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Pine Needle Pyrolysis: Bio-waste into Biofuel

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Pine Needle Pyrolysis: Bio-waste into Biofuel

By

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Submitted in partial fulfillment of the requirements of the Department of Natural
Sciences and Mathematics and the Honors Program
Dominican University of California
2017

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DEDICATION

I would like to dedicate this thesis to my recently departed High School hero and professor, Dr. Jim Olwell. Without whom I would have given up on my love for math and science, and would not be standing here today.

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This thesis is the culmination of many years of study, research and experimentation. This project would not have been possible without the support of my professors, my friends, my family and the staff at Dominican University of California and for that I thank them.

First and foremost I would like to thank Dr. Frost, without his guidance and support my thesis would not have been possible. I want to thank him for his confidence in my ability and his forward thinking mentality, these helped me stay on task during the slow days and kept me determined when the workload seemed almost impossible to handle.

Secondly I'd like to thank the Dominican University of California's Lab Manager Christopher Endicott. While he may have supported this project primarily as a technical support, assisting in the development and implementation of numerous apparatuses, Chris also served as an integral support system and idea backboard. Without him this endeavour would have surely ended up in smoke.

Thirdly I'd like to thank my friends, my wonderful family who stood by my side and gave me a rock to come home to when our experiments were unsuccessful. Last but not least I'd like to thank my lab partner Sierra Carlson. Together we pushed through the snags and bumps in the road to turn out the best data we could.

ABSTRACT

This project explores the alternate uses of biomass. In particular it focuses on pine needles as a source for biofuels. Pine needles are of interest because in certain Mountain communities they are collected and removed from residential properties. By removing the pine needles, communities create a “defensible space” to prevent wild fires from destroying homes and property. These needles are often placed in regional landfills. The South Tahoe Refuse and Recycling Services alone has more than 4,340 tons of pine needles dumped at their facility annually. This large amount of biomass can be a potential energy source.

The focus of this research is on the anhydrous pyrolysis of the pine needles to create synthesis gas and other byproducts. A large portion of the material that remains after pyrolysis is biochar and will be the subject of future research. Normally biochar from yard waste and crop burning may be ploughed into the soil in crop fields to enhance their fertility and stability of the soil, and for medium to long-term improved carbon sequestration of these agricultural plots. One of the additional products of this process is a complex mixture of viscous liquid products containing furfural, furan, and other dehydration products from sugar decomposition. Paired with the syngas these two products can be subjected to further processing in order to create other chemicals fuel products.

This research focuses on the gaseous product produced from the pyrolyzing of the pine needle sample. With Fischer Tropsch technology applied, it should be possible to oligomerize this gas to methanol and higher carbon number products. Later the

carbon based products could be used directly in gasoline as supplemental fuel components. The components will reduce the carbon footprint of gasoline without raising the ethanol content of the fuels above the threshold level of 15%; a level above which many automobile manufactures refuse to recommend for their vehicles. To demonstrate the feasibility of this process we will discuss research done with an iron based Fischer Tropsch catalyst supplied by Emerging Fuels Technology, Tulsa, Oklahoma, and synthesis gas models of hydrogen and carbon monoxide. Possible steps forward in this research will be discussed in the latter part of the thesis. If successful with further research we could have a new renewable energy source at or disposal.

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LIST OF TERMS

Biomass: organic matter, especially plant matter, that can be converted to fuel and is therefore regarded as a potential energy source

Anhydrous Pyrolysis: a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen and water

Biochar: a solid material obtained from thermochemical conversion of biomass in an oxygen-limited environment

Furfural: a colorless, oily liquid, $C_5H_4O_2$, having an aromatic odor, obtained from bran, sugar, wood, or corn cobs by distillation: used chiefly in the manufacturing of plastics and as a solvent in the refining of lubricating oils

Furan(Furfuran): a colorless, liquid, unsaturated, five-membered heterocyclic compound, C_4H_4O , obtained from furfural: used chiefly in organic synthesis

Syngas: a synthetic natural gas derived from matter

Fischer Tropsch: the synthesis of hydrocarbons by the catalytic hydrogenation of carbon monoxide. Named after Franz Fischer and Hans Tropsch, German chemists.

Oligomerize: to react together to form a polymer consisting of at least 2 and as many as 100 monomers

Infrared Spectrometer: the study of the interactions of matter with infrared radiation; used as an analytical tool to identify (mostly organic) compounds.

KBr method: solid phase method of taking the infrared spectra of a sample using potassium bromide (KBr); which is an IR-transparent material.

Nuclear Magnetic Resonance(NMR): a research technique that determines the physical and chemical properties of atoms or the molecules in which they are contained.

INTRODUCTION

The Webster definition for pyrolysis is: the chemical decomposition of organic substances by heating to high temperatures. Anhydrous Pyrolysis is one of many procedures that can be used in order to carry out biofuel synthesis. Any cellulose biomass can be put through this form of pyrolysis. This process is usually completed using this form of biomass which is to be ignited in an air evacuated system, as depicted in Figure 1.¹ This form of biomass comes to produce a light crude product along with biochar and syngas.

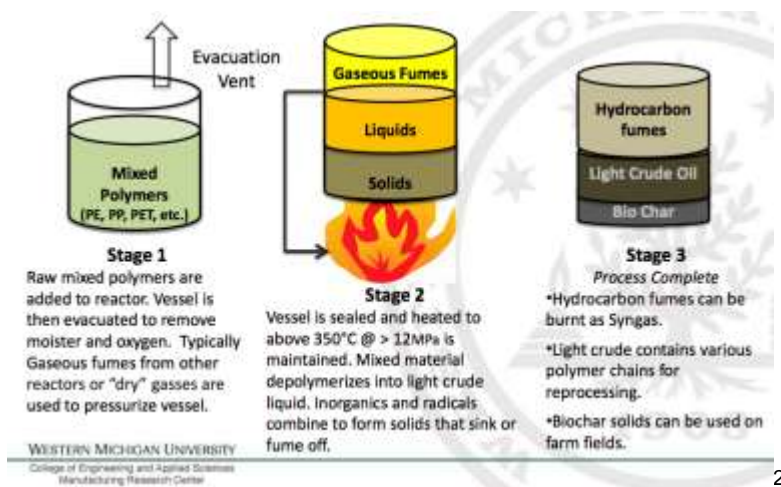


Figure 1: Basic Anhydrous Pyrolysis Process with Polymers

Syngas is short for synthesis gas; usually comprised of a mixture of carbon monoxide, carbon dioxide, and hydrogen.³ The most viable syngas can be produced from a dried biomass high in cellulose/carbon content. The light crude products can be reprocessed into: virgin polymer feedstock such as polystyrene, polyethylene, and

¹Evans, George. "Liquid Transport Biofuels – Technology Status Report" Archived September 19, 2008, at the Wayback Machine., "National Non-Food Crops Centre", 14-04-08.

² Johnson, Matthew., & Derrick, Sean. n.d.GMI Pyrolysis of Mixed Polymers Review. Wmich.edu. Retrieved March 10, 2017, from <http://www.wmich.edu/mfe/mrc/greenmanufacturing/pdf/GMI%20Pyrolysis%20of%20M>

³ Beychok, M.R., Process and environmental technology for producing SNG and liquid fuels, U.S. EPA report EPA-660/2-75-011, May 1975

polypropylene (PS, PE, PP), short chain fuel products (Gasoline, Jet Fuel), Esters (Diesel) with the addition of a process catalyst.⁴ The synthesized gas derived from the anhydrous pyrolysis can then be used as an intermediate for the production of various fuels or lubricants via the Fischer-Tropsch catalyzed process, as demonstrated in Figure 2.⁵ As a result various products will be formed which may also be separated and utilized for various purposes.

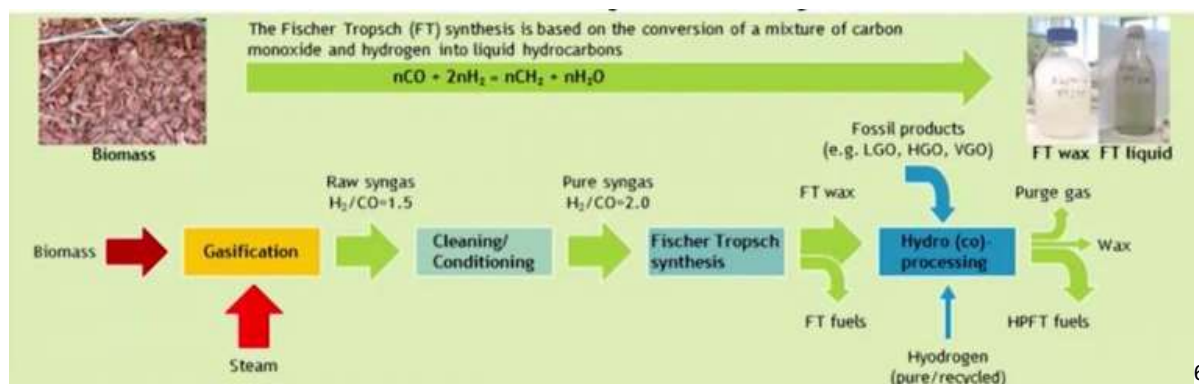


Figure 2: Anhydrous Pyrolysis with Fischer Tropsch Addition

When selecting a biomass for pyrolysis it is important to choose something rich in carbon that can be collected and processed in abundance. Needing a large source of biomass limits the options, truly narrowing it down to naturally occurring biomass waste. A strong candidate is pine needles; not only are they abundant across the natural landscape of our planet, but they are also cleared annually only to sit in a landfill. In California pine needles are a frequent nuisance to residents and infrastructure, serving as a constant threat for wildfires. The South Tahoe Refuse and Recycling Services

⁴Johnson, Matthew., & Derrick, Sean. n.d.GMI Pyrolysis of Mixed Polymers Review. wmich.edu. Retrieved March 10, 2017, from <http://www.wmich.edu/mfe/mrc/greenmanufacturing/pdf/GMI%20Pyrolysis%20of%20M>

⁵Boehman, André L.; Le Corre, Olivier (2008). "Combustion of Syngas in Internal Combustion Engines". *Combustion Science and Technology*. Taylor & Francis. 180 (6): 1193–1206. doi:10.1080/00102200801963417.

⁶Greg.tv. Greentech-Germany: Article Files http://www.greentech-germany.com/res/articlefiles/755299_86f3bc63230eff555518e171a6806b44.jpg

alone has more than 4,340 tons of pine needles dumped at their facility annually.⁷ Collectively we have hundreds of thousands of tons of pine needles sitting in landfills annually, all across the globe. The annual collection of the needles would provide a steady flow biomass for the synthesis of syngas.



Figure 3: Pine Needles Waiting to be Used

Due to the abundance and viability of this particular biomass, pine needles were the readily available choice made for the remainder of the thesis. The focus of this thesis research is on carrying out the anhydrous pyrolysis of the pine needles to create synthesis gas (syngas) and other byproducts. This process will produce a complex mixture of viscous liquid byproducts containing furan, furfural, and additional relatively low molecular weight products derived from the breakdown of sugars. The products derived from the experiment will be subject to testing in order to identify and determine what compounds were produced. These compounds will be identified using an Infrared Spectrometer (IR). A large portion of the material that remains after pyrolysis is biochar.

⁷n.d.Resource Recovery Facility. Recycling at STR. Retrieved March 22, 2017, <http://www.southtahoerefuse.com/RRC.html>

Products outside of the syngas will be the subject of further future research. If the IR reveals that a viable syngas is full of low molecular weight hydrocarbons, there will be a new naturally abundant biomass that could be an alternative energy source.

METHODS

This experiment was born from the hypothesis that pine needles can be used as a form of biomass when synthesizing biofuels. With the aid of Christopher Endicott, Lab Manager of Dominican University of California, a makeshift pyrolysis system was devised in order to properly put the pine needle sample through Anhydrous Pyrolysis.

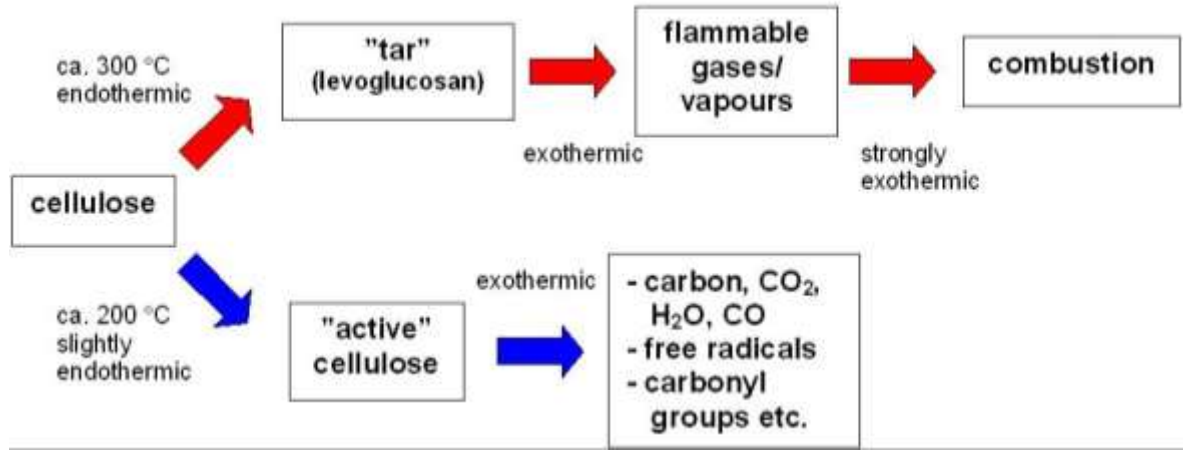


Figure 4: Schematic for Cellulose Pyrolysis

Before a sample could be gathered and tested, it was imperative that we make sure the system was properly constructed. Dry runs were conducted in which a gas collector bag was replaced with a vessel of water at the end of the system to measure any change in air pressure.



Figure 5: Dry Run Set Up

For the first half of the experiment, we took ~7.5 grams of thoroughly blended pine needles and placed them in the oven for several hours. Once our biomass was thoroughly dried, it was put through the process of pyrolysis within a Nitrogen purged apparatus to produce a syngas. When the apparatus was deemed sealed and successful, the water vessel was replaced with a pre-weighed gas bladder. Trials were then conducted with the same ~7.5 grams of blended pine needles in order to produce a testable syngas sample.



Figure 6: Final Set Up w/ Bladder

The syngas was formed by the rapid heating of the dry pine needles in the absence of air, the gas mixture was then sent through an apparatus essentially causing water displacement allowing the capture of the synthetic gas in pre-weighed gas bladders. As a byproduct of this pyrolysis a viscous liquid was collected in a pre-weighed flask. Once pyrolysis was complete, some of the gas was released through a tube and was ignited using a match.

The second half of the experiment consisted of taking our pre-weighed containers and reweighing them to determine the amount of each product collected. After the masses were recorded, we injected an aliquot of our gas sample into an infrared gas cell. When gas analysis was complete we performed a KBr method - IR test on the biochar and viscous liquid byproducts. Using the IR we captured the spectra of our syngas and byproduct. Using the IR we were able to determine the components of our various products.

RESULTS

From a mere ~7.5 grams of sample of biomass, we typically produced ~1.75g of syngas, with ~2.23g of viscous byproduct, and ~3.5g of biochar. Our byproducts collected contain furfural, furan, and various additional products resulting from the dehydration and decomposition of complex sugars.

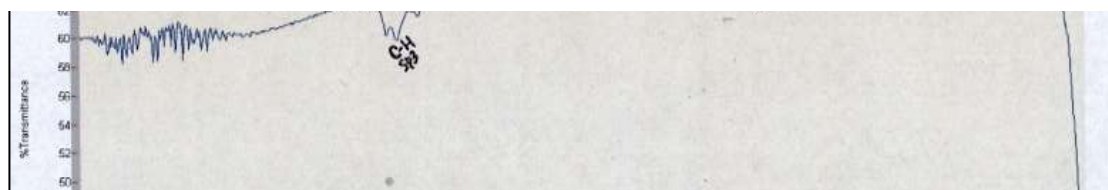


Figure 7: Typical IR spectra for our byproduct.

The syngas collected is believed to contain hydrogen, carbon monoxide and low molecular weight hydrocarbons that may be used with further treatment. We produced the type of syngas we were looking for; the IR spectrum gives us the qualitative data we needed. Regrettably we were unable to put the sample through an Nuclear Magnetic Resonance (NMR) spectrometer to identify our hydrogen content.

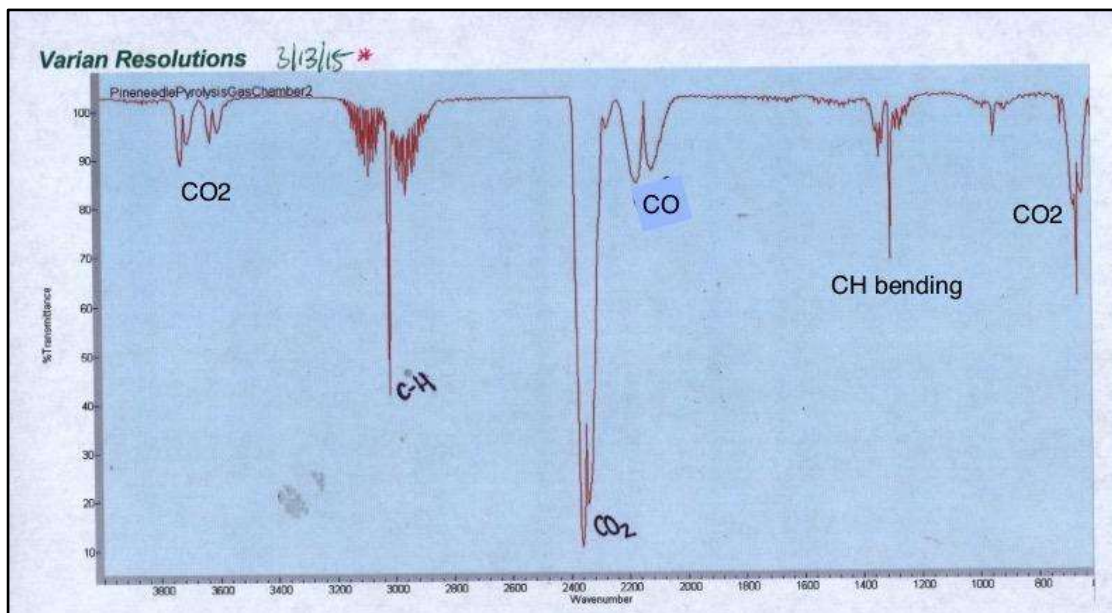


Figure 8: Typical IR spectra for Our Syngas

From the peaks identified from our IR spectra, we compared the intensity of the identified peaks; to estimate the approximate ratio between the various functional groups. Although our real world test came when we ignited our streams of syngas with matches. The flammability of our gas stream further supported the notion that we had produced a viable syngas.

Due to a lack of analytical tools to directly determine the presence of hydrogen in our syngas. An additional experiment needed to be carried out, and the following was performed. Methyloleate was catalytically reduced to methylstearate using the palladium on carbon (Pd/C) catalyst. This provides evidence of the presence of H₂ in our syngas.

DISCUSSION

This thesis project proved to be quite educational and beneficial in its process. By creating a viable syngas we have shown that pine needles could possibly be used as an alternative source of fuel. The other byproducts, viscous liquids and biochar, were unable to be tested thoroughly due to limited resources and time. Further research will delve deeper into the contents and possible applications of the viscous byproduct and the biochar.

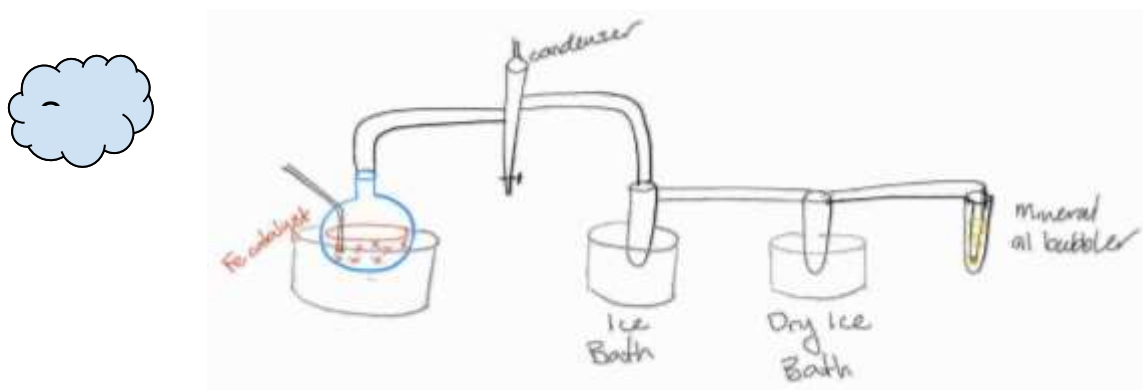
The research carried out currently focuses heavily on the gaseous products. With Fischer Tropsch technology applied to our produced syngas, it should be possible to oligomerize this gas to methanol and higher carbon number products. Further into processing the carbon based products could be used in gasoline as supplemental fuel components.⁸ These components can reduce the carbon footprint of gasoline fuel without raising the overall ethanol content of the fuels above the threshold level of 15%. Fuels containing any levels above the 15% are not recommended by car manufacturers to use within their vehicles.⁹

⁸ Frost, Kenneth. 2017-Personal Communication

⁹ Towards Sustainable Production and Use of Resources: Assessing Biofuels (PDF). United Nations Environment Programme See Table 3.3. 2009-10-16. Archived from the original (PDF) on 2009-11-22

CONCLUSION

This thesis project proved to be quite educational and beneficial in its process. Though the creation of this experimental process took a large amount of time to draft and fine tune, the collective drive of the team drove this project home. By creating a viable syngas we have shown that pine needles could be used as an alternative resource for fuel. Due to limited resources and time we were unable to explore the following portion of this process in which our syngas would be put through Fischer Tropsch synthesis with the aid of a catalyst. If we had a pressure vessel at our disposal, or the materials to make one, we would have been able to experiment with the Fischer Tropsch process.



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Figure 9: Theoretical Future Apparatus Design

In further research we would like to carry out the Pyrolysis process, with the aid of Fischer Tropsch catalyst treatment to our syngas, in the hopes of creating hydrocarbons of varying molecular weight. These derived compounds can be used

¹⁰ Frost, Kenneth. 2017-Personal Communication

directly or indirectly within fuel itself. Using computer software we can predict just how much energy can be produced from one mol of our hydrocarbons in comparison to methane (natural gas). With all calculations considered, if the program Gaussview is accurate, the 4,000 tons of pine needles sitting in South Lake Tahoe could be transformed into enough natural fuel to power 528 homes annually. That is almost 10% of the homes in that area. If further research were to determine the Anhydrous Pyrolysis, with Fischer Tropsch processes added, of pine needles successfully created the hydrocarbons used in diesel, gasoline and jet fuel, we would now have a new abundant natural resource. Thus taking us further away from crude oil dependency.

RESOURCES

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