuels, costing approximately $1.1 trillion [27]. While synfuel is cheaper than other renewable energy sources, it is still costlier than the existing crude oils. Cobalt, iron, and ruthenium are commonly used catalysts in synfuel production plants. Metals like cobalt and ruthenium are neither particularly abundant nor cheap—the estimated price of synthetic fuel range from $3.80 to $9.20 per gallon. In contrast, the regular crude oil price is $2.60 to 2.73 per gallon. Some researchers predict that the final cost will achieve around $3.78 per gallon once the production scale increases [31], but the price is not competitive, considering that drivers want efficient fuels at a lower price. Therefore, to make the use of synthetic fuel mainstream, researchers should work on lowering the production cost of the FT process.

The National petroleum council presented a goal of producing 5.5. million barrels per day Coal to liquid (CTL) fuel using 1439 Mt coal by 2030, but according to the studies conducted by independent organizations to achieve this goal, 1466 to 2100 million ton (Mt) coal will be consumed, which is more than the coal extracted in the USA. Hence, it can be said that this goal is not realistically achievable within 20 years [11].

Some scientists oppose the use of coal to produce synfuel. A recent study predicts that, although the Fischer-Tropsch process produces clean fuels, the plant itself releases a significant amount of pollutants to the environment. Researchers estimate that synthetic fuels' utilization might double the carbon dioxide in the atmosphere in 30 years, also mentioning that it cannot be the ultimate solution, and the government should invest more in renewable energy sources [32]. A well-to-wheel analysis has shown that DCL generates 90% and ICL emits 80-110% more carbon dioxide than conventional fuels due to the mining process [24]. Research also shows that the biggest user of the Fischer-Tropsch process, South Africa is the 14th largest emitter of carbon dioxide, where 50% of the emissions are due to coal-based synthetic fuel plants [33].

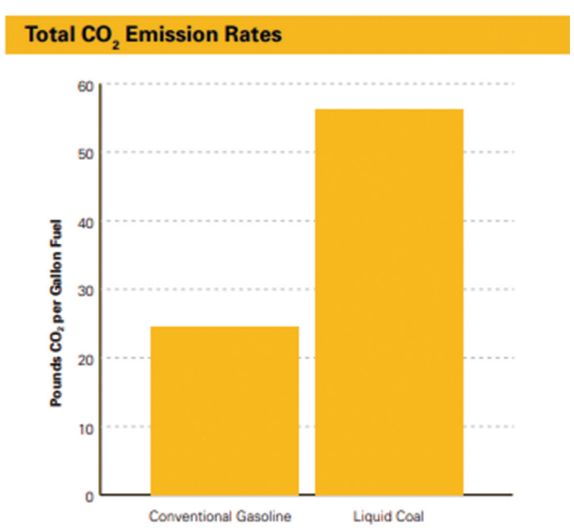

Figure 8: Comparison between gasoline and liquid coal-based fuel [34]

Researchers have introduced an alternative way of using coal to address these issues to produce synfuel, known as coal-biomass to liquid or CBTL process. One of the main concerns regarding the CTL process is that the production process causes carbon emissions. However, biomass is a carbon-neutral compound that reutilizes the atmospheric carbon dioxide such that its addition to the typical CTL process will reduce the carbon footprint. During this process, both biomass and coal are gasified into syngas and converted into synfuel. In the direct CBTL plant, coal and biomass are directly converted into syncrude using the hydrogen produced from the gasification of coal/biomass in the catalytic two-stage liquefaction (CTSL) unit. In the indirect CBTL plant, coal and biomass are pre-processed and sent to two different gasification units, syngas production unit or CTSL unit, and later the produced syngas is sent to FT unit or hydrogen production unit [35]. By utilizing two different gasifiers for coal and biomass, the production cost and carbon footprint both increase. Therefore, researchers are trying to apply thermal pre-treatment and torrefaction, in which biomass is moderately heated in a low oxygen environment, reducing the O/C ratio and increasing the outcome of carbon dioxide and hydrogen during gasification, which is later converted into an energy-dense, homogeneous, similar to coal solid [36]. The amount of carbon dioxide produced by FT is higher because the iron-based catalysts have a higher water-gas shift reaction activity than cobalt-based catalysts, but carbon capture and storage (CCS) technology can address this problem by capturing carbon dioxide and protecting the downstream catalysts. CCS technology utilizes amine groups (secondary and tertiary) to capture carbon dioxide because of the lower solvent loss, lower heating requirement, and corrosivity. An increase in the carbon/hydrogen ratio does not change the conversion rate of carbon as lighter hydrocarbons are produced (C1-C20), but the carbon consumption by CCS increases. Furthermore, the biomass type does not have a significant impact on the efficiency and yield of hydrocarbons, yet the thermal efficiency may vary slightly as the products from wood chips are lower due to the presence of oxygen [35].

Biomass	Wood Chips	Bagasse	Torrefied wood
Feedstock			
Dry coal (ton/hr)	153.8	153.4	153.3
Dry Biomass	13.5	13.3	13.8
Product			
Gasoline (bbl/day)	4050	4050	4050
Diesel (bbl/day)	5950	5950	5950
C capture by FT (%)	36.3	36.4	38.2
Thermal efficiency	46.1	46.8	47.9

Table 3: Impact of Biomass type [35]

Although there is an immense possibility in this sector, it is not a competitive fuel alternative due to the lack of capital and infrastructure. Also, there is not much research available on this topic, but it has a huge potential considering the environmental impact.

Considering the advantages and shortcomings of synfuel production, it can be said that synfuel cannot be the ultimate solution to the energy crisis. Crude oils have been the primary source of energy since the beginning of industrialization, but as the concern about its environmental impact is rising, scientists are looking for new solutions. Although many people consider batteries and electric cars as a unique solution, it is not entirely true. The energy density of such batteries is approximately 1% of crude oil-based fuels [37]. Although 48 GW of coal capacity has been shut down in the United States in the last five years, however, a study predicts that coal will supply 30% of energy demand. But the retirement process of coal will slow down this year, and the low price of coal will make the CTL process more cost-effective than other sustainable energy sources [38].

And many researchers have shown that the synfuels produced through the Fischer-Tropsch process are equally efficient as crude oils and a clean source of energy. However, the carbon dioxide and pollutants released by the production plants during the process concern environmental scientists. Furthermore, the high production cost makes it difficult for synfuels to compete with existing fuel sources. Therefore, the future of synfuels does not look very promising. However, if researchers can make the production process less environmentally hazardous and cost-effective, it can become another possible fuel source for transitioning towards greater sustainability.

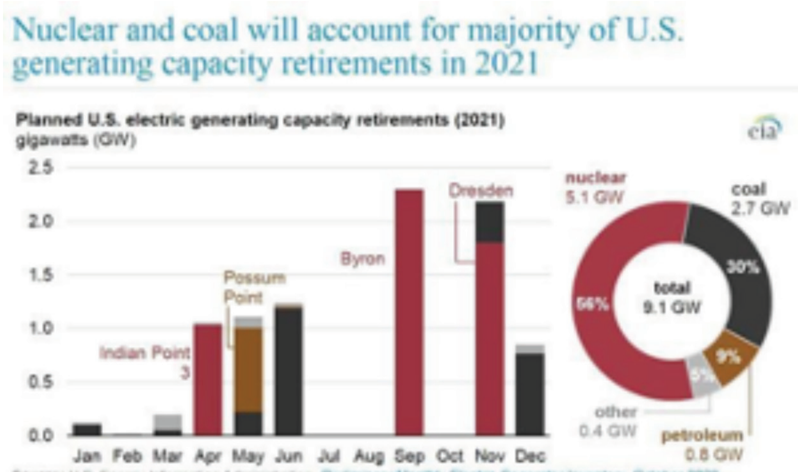

Figure 9: Future of coal [38]

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https://www.petro-online.com/news/fuel-for-thought/13/koehler-instrument-company/dr-raj-shah-director-at-koehler-instrument-company-conferred-with-multifarious-accolades/53404

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