3. Identify the technology

a. <u>What is hydrothermal pyrolysis</u>

Definition

By language, hydrothermal means something related to the action of heated water in the earth's crust while pyrolysis is decomposition brought by high temperature. Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures (high temperature) in the absence of oxygen or any halogen. So, generally hydrothermal pyrolysis is thermal decomposition of organic material at elevated temperature in the presence of water.

Overall concept

Hydrothermal/Supercritical pyrolysis of biomass is a well-known process that is used to convert moisture-rich carbonaceous materials to liquid fuels such as bio-oil. The destruction process by hydrothermal pyrolysis reaction proceeds through hydrolysis, oxidation and gasification. Hydrothermal reaction involves applying heat under pressure to achieve reaction in an aqueous medium. It has been attracting worldwide attention because of the fascinating characteristics of water as reaction medium at elevated temperatures and pressures (Savage, 1999).

Process flow in proposed technology (shown in block diagram in Q4)

The biomass slurry undergoes a conversion reaction to biocrude, aqueous, and gas phase products. The hot effluent from the HTL reactor is sent to a settler/filter to separate fine particles from the hot liquid. The filtered solids are mainly composed of precipitated minerals with some unreacted biomass or char. Further processing of the separated solids is not considered in this model and the materials are assumed to be disposed as solid wastes. The liquid effluent from the settler/filter exchanges heat with the incoming biomass-water slurry and is then depressurized. After cooling to 117 °C and depressurization to 0.1 MPa the products go through a 3-phase separator, SP-210, and exit in the gas phase, aqueous phase and biocrude product streams S208, S209, and S213 respectively. (U.S. Department of Energy, 2014)

Feedstock characteristics

One of the critical feedstock characteristics of hydrothermal pyrolysis that needs to be considered in HTL processing of food waste is the moisture content. HTL processing works best with solids contents in the starting feedstock that are around 20-35 wt %. Feedstocks with moisture contents significantly lower than this may prove difficult to handle, due to higher viscosities (Keener).

Operating conditions

The operating conditions that affect HTL of foodwaste include temperature, pressure, residence time within the reactor (also referred to as retention time), pH, solids content and the oxygen to carbon ratio. HTL processing typically occurs under the range of system operating conditions summarized in the table below.

Control Factors	Typical Range
Temperature	250-400°C (482-752°F)
Pressure	5-20 MPa (725-2900 psi)
Residence time	0.2-1.5 hrs.
pH	6.5-7.5
Total solids content	20-25 wt.%
CO to volatile solids ratio	0.11

Inert and/or reducing gases (i.e. N2, CO) and catalysts have been used to improve the bio oil yields in HTL processing of biomasses, including food waste (Keener).

Product

HTL processing of food waste yields 4 product streams: bio oil, synthesis gas (syn gas), solids and an aqueous phase. The feedstock and processing conditions will impact the exact makeup and distribution of these product streams (Keener).

- Bio Oil

The bio oil produced from the liquefaction of food waste is a complex mixture of hydrocarbons. The bio oils produced from liquefaction typically have a lower oxygen content and a higher heating value than those produced by pyrolysis. Bio oil yields have ranged from 20 wt% to 70 wt%, with respect to volatiles, depending on feedstock and processing conditions. The bio oil is mostly made up of carbon, hydrogen and oxygen, with lesser amounts of nitrogen, sulfur, ash and water (Keener).

- Syngas (Non-condensable gas)

The syngas produced in the liquefaction of manure is mostly comprised of carbon dioxide. The use of CO as a reducing process gas will also increase the amount of CO2 produced as syn gas (Keener).

b. Why hydrothermal pyrolysis?

Hydrothermal pyrolysis or hydrothermal liquefaction (HTL) is an important wat to produce infrastructure-compatible fuels from bio-oils (Elliot, 2014). This process can be conducted with a simple thermal upgrade and existing refinery technology to subsequently obtain all the liquid fuels. HTL process is known to only consume 10 – 15 % of the energy in the feedstock biomass because it recycles the heat energy in between the heating and cooling of the process medium. With that, HTL process yields around 85 – 90 % of energy efficiency, making it very energy-efficient. (Comparative analysis of fast pyrolysis and hydrothermal liquefaction as routes for biomass conversion to liquid hydrocarbon fuels))

In addition to that, why we chose this promising process is that it accepts all biomasses from modern society – sewage sludge, manure, wood, compost and plant material along with waste from households, meat factories, dairy production and similar industries. This is perfect since our focus in this project is the waste from TESCO supermarket, which mainly is wet food waste. This process is environmentally-friendly because this is basically a pressure cooking which means no harmful solvents are involved. (University of Illinois at Urbana Champaign)

From the name itself, this process involves water at high pressure to decompose the waste. Hydrothermal liquefaction (HTL) is a promising technology to treat the wet waste stream because water is used as the reaction medium and easily separated from the product. In contrast, most other biomass conversion routes generally require dry feeds or distillation to remove water from the product. As a result, HTL is more energetically favorable for processing wet feedstocks such as food waste and slop. (Jennings). This means that, HTL requires no drying beforehand (note that drying process is expensive) or use only limited amount of the biomass. The recovery of the carbon content from the feedstock is fairly high; that is more than 70 %. The product oil from this process is also storage stable and has low upgrading requirements. (UNIVERSITY)

Why not other technologies?

In the standard pyrolysis technology, although also very efficient, this process requires drying of biomasses prior treatment. As per mentioned before, drying process is costly, which is what we want to avoid. Furthermore, the oils produced may be hazardous waste and they require special storage, disposal and proper further treatments. (Pyrolysis)

For anaerobic digestion, it is a very complex and expensive technology. Because this technology relies on anaerobic bacteria to complete the decomposition of the waste, this process is highly sensitive to temperature. The bio-digester must be kept at a consistent temperature, as rapid changes upset bacterial activity. (Anaerobic Digestion Basics)

From our studies, hydrothermal pyrolysis or HTL's benefits overpowers the other technologies available in the industry. Thus, our choice is the ideal technology for this project.

c. Sustainability principle of hydrothermal pyrolysis technology

Basically, sustainability can be define as the study of how natural system functions, remain diverse and producing everything it needs while the ecological resources are maintained. There are three main pillars of sustainability which are:

i. Economic development

ii. Environmental development

iii. Social development

In terms of **economic development**, hydrothermal pyrolysis is economic efficient whereas the pyrolysis process only consume approximately 10-15% of the energy in the feedstock biomass. However, in return it will yield an energy efficiency of 85-90% (AARHUS University, 2013). Basically in any department of sustainability, we want to increase the efficiency of the production while reducing its cost as well as the effect to the final product. Moreover, some comparisons have been conducted whereas the efficiency of hydrothermal pyrolysis is higher than the anaerobic digestion, solid-solid extraction and ethanol fermentation. It means that this hydrothermal pyrolysis technology has lower maintenance and operating cost compared to others although it will need a very huge capital to start this technology. However, in any technology, we need to invest more for the future needs.

Other than that, economic values do not depend solely on the price of the oil and gas as this hydrothermal pyrolysis is a process of producing bio-oil as the final product. There are no technology processes that can achieve economic efficiency as high as hydrothermal process so far. This is because dry process such as hydrothermal pyrolysis has a very large amount of energy production whereas for the wet processes, it can only convert up until half of the energy in the feedstock as bio-oil. Hence, we can conclude that this hydrothermal pyrolysis can have a higher quality of it's final product of oil compared to to others. Therefore, it can also increase the value of this technology in terms of economic.

Next, it will provide job opportunities to the people around the areas. Although this technology have low operating as well as maintenance cost, however it still need human power to make it operate. Therefore, some training course can be provided for those who wants to apply in the job to be in this technology. This is because there are people or undergraduates who are still looking for jobs around this area hence it will be more cost saving to employ local people instead of bringing in researchers from foreign countries.

Lastly, it must meet the supply and demand of people. This is because some people just more comfortable to dispose their food waste in the waste area and this kind of technology is still new especially to our country. However, different countries such as United Stated of America, Singapore, France and many more have been using this kind of sustainable solution for decades. People may take sometimes to meet the demand of this technology but give or take in a decade, it will be very environmental helpful to our country provided the supply of this technology is continuously provided.

In terms of **environmental development**, this technology minimize the generation of hazard or pollution to the environment around it. According to AARHUS (2013), this is because the water from the hydothermal pyrolysis process can be recycled into another process because due to the pyrolysis process, the water has very low amount of carbon contents. Moreover, this water can be purified and hence can be used to make drinking water provided there is water treatment and minerals in it. Although this seems to be a long-term goal, it is actually one of the best way to dispose waste and change it to bio-oil as well as use the water in the hydrothermal pyrolysis in drinking water processes. This process is mainly known as recycling as most of the product can be used in different process that can lead to environment benefits. Other than that, hydrothermal pyrolysis will produce a bio-oil which will recover more than 70% of the carbon content in the feedstock in one way single pass. Next, the oil will be storage stable. Due to its high fraction of middle distillates in the crude oil, it requires very less upgrading requirements compared to the normal pyrolysis oil.

Next, this hydrothemal pyrolysis can minimize the usage of non-renewable energy resources. This is because the energy form the wet waste that undergoes the hydrothermal pyrolysis does not compete for food production. However, in return it will be very useful in feed stock whereas it can provide a very one virtuous cycle. In fact, the renewable oil produced from the process can make up to the world supply and demand of renewable fuel. Due to increasing number of people as well as vehicle to the extent of space venture, oil has a very high demand throughout the world. Lately, the amount of oil in the world had decreased hence a more conventional or sustainable oil will be needed to solve this problem. Although this bio-oil can only come up to 25% of transportation fuel compared to the normal fossil fuel, it is more than enough for an alternative oil and the energy produced is relatively high compared the one from anaerobic digestion, solid-solid extraction and ethanol fermentation.

Other than that, this hydrothermal pyrolysis can minimize the usage of raw materials. This is because the wet medium shows that this pyrolysis can make up to moist and wet waste product. Compared to other waste product in the world, the wet waste is the most amount in the world and harder to dispose properly compared to the dry waste. Based on the research conducted, hydrothermal pyrolysis can accept all type of biomasses up from sewage, wood, compost of plant, household, meat factories waste and many more of the similar industries. For instance in this project, we are looking for a technology to dispose the wet product from the TESCO Sri Iskandar properly and in a way to find a sustainable way to change it to wealth. Mostly the wastes found here are vegetables, meat products, fish products, dairy products and bread products that has expired or damaged as well as some of the dry waste.

Lastly, this hydrothermal pyrolysis follows up recycle and reducing power usage (Diamond, J. 2005). This technology recycles the waste and the water produce from the hydrothermal pyrolysis can be process later to make drinking water. Other than that, if the management allow this technology, it can actually be used to generate their own electricity power in that area since it carries 25% of power compared to the normal transportation fuel.

In terms of **social development**, hydrothermal pyrolysis can reduce the generation of hazard that can affect the people's health. Basically this pyrolysis burns the product without using oxygen and the water from the hydrothermal part can and will be used in the next process. Moreover, this waste management can give more pleasure to the society compared to the other technologies. For example, anaerobic digestion can be performed in terms of batch reactor or in continuous flow stirred reactor but both ways will produce odour problem to the society which will be unpleasant for them. Moreover, some technologies require big reactors in series and this will be consumed the space in one area. Some area may be wasted for housing area since there should be some distance for the industry to take place from the closest housing areas.

Other than that, if this technology is implemented and built in Sri Iskandar, it will cover up a lot in terms if the transportation reduction. Since most of the transportation in the world uses fossil fuels, we can conclude that unnecessary movement should be reduced. The food waste form the TESCO can directly be send to the hydrothermal pyrolysis industries and process it to be bio-oil. In terms of transportation distance, the company can uses around 30% of the oil products to be used for the vehicle used to transport the food waste. The other remaining 70% of bio-oil can be used either as the power generation energy or invest it as the future oil fuel for vehicles.

Lastly, this hydrothermal pyrolysis technology can be used to teach and encourage people to change to a more sustainable lifestyle as well as find a better way to dispose their food waste either for the household waste or industrial waste. In modern days, we are looking for a supply that can accommodate the world demand without realizing we are actually compromising the future needs. Basically, sustainability is how we meet the needs of society in ways that can continue indefinitely into the future without damaging or depleting natural resources. In short, meeting present needs without compromising the ability of future generations to meet their own needs. Therefore, we need to start to teach the younger generation on how each of the technologies profits and perform best economically and sustainable. Hence, this technology can not only give benefit in environment, it can as well educate the people and raise their awareness regarding sustainable development.

d. <u>Catalyst involved</u>

Hydrothermal liquefaction (also known as direct liquefaction) is essentially pyrolysis in hot liquid water. As such, it does not require a catalyst, but a significant amount of research and development on catalytic methods in hydrothermal liquefaction has been undertaken. The most commonly considered ‘‘catalyst’’ has been the use of alkali to modify the ionic medium to favor certain base-catalyzed condensation reactions, which can lead to aromatic oil formation, in preference to acid-catalyzed polymerization reactions, which lead to solid product formation. Alkali catalyst is also used in the process to limit the amount of secondary reactions of the oil phase to char during processing. (Douglas C. Elliott, 2015)

The usage of catalyst in hydrothermal pyrolysis depends on the type of waste used. This statement is also supported by Jason who stated that ultimately the characteristics of the biomass used in the process dictate the types of catalyst that will be effective. One of the catalysts that is largely used in the industry is Ceria-base catalyst CeO_2 and ZSM-5. These catalysts have been reported by (Notsawan Swadchaipong, Nutnan Kanestitaya, Itsara Rojana, Tanes Utistham and Unalome Wetwatana, 2013) to possess some properties that could possibly help in this pyrolysis process.

Preparation of Ceria-base catalyst

Ceria-base catalyst was prepared by using hydroxide precipitation method. Cerium (III) nitrate hexahydrate was dissolved in 150ml of analytical grade deionized water. It was precipitated using ammonium hydroxide to a final pH in the range of 7-8. Ammonium hydroxide solution was added drop by drop by burette (flow rate = 5cc/min) while being stirred for 4 hours until cerium hydroxide, $Ce(OH)_4$ was totally precipitated. The precipitate was then recovered, washed with deionized water and ethanol to prevent agglomeration. Then it is calcined under the reducing condition to convert to CeO_2. (Notsawan Swadchaipong, Nutnan Kanestitaya, Itsara Rojana, Tanes Utistham and Unalome Wetwatana, 2013)

Preparation of ZSM-5 catalyst

Preparation of ZSM-5 catalyst is very complex and requires a lot of processes. Basically to prepare this catalyst, Aluminium chloride tetraproply, $AlCl_3$ and ammonium bromide were used as metal source and organic template respectively for ZMS-5 preparation. The substance will undergo several methods which are: Gel precipitation and decantation solution, crystallization, first calcinations, ammonium ion exchange and lastly second calcination (ZMS-5 catalyst produced) (Notsawan Swadchaipong, Nutnan Kanestitaya, Itsara Rojana, Tanes Utistham and Unalome Wetwatana, 2013)

Functions and amount needed for these catalysts?

According to freedictionary.com (n.d.), catalyst is used to increase a rate of chemical reaction without itself undergoing any chemical change. Based on the experiment done by (Notsawan Swadchaipong, Nutnan Kanestitaya, Itsara Rojana, Tanes Utistham and Unalome Wetwatana, 2013), the effects of catalyst and optimum operating condition such as temperature, pressure and retention time is studied. 150g of food waste with moisture content greater than 80% was selected for this hydrothermal process. The amount of ceria catalyst is varied from 0 to 3g.

Based on this experiment, both catalysts were found to help decreasing 4.13% of the final pressure. Yield of the bio-oil in the presence of Ceria A and Ceria B also were found to be increased by 12.9% and 12.0% respectively. The performance of ZMS-5 catalyst towards the hydrothermal pyrolysis reaction was tested under sub-critical condition.

As a conclusion, it can be seen clearly that catalytic reaction has an ability reduce the operating condition such as temperature or pressure and increase the yield of the product within the stipulated time. In this experiment studied by (Notsawan Swadchaipong, Nutnan Kanestitaya, Itsara Rojana, Tanes Utistham and Unalome Wetwatana, 2013), Ceria catalyst that has been used to reduce the pressure of the system and yield more than 12% of the final products.

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