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Supercritical Water Gasification and Pyrolysis – Cleaning up the Great Pacific Garbage Patch

Kelly L. Emery

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Supercritical Water Gasification and Pyrolysis – Cleaning up the Great Pacific Garbage Patch

An Undergraduate Thesis

By Kelly L. Emery

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Thesis Advisor: Name: Dr. Jamie L. Shamrock

Thesis Reader: Name: Amanda Gangwish

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Preface:

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Introduction:

This research paper is a comparative meta-analysis of gasification of hydrocarbons in supercritical water, specifically concerning the great pacific garbage patch (GPGP). The research explores two ways to clean up the GPGP while also harnessing the waste as biofuel. This research compares the environmental and economic outcomes between supercritical water gasification and pyrolysis. I will be comparing which thermochemical process of converting hydro-pollution into usable, methane-rich gas is most economically beneficial and environmentally sustainable. The relevance of this use of plastic refuse is that it would not just be diverted to a different landfill or back right where it started in the first place, but rather serve a new purpose: A source of energy that will not run out quickly. The application of this to the Great Pacific Garbage Patch (GPGP) is that this process can be used to clean up the material and give an economic incentive to do so by harnessing energy from the broken-down materials. (Bai, 2019) This is relevant to the GPGP because the materials are not all solids. The GPGP is not a giant solid object floating through the pacific gyre.

The Patch is primarily supercritical water and a mixture of water-soluble/broken-down microplastics floating in the east, west, and the subtropical convergence zone of the Pacific Ocean. This breakdown of chemicals makes a thick gelatinous-like material. Because the material is viscous in nature, it is much easier for fish to get caught in the matrix of the supercritical water, consume the material as if it were food, or simply ingest it into their diet – affecting their offspring and the food we eat. Both of these ways of harnessing the energy from the waste tie back to the main problem of cleaning up the GPGP without causing further harm to the environment and solving a growing issue. (Gilsam, 2021) The benefits of cleaning up the GPGP outweigh the negatives. Human health, migration patterns in marine life, economic opportunity, and sustainable energy consumption are just a few of the many ways that this topic can affect everyone, whether they live in a land-locked state like Nebraska, or they are over 50% of the population of the world that lives by a coast.

Hypothesis:

My hypothesis is that gasification will be a more applicable method of converting waste because of gasification's ability to convert dry feedstock, such as plastic, into bioproducts. I hypothesize pyrolysis may be more economically feasible or beneficial because of its current uses in the waste industry. (Bioforcetech, 2020)

Gasification	Gasification is achieved by the partial combustion of the biomass in a low oxygen environment, leading to the release of a gaseous product (producer gas or syngas). So-called "allothermal" or indirect gasification is also possible. The gasifier can either be of a "fixed bed", "fluidised bed" or "entrained flow" configuration. The resulting gas is a mixture of carbon monoxide, water, CO_2, char, tar and hydrogen, and it can be used in combustion engines, micro-turbines, fuel cells or gas turbines. When used in turbines and fuel cells, higher electrical efficiencies can be achieved than those achieved in a steam turbine. It is possible to co-fire a power plant either directly (i.e. biomass and coal are gasified together) or indirectly (i.e. gasifying coal and biomass separately for use in gas turbines).
Pyrolsis	Pyrolsis is a subset of gasification systems. In pyrolysis, the partial combustion is stopped at a lower temperature (450°C to 600°C), resulting in the creation of a liquid bio-oil, as well as gaseous and solid products. The pyrolysis oil can then be used as a fuel to generate electricity.

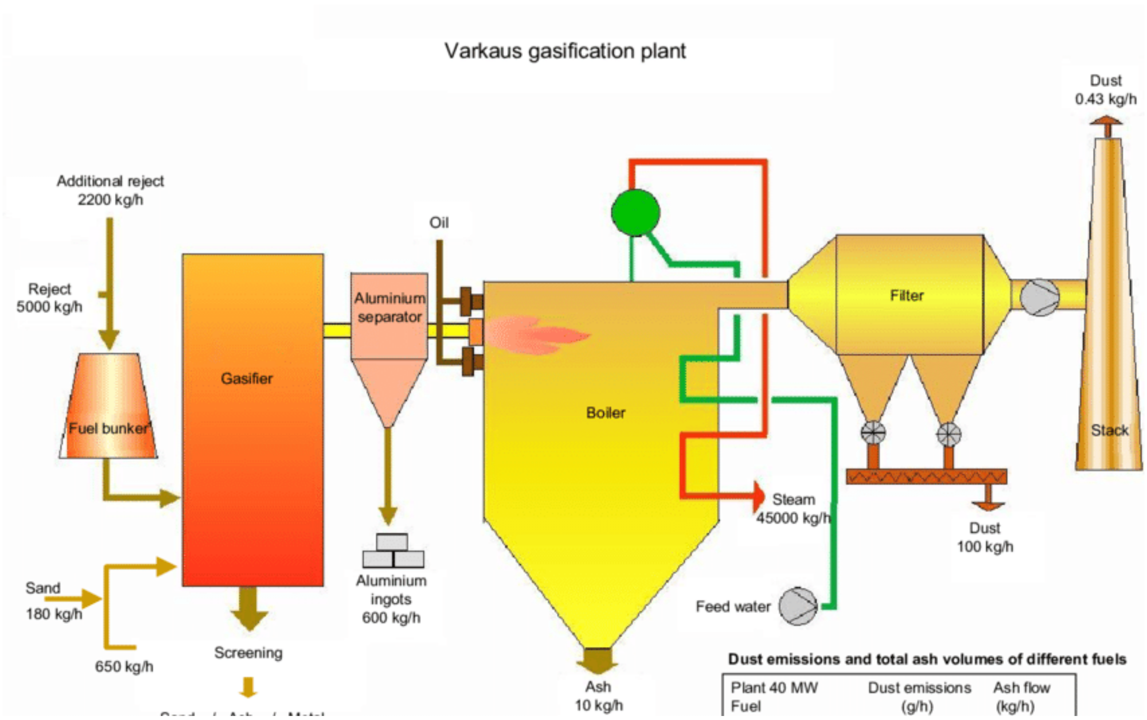
(Irenia, 2012)

I used this model for explanation in the proposal on its own in order to best explain the process without comparing several different diagrams and machines that I have found. This explanation and process is not the only way for pyrolysis to occur – but is the simplest breakdown of the steps of the processes. Pyrolysis is a subcategory of gasification - the difference is that Pyrolysis is limited to 300ºC and 600ºC and does not have the second step of gasification of the char by-product into CO and H2. (Irenia, 2012)

Introduction to gasification:

A supercritical fluid is any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist, but below the pressure required to compress it into a solid. (Withag 2012) This is important to understand the topic and the "sludge water" that lives within the GPGP. Gasification is the process of converting this water into a gas – in this case, a methane-rich usable gas. Low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), and polystyrene (PP) are the plastics I will be focusing on so far that are present in the pacific garbage patch. Water-soluble plastics, oil, and water mixtures can create synthetic natural gas (SNG) with the gasification process. The gasification of hydrocarbons in supercritical water is based on the characteristic that supercritical water acts not only as a solvent but also as a reagent (Pinkwart, 2004). Basically, there is no melting of the plastics but instead taking a solid to a liquid and then taking it straight to the form of gas within seconds. This reduces the volume of greenhouse gasses (GHGs) that the process creates. When the transformation is complete, semi-natural gas rich in methane remains that can be used as energy and stored easily without extreme environments. (Kotrba, Ryan n.d) This process applies to cleaning up the GPGP and is used in cleaning oil spills within the fracking industry. (Chu) Large oil spills are not as common; however, oil sludge infects the Pacific in a variety of areas over the long term. Oil spills can never be 100% cleaned and rarely cleaned quickly enough. According to the National Oceanic and Atmospheric Administration, the Coast Guard is primarily responsible for cleaning oil spills. This process happens slowly and usually heavily relies on non-profits for funding and a quicker reaction to cleanup (U.S. Department of

Commerce, 2020). The mixture of supercritical water or plastic sludge can be safely disposed of, but we also need to consider recovering the lost energy. With the gasification of supercritical water and mixtures – these fuels can be retrieved into usable energy again. (Peng) With supercritical water – the organic matter is higher, which is viable for gasification through increasing temperature and then pressurizing the gas by cooling the pressurizer. (Chu. 2021) The products we are focused on yielding are CH_4, C_2H_4, C_2H_6, CO, and H_2 - They are the most commonly used natural gases. (Leonard 2012)

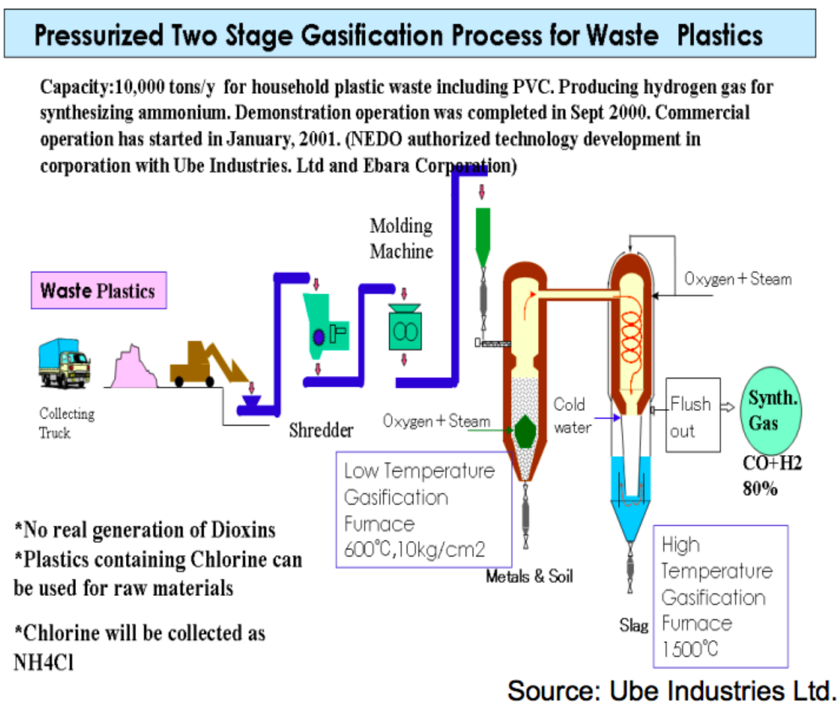


(OPET, 2002)

The diagram above is of the Varkhaus gasification plant in Finland – this was the first gasification plant in Finland and is used for gasifying aluminum and plastics after the recycling process. (OPET, 2002) In this specific process, aluminum is removed from the gas and recycled, while the gas product is used to fuel other parts of the recycling plant and this machine. This model is referred to as a commercial Circulating Fluidized Bed (CFB) gasifier. (OPET, 2002) The process starts with a refractory line reactor where the gasification takes place. Then a cyclone separates the materials that cannot be gasified (metal and soil). Then the selected approved material sinks to the bottom of this cyclone and goes through a return leg into the bottom part of the gasifier. The temperature stays between 800^{o}-1000^{o}C to convert the material. (OPET, 2002) The gas is then fed to a separate part of the gasifier, where the gas dries and is separated into containment chambers that separate synthetics gas (syngas) and biofuel. In the above model, they use pyrolysis as well as gasification to condense the product into fuel and gas and then re-feed the fuel through in order to create a more usable gas for their needs. (OPET, 2002)

Although the above model used both processes, I still see this diagram as a valuable tool in understanding the gasification process and whether or not it is possible to have a gasification process on its own without the need for condensing or drying (pyrolysis).

Figure8

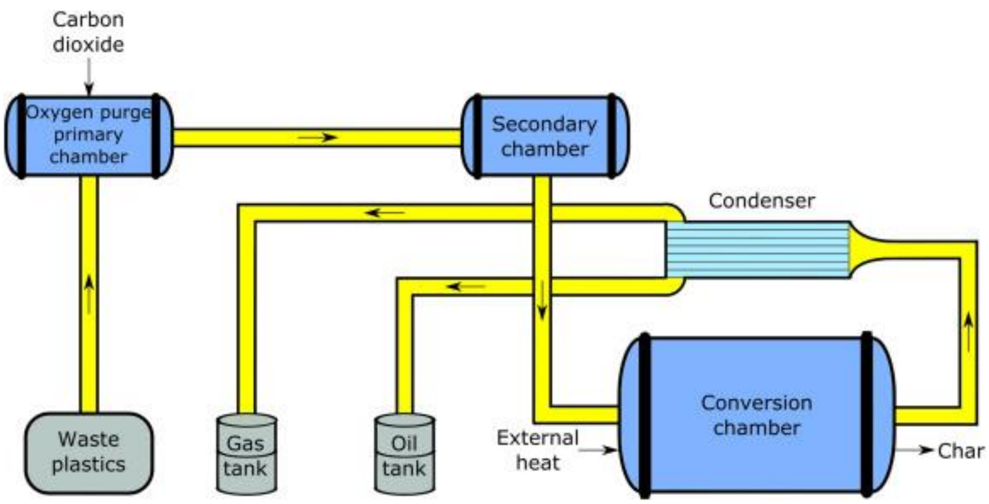


(Takashi, 2009)

The above diagram shows a two-step gasification process from UBE Industries Ltd. It has been in full operation since 2002, and UBE Industries have maintained and improved on it. (Takashi, 2009) This type of gasifier is unique because all forms of plastics can go inside, including PVC. This is important for two reasons. First, PVC is widely known as non-recyclable and usually not accepted in the pyrolysis process. (Takashi, 2009) Secondly, collected material from the GPGP contains multiple plastic types that would be difficult to separate in their current gelatinous form. The plastics then go through high temperatures or quick gasification. The ash and water are discarded and used for cement, and the gas is purified with an alkaline treatment, allowing it to be accepted as de-chlorinated material gas. (Takashi, 2009)

Introduction to Pyrolysis:

Pyrolysis - (devolatilization) is the thermal degradation of an organic substance in the absence of air to produce char, pyrolysis oil, and synthesis gas, for example, wood conversion to charcoal. (Onwudili, 2016) PP produced the highest yields of these hydrocarbon gases. Hydrocarbons are compounds composed exclusively of carbon and hydrogen. They are the dominant components of crude oil, processed petroleum hydrocarbons (gasoline, diesel, kerosene, fuel oil, and lubricating oil), coal tar, creosote, dyestuff, and pyrolysis waste products. (S.M. Al-Salem, 2007) For all four plastics mentioned above, the methane product accounted for more than 75% of the hydrogen atoms, indicating effective methanation or other methane-formation mechanisms. (Kotrba, Ryan, n.d) Pyrolysis works by random depolymerization - breaking down the bonds within the waste plastics to create liquid hydrocarbons that can be used as fuel. With the system from Polymer Energy LLC, a division of Northern Technologies International Corp., we can expect 78% of every pound of plastic to be turned into liquid fuel. The prediction for the pyrolysis reaction is that the yield will be around 75-85%.



(Kalargaris, 2017)

The image above is an example of a pyrolysis condensing machine and the process. Approximately 1-2 cm pieces of plastics are put into the primary chamber to start. Then, carbon dioxide is forced into the primary and secondary chambers to push the plastics to the bottom and ensure no oxygen makes it to the conversion chamber. (Kalargaris, 2017) It is in the conversion chamber that fast pyrolysis occurs. (The temperature must be maintained around 700º-900ºC.) As seen in the diagram, the outcomes of the conversion chamber are gas and char; the char makes up about 10% of the yield of the product. (Kalargaris, 2017)

In the condenser, the gas is cooled down to 20ºC to separate the gas and oil. The oil is then filtered and the final two products are completed. It is important to note that the primary plastics used in this model are styrene, butadiene, and polyester plastics. (Kalargaris, 2017)

Methods

The approach for this research paper is a meta-analysis and systematic literature review. To grasp the economic feasibility of pyrolysis and gasification, many sources and analyses have been considered to find the average and most comprehensible conclusion. According to almost all sources on the subject of waste gasification, the technology and advancements are new, and parts are yet to be refined. Because of the ongoing and new research being done, gasification processes had multiple cross analyses between different reactors and processes. Through research, it was inconclusive as to which method is both environmentally most sustainable and economically profitable. As a result of the lack of conclusion, the economic comparison will focus on Plasma Gasification. Pyrolysis was more straightforward in that it has already been used in the recycling and waste treatment industries in a separation 2-fuel process.

Sustainability:

Considering the environmental impact of these processes is a crucial part of resolving the already existing pollution problem in the GPGP. Taking pollution from the ocean or landfills and turning it into unsustainable fuels that produce GHGs is a significant concern in the process. To measure sustainability, we will discuss the energy intake for the waste processing plants to operate a the products they make and sell for energy consumption. Data collection was taken from multiple resources to create a holistic picture of the environmental sustainability of pyrolysis outputs syngas, slag, , oil and plastic gasification syngas and slag.

Economics:

Economic analysis plays a critical role in the recommendation for plastic waste treatment. Whether or not the model is adopted as a business model depends on its feasibility. Data collection for economic analysis was also taken from multiple resources and did not follow one particular case study but an average view of cost and production. To keep the research unbiased, quotes of prices and profit were taken from reports and scholarly reviews rather than private companies. This ensured that the profitability of gasification or pyrolysis was not inflated for business purposes or investors.

To keep sustainability and economics separate, I will discuss the outcomes of each category in the discussion section of this paper; then I will base my recommendation on the weight of both results.

Research questions:

Can plastic waste pyrolysis or gasification be environmentally sustainable and a potential solution to the Great Pacific Garbage Patch?

Is plastic waste pyrolysis or gasification plants an economically sound business model? Which plastic waste process is economically most profitable?

Results

Choosing the correct type of gasification:

There are multiple different types of gasification in terms of plastic waste to energy. The two I compared are the most efficient and modern in terms of the best available technologies. I compared fluidized bed gasification and plasma arc gasification. Other gasification methods are viable; however, some were not considered due to the lack of scholarly, unbiased research on the methods. The results from the feasibility of both gasification types are that, specifically plasma arc gasification is more efficient. The conversion capacity of a plasma gasifier can reach up to 100%, as opposed to a circulating fluidized bed gasifier which can only reach up to 95% conversion capacity. According to research done by Pentakota, Plasma gasification is also automatic, meaning that it feeds itself. The energy made from the gasification technology would have enough to sustain itself and produce a profitable amount of product. Plasma Arc gasification also requires only 1.088 acres of land per municipal waste compared to a fluidized bed gasifier which needs around 10 acres of land for the same amount. (Pentakota, 2016) The land use brings down the initial cost of starting a gasification plant. The byproducts from a plasma gasifier do not need to be treated before being sold to third parties; however, there's a considerable variation in the upfront capital initial cost of plasma and circulating fluidized bed gasification. The cost to set up a plasma arc gasification plant with the current technology is around 1,083,655 USD.

In contrast, the initial setup cost for a circulating fluidized bed gasification plant is around 131,671 USD. The price difference is due to the lack of development in plasma-arc gasification - a new technology in the world of waste-to-energy. Recommending plasma-arc gasification comes from its benefits in sustainability and long-term profits. The process has high thermal efficiency, and as a result, MSW containing moisture around 50% can be gasified without need for pre-drying. The newest technology in the waste-energy industry means that old less efficient gasification models will eventually become less profitable with competing plasma arc gasification (Pentakota, 2016).

Pyrolysis:

Plastic waste pyrolysis is already used widely in the waste industry and the sustainable methods did not need to be compared. The methods of pyrolysis are described in the pyrolysis section of the introduction. Each source was consistent in the methods of pyrolysis plants.

Cost analysis:

Cost comparison	**Gasification**	**Pyrolysis**
Capital cost	$1,084,000	$1,272,000
Profit ($/Ton)	$279	$443.4
Rate of return	25% (4 years)	19.8% (5 years)
Operating Cost ($/Ton)	$32/ton.	$15.77/ton

The numbers listed in the table above were calculated and estimated from several sources to create a holistic picture of average costs and economic values. (Hamid, et, al. 2021), (Ducharme 2010), (Homolka, 2019). The sources were chosen due to the similarity in size and operation intention of the plants. These are smaller-scale plants that have been researched by academic research in order to prevent company-bias in reporting profitability.

The capital cost of the plants is similar, with plasma gasification starting at $1,083,655 and pyrolysis starting at $1,272,070 (Hamid, et, al. 2021). One of the biggest barriers to both of these technologies is the high capital investment and upfront costs of these power plants. (Ducharme 2010) With the production cost of gasification being significantly higher, the profit falls lower. The profit of products was calculated by the following formula:
Selling price - Production cost = Profit.

The temperature for gasification to occur must be between 800º-1000ºC to convert the material (OPET, 2002). Pyrolysis does not need as high of temperature, needing to be maintained around 700º-900ºC (Kalargaris, 2017).

Both of these estimates are made by calculating labor cost, fuel cost, repair cost, and maintenance cost.

Gasification profit
Electric products selling price = $286/ton.
Hydrogen products selling price = $197/ton
Total selling price= $486
Production Cost (4/ton) = $207
Profit = Selling price - production cost = $279/ton
(Homolka, 2019)

Pyrolysis Profit
Selling Price = $550/ton
Production Cost ($/ton) = $106.6/ton
Profit = Selling price - production cost = $443.4/ton
(Hamid, et, al. 2021) , (Ducharme 2010)

Because the technology is new in the realm of gasification, there is no direct standardized price; therefore, estimates in the above chart have been made from the most recent academically reviewed models available

Other costs:

There are many smaller variables that affect the operating cost of both power plant models. The cost of transportation of waste materials was not clear within the research. The cost of transportation greatly varies and depends on multiple factors. The factors that would need to be considered are the distance from source and factory, vehicles used to transport waste, labor cost, country of operation, legal fees, and fuel price for vehicles. Within these calculations, the transportation cost is omitted from the model.

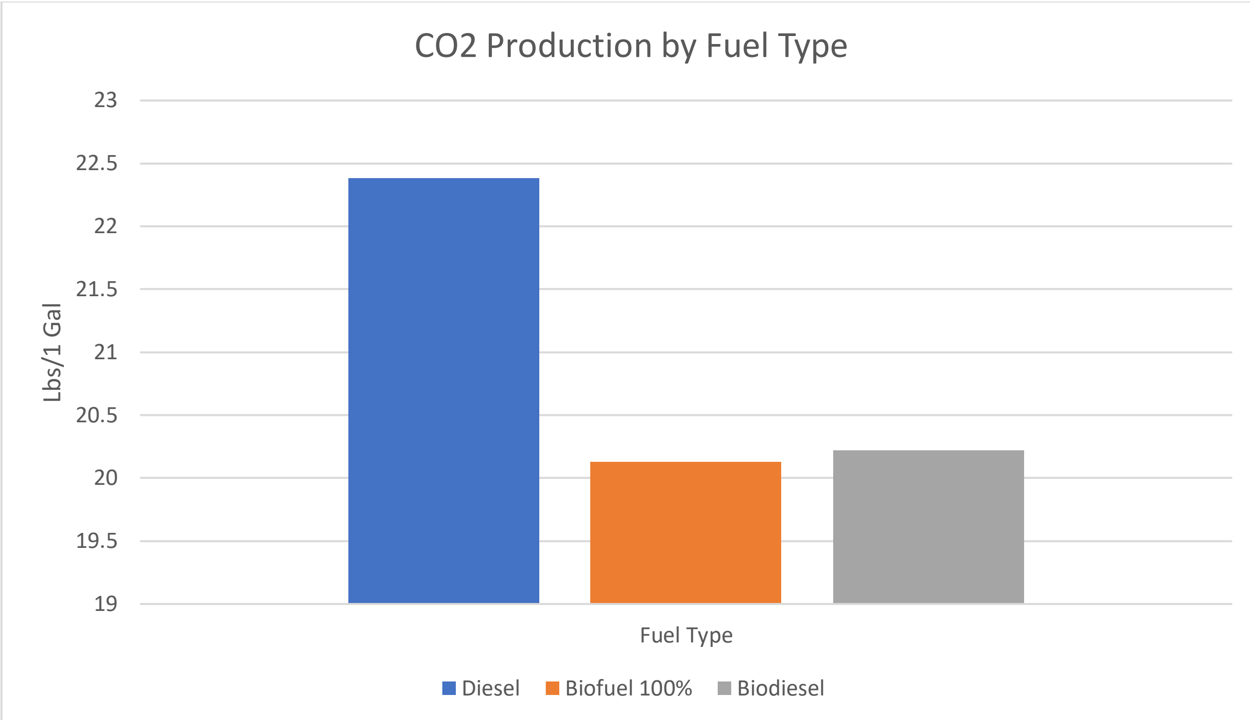
The country of operation is an important factor in the research and economic model process. With the model produced, economic research was conducted in India and Pakistan. These countries are similar in cost of labor. I deemed the similarities of production costs to be similar based on the economic average cost of labor in both countries, selling price of products, geographic similarities in their respective regions. Cost of labor in India was, on average, 1.7 dollars per hour in 2015 (Statista, 2020), and in Pakistan, 1.23 dollars per hour in 2012. (NationMaster, 2013). Many of these factors could change significantly depending upon the local or national economies in which they are employed globally.

Discussion

Sustainability:

Liquid fuel products:

Pyrolysis produces two fuel types – biofuel and syngas (synthetic gas). These gases are identical or very similar in operation and structure (T. Mendiara et al., 2018). Gasification can produce syngas. One problem with syngas is the lower calorific value, indicating a lower efficiency as they burn at a lower temperature than traditional fossil fuel natural gases. (T. Mendiara et al., 2018). Pyrolysis fuel is unable to be efficient on its own at this time. Most literature references the biofuel with other forms of biofuel such as ethanol or organic pyrolysis biofuel, or the fuel must be mixed with diesel to make biodiesel (Kalargaris, 2017). The emissions for CO_2 were higher in the combined biodiesel in several studies, but the overall emission of diesel still outweighed the emissions of the biodiesels. Blending pyrolysis biofuel with diesel is possible or efficiency at 25%-40% when mixed with diesel. (Kalargaris, 2017).

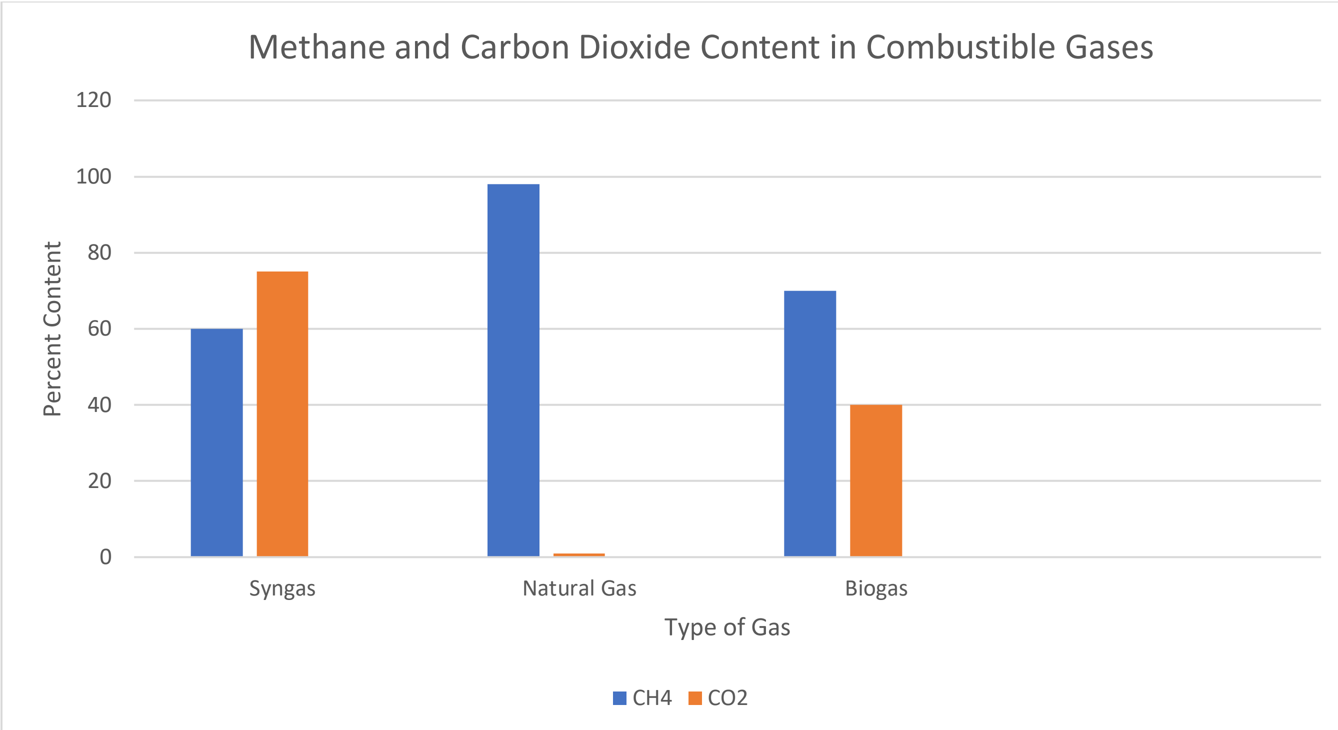


Biodiesel (B20) produces about 20.22 pounds of CO2 per gal.
B100 (100% biodiesel) produces 20.13 pounds of CO2 per gal.
Diesel fuel produces 22.38 pounds of CO2 per gal.
(EIA, 2014)

Gas Products:

I compared the three gasses in this research: natural gas, biogas, and synthetic gas. Synthetic gas includes the products that are produced through gasification and the pyrolysis processes. These three gaseous products were chosen based on their popularity among energy use via combustion. Generally, the combustion of synthetic gas produces much more CO_2 than natural gas due to the vast spread of treatments done to synthetic gas. The table below shows the chemical variations seen in these products with respect to greenhouse gas

Type of Gas	CH4 Content	CO/CO2 Content
Syngas	40-60% vol. (Othman, 2016)	45-75% vol. (U.S. Department of Energy, 1999)
Natural gas	87-98%.vol. (Ortech, 2017)	0.05-1% vol. (Ortech, 2017)
Biogas	50-70% vol. (Tanigawa, 2017)	30-40% vol. (Tanigawa, 2017)



This chart includes only the highest percentage from each category to represent each gas product's maximum CH4 and CO2 content.

When comparing the composition of these gasses, there is no question that syngas produces more CO2 than the other three analyzed gases. This information shows that the other alternative uses a significantly larger amount of methane for combustion. It is important to note that methane is ~25 times more efficient at trapping heat within the atmosphere (EPA, 2021). I would suggest that syngas and biofuel are more sustainable alternatives to natural gas and should be considered for use as a more sustainable, or at least less-detrimental, alternative energy source than natural gas. The ultimate goal is to reduce GHGs and specifically GHGs that are more heat-trapping in Earth's atmosphere. Concluding the gas-sustainability discussion, I would say syngas, a gasification product, is more sustainable than biogas and Natural gas.

<u>Economics</u>:

While gasification has a higher rate of return due to lower capital cost, it is not as profitable long-term due to the length of the payback period required for investors to recoup their initial investment. While the initial investment is lower than pyrolysis, gasification has a higher operating cost per ton (determined by operating costs/total annual production) than the higher temperatures required in the gasification process. This directly reduces profit and reduces investor returns.

The rate of return is better with gasification because of its lower capital cost; however, it is not as profitable in the long term. The payback period or rate of return indicates the amount of time investors would need to make back the money they initially invested. The operating cost per ton was found by operating cost divided by total production per year. Because of the high temperature needed in gasification, the operating cost is higher and directly affects the profit.

When comparing the two logistically, pyrolysis requires the waste product to be dried and pretreated more so than gasification. However, gasification and pyrolysis both required PVC to be removed from the raw material. Essentially, both these processes need a pre-treatment to sort out PVC or polyvinyl chloride products from the raw materials in order to operate. In addition, pyrolysis also needs a drying process at around 15-20%, whereas gasification can take raw materials with up to 50% water content - which concludes that the gasification stock does not necessarily need this drying treatment (Zaman et al., 2017). Even so, the drying process takes minimal energy as the material is put into a centrifugal dryer, and the moisture content is removed from plastic at 25ºC. (Hamid, et al., 2021) My initial hypotheses were that pyrolysis would be more expensive because of the need for drying, which adds an extra pre-treating step to the process. However, because the cost of energy is still lower than that needed to produce the consistent higher temperatures of gasification, pyrolysis has the potential to produce more profit for investors.

<u>External Factors:</u>

While I analyzed the economic benefits of investment in both gasification and pyrolysis plants, the viability of government versus independent ownership should be considered. Proposing that these plants run through Government funding in lesser developed countries would significantly reduce the need for high economic profitability. In this model, the government would need to break even in order to pay back investors rather than focus on profit. The rate of return would be less critical – rather, the employment potential for citizens with the municipality would automatically improve the economic and social potential. The use of these plants would give the ability for cheaper energy to be given back to the general public, stimulation of the economy through job opportunities, and lowering unemployment rates, and stimulation of the education sector within the area due to needing specialization and skilled workers. The economic values used for this paper were mainly taken from two sources sourced from India and Pakistan [see pg 9]. Both have overpopulation issues, high unemployment, and face massive littering problems that hinder tourism (Mohan, 2019). Creating employment through plastic collection would benefit the environment and the respective countries economically through increased tourism while generating more reliable energy for the area. While I truly believe that these models can produce profit for independent companies and investors, government-funded research has a long-standing history of propelling technological advances towards more efficient forms of profit development. In addition, a municipally run program has the potential to benefit the area and its citizens socially, environmentally, and economically.

The variability of the figures presented is evident throughout the research. As these processes are areas of emerging technologies and development, the exploration and technological advancements are ongoing, and the literature lacks abundant, controlled, and directly comparable research. Other variables that would affect the economic viability are the country in which the plants are built, transportation distances, government or private funded plants, and specific labor availability. The degree of sustainability depends on transportation factors, purity of raw waste, technological equipment choices, and disposal of byproducts. Another note to be taken into consideration when reading this research is that the technical and economic situation of plastic pyrolysis and gasification plants will vary widely based on the size of the energy plants.

Summary and Conclusions

My future recommendations for research within this field is simply more research. Gasification, specifically plasma Arc gasification, is a new technology that has yet to be refined in the sector of plastic waste to energy. In order to gain more information on gasification and pyrolysis, I suggest that future studies and research be conducted on a bi-annual review basis by either municipal-funded research or university graduate research programs. This would allow for the subjects to be developed further. Difficulties within the analysis were mainly the lack of standardized information within the industries. After comparing the two processes, I was able to see the similarities and many differences between the two. However, I believe both of these should work hand-in-hand simultaneously in reducing greenhouse gas emissions relative to typical hydrocarbon usage, reducing plastic waste in the GPGP, and improving the environment for future generations to come.

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