FINAL YEAR PROJECT II

DISSERTATION

TITLE: HYDROTHERMAL CARBONISATION OF PALM OIL MILL EFFLUENT (POME)

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CERTIFICATION OF APPROVAL

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Approved by,

____

(Mr Azizul B. buang)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Ng Tze Yi

ABSTRACT

Hydrothermal carbonisation (HTC) is a thermochemical process that converts organic wastes into a coal-like material named ‘biochar’ or’ hydrochar’. The process involves application of high temperature and pressure to solid biomass in a suspension with water for several hours.

Palm oil refining industry is one of the largest industries in Malaysia. Consequently, the volume of Palm Oil Mill effluent (POME) generated would be massive. This polluting oily waste water always causes environmental issues and requires certain cost for its treatment before discharge. The objective of the project is to verify the potential of HTC process to upgrade or treat POME, to study the effect of temperature, formaldehyde concentration, pH value and feed solid:water ratio towards hydrothermal carbonisation of POME and also the significance of each factor to the quality of hydrochar generation and lastly to select the optimum operating condition. Based on literature review, most researches are commonly done with the solid biomass. However, there are no wide studies on HTC process on waste in sludgy liquid form for example palm oil mill effluent.

In this project, the scope will be focusing on producing hydrochar from POME. The quality of hydrochar will be analysed using Heating Value Analysis, Ash Content Analysis, and Carbon content. Taguchi method is implemented in this project to simplify and reduce the duration required for the project. This method adds the context of quality engineering into the common HTC studies.

The result of the experiment shows that HTC process has high potential to upgrade POME to higher value product. Increasing temperature and humidity reduces yield and ash content but increases heating value and carbon content. Increasing formaldehyde concentration gives positive results to all the parameters. The effect of temperature and formaldehyde concentration is more dominant in HTC process. The suggested operating conditions for HTC process are 270^{o}C, 2.5 wt% Formaldehyde concentrations and 88.05% humidity which is the originally obtained POME.

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ABBREVIATIONS AND NOMENCLATURES

HTC	Hydrothermal Carbonisation
CHN	Carbon, Hydrogen, Nitrogen
POME	Palm Oil Mill Effluent
MT	Mega tonnes
EFB	Empty Fruit Bunch
OMW	Olive Oil Mill Waste Water
SN	Signal to noise ratio

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Organic waste can be defined as waste that is biodegradable. It includes food waste, agricultural waste, sewage and animal faeces. Among all the sources, agricultural activities contribute most of the organic wastes for most of the countries including Malaysia. Nowadays, these wastes are normally managed by disposing to landfill, composting or energy harvesting.

Palm oil industry is selected in this project due to its significant role in Malaysia. According to the data obtained from indexmundi.com, Malaysia is currently second largest crude palm oil producing country. It is showed in figure 1.1

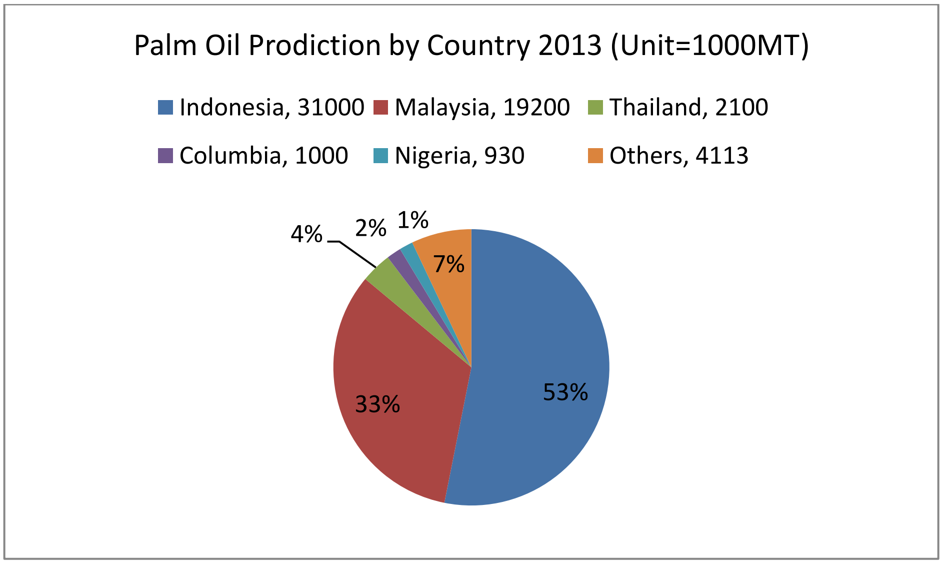


FIGURE 1.1 Palm Oil production by country
("Palm Oil Production by Country in 1000 MT," 2013)

The project is targeted to find a novel approach of fully utilising the oily and high solid content wastewater produced by palm oil refining industry. The polluting wastewater is commonly called Palm Oil Mill Effluent (POME) or Oil Palm Slurry (OPS). In addition, POME is a waste product generated from sterilization, hydro cyclone waste, and separator sludge throughout crude palm oil extraction process where separator sludge and sterilizer effluent are the major culprits contributing to the highly polluting characteristics of POME. (Poh, Yong, & Chong, 2010) Unlike other palm oil industry waste such as empty fruit bunches (EFB) and palm kernel shells which can be directly used as biomass fuel for electricity generation and heating utilities, POME is a wastewater that contains both high amount of water and solid. This characteristic has caused higher cost and efforts required to treat POME as wastewater or to dry it for further utilisation. Hence, POME is selected as the targeted research material since it is very abundant in Malaysia and yet to be utilised as much as other palm oil industry waste products such as empty fruit bunches (EFB). According to the literature review process, it is clear that there are researches done on most solid palm oil industry wastes but there are little or no researches that had been conducted on sludgy liquid waste such as POME. The most similar research would be HTC process on Olive Oil Mill Effluent.

With the increasing awareness of renewable energy due to the worries of depleting fossil-fuels, researches based on organic waste energy recovery are increasing by years. With the fact that fossil fuels are originally comes from organic matters, it is highly possible to recover energy from organic wastes. Some of the common methods include pyrolysis, gasification and hydrothermal treatment.

In order to treat POME, Hydrothermal carbonisation (HTC) is proposed to upgrade the waste into more useful products such as fuel. Hydrothermal carbonization (HTC) is a thermal conversion process in the presence of water. In the process, the water together with solid biomass is heated up in a confined volume and hence both the pressure and temperature of water will increase above normal water boiling point. HTC method has been shown to be environmentally and energetically advantageous for the conversion of wet feed stocks to a carbon-rich, energy-dense solid material often referred to as “Hydrochar”. (Lu, Flora, & Berge, 2014) The main reason of selecting this treatment method is the HTC process does not require drying. According to Elliott (2011), the role of water is important as it provides a mean to access ionic reaction conditions.(Elliott, 2011) In addition, HTC hydrochar has H/C and O/C ratios similar to that of coal, and higher calorific (heating) value comparable to coal so can be used as fuel. (Danso-Boateng et al., 2013) At lower temperatures, hydrothermal processing leads to carbonization reactions and the primary product is a biochar. At intermediate temperatures, below the critical point of water, the process is hydrothermal liquefaction and the primary product is a biocrude. Above the critical point, gasification reactions predominate and the primary product is a syngas.(Biller & Ross, 2012)

The purpose of this project is to verify the potential of POME to undergo hydrothermal carbonisation. The judgement will be made through the heating value of generated biochar, biocrude and also chemical analysis on the biochar, biocrude and remaining aqueous solution. Product of gasification will not be tested since it is insignificant in the temperature range of hydrothermal carbonisation process. A few parameters would also be tested which include effect of temperature, effect of additives concentration and also solid:water ratio. The significance of each variable to the quality of hydrochar product will also be judged.

Another creativity that had been included in this project would be the integration of Taguchi Method, a famous Quality Engineering design of experiment method. Since there are 3 variables that are targeted to be tested, this method is selected. The Taguchi method is optimal to be used when there are 3-50 variables in the experiment. However, the method assumes few interactions between variables, and only minimal variables contribute significantly.(Fraley, Oom, Terrien, & Zalewski, 2007) The biggest advantage of this method is its ability to cut down the number of experiments required to observe the influence of each parameters to the targeted outcome and also the significance of each parameters to the outcome relatively.

1.2 PROBLEM STATEMENT

As mentioned before, Malaysia is the second largest crude palm oil producing country. In fact, the industry is still experiencing some growth in the past few years. Figure 1.2 shows the annual production of crude palm oil in Malaysia

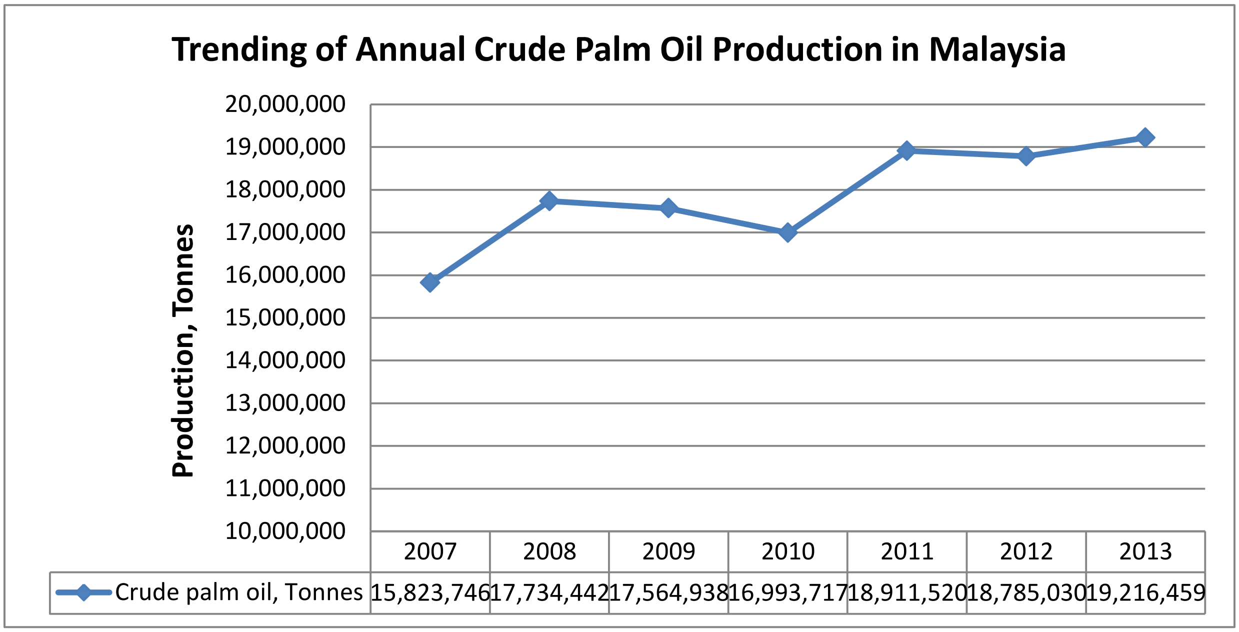
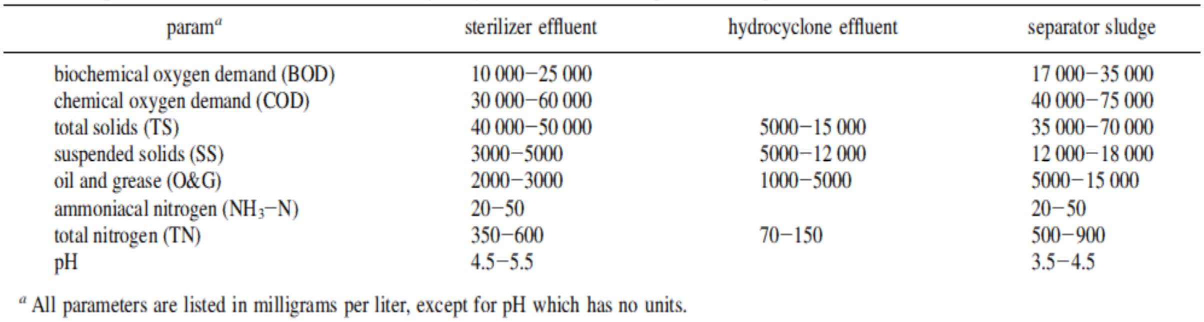


FIGURE 1.2 Annual Palm Oil Production Trending Curve ("Production Statistics," 2013)

The growth of palm oil extraction industry had definitely increased all the waste including POME. Based on the fact that 3 tonnes of POME is being generated from a tonne of crude palm oil produced in palm oil mills (Poh et al., 2010), Malaysia generated approximately 57.65 million tonnes of POME in year 2013.

Referring to table 1 and table 2 regarding the properties of POME and the POME discharge limit set by Environmental Quality Act 1974, POME is a very polluting wastewater with high solid content.

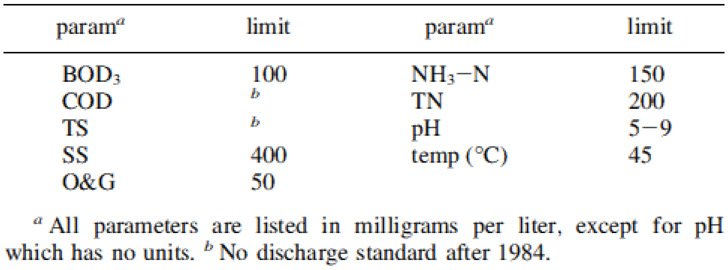
TABLE 1.1 Properties of POME (Poh et al., 2010)



param[a]	sterilizer effluent	hydrocyclone effluent	separator sludge
biochemical oxygen demand (BOD)	10 000−25 000		17 000−35 000
chemical oxygen demand (COD)	30 000−60 000		40 000−75 000
total solids (TS)	40 000−50 000	5000−15 000	35 000−70 000
suspended solids (SS)	3000−5000	5000−12 000	12 000−18 000
oil and grease (O&G)	2000−3000	1000−5000	5000−15 000
ammoniacal nitrogen (NH_3−N)	20−50		20−50
total nitrogen (TN)	350−600	70−150	500−900
pH	4.5−5.5		3.5−4.5

[a] All parameters are listed in milligrams per liter, except for pH which has no units.

TABLE 1.2 POME discharge limit(Poh et al., 2010)



param[a]	limit	param[a]	limit
BOD_3	100	NH_3−N	150
COD	[b]	TN	200
TS	[b]	pH	5−9
SS	400	temp (°C)	45
O&G	50		

[a] All parameters are listed in milligrams per liter, except for pH which has no units. [b] No discharge standard after 1984.

Besides, in order to treat the highly contaminated POME, high cost is required. Assuming a Compact Tertiary Plant design, estimated cost for POME treatment of 30 tonnes Fresh Fruit Bunches hr^{-1} palm oil mill is RM 1.4 million. (Sulong & Wahab, 2008) The figure does not include the operating cost of the treatment plant. In addition, normal waste water treatment will generate sludge which will require the plant to pay for the high disposal cost. Hence, the cost will be more justified if the waste can be used to generate income or to cover some utility cost.

Thus, if hydrochar can be generated successfully from POME, it can be used as a fuel for heat utilities and power cogeneration. However, compare to other types of palm oil industry waste, the moisture content in POME is relatively high and most utilisation methods requires drying of biomass. Therefore, the selected method to be studied is hydrothermal carbonisation.

In addition to this problem, there is little or no researches on HTC process of POME conducted. The most HTC researches done for HTC process using waste from Palm oil Extraction Industries are based on Empty fruit bunches (EFB). Information about the HTC process would be discussed more in the literature review.

1.3 OBJECTIVES

The objectives of the project include:

1. To verify the potential of HTC process to upgrade or treat POME through heating value analysis and chemical analysis

2. To study the effect of temperature, additives concentration, pH value and feed solid:water ratio towards hydrothermal carbonisation of POME.

3. To identify the significance of each parameters towards the quality of hydrochar

4. To select optimum operating parameters for HTC process of POME

1.4 SCOPE OF STUDY

The experiment will use POME collected from actual palm oil mill and gone through hydrothermal carbonisation. To increase the effectiveness of the process, the experiment is repeated for different operating parameters:

1. Reaction temperature
2. Presence of formaldehyde and the concentrations
3. Solid:water ratio

Besides, the following analysis will also be done on the solid and liquid samples to know the quality of products.

1. Heating Value Analysis
2. Ash Content Analysis
3. Carbon, Hydrogen, and Nitrogen (CHN) Analysis

Taguchi method of design of experiment is used to distribute the four operating parameters. Data analysis will be done to verify the effect of the four operating parameters to the heating value, ash content, carbon content and their significance to the process.

1.5 RELEVANCY OF THE PROJECT

This project is important as it deals with current issue in one of the largest growing industry in Malaysia which is Palm oil refining industry. In addition, POME is costly to be treated while Hydrothermal Carbonisation method has potential to upgrade the wet biomass to fuel. It is also a highly polluting waste if discharged without treatments and expensive to treat. Besides, this project is relevant as hydrothermal carbonisation of POME as a sludgy liquid waste has not been widely addressed yet.

1.6 FEASIBILITY OF THE PROJECT

Although the project is not yet done by any parties, there were similar project that utilise other types of biomass sources. Hence, sufficient information is required to complete the project. The project deals with plenty of scope of experiments whereby 3 parameters are tested while judgement is done based on 4 parameters in the reaction product. Furthermore, the number of experiments is trimmed by using Taguchi's method in Design of Experiment. It is positive that this project can be completed within the time allocated with helps and guidance from the supervisor and the coordinator, and smooth process in acquiring equipment and materials.

CHAPTER 2

LITERATURE REVIEW

2.1 HYDROTHERMAL CARBONISATION

The hydrothermal carbonization process (HTC) is a type of thermal conversion process. Similar to formation of coal, the solid content of biomass is being heated up in a confined space. With increasing temperature, the pressure in the confined volume will increase. Under high temperature and pressure environment with lack of oxygen due to presence of water, the carbonisation takes place. Consequently, the product formed would be similar to coal. The diagram below shows the reaction flow of HTC process.

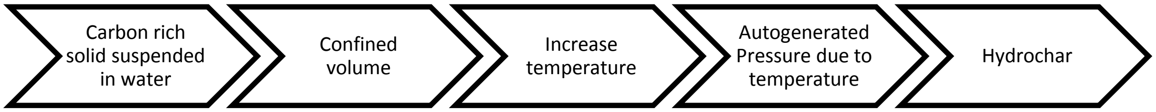


FIGURE 2.1 HTC Process Flow

Some other form of thermal conversion processes includes pyrolysis and gasification. The most obvious advantage of hydrothermal process is it requires lower temperature compare to pyrolysis and even biodiesel production which will greatly reduce energy cost to produce the fuel. This is supported by the fact that pyrolysis requires temperature approximately 400^{o}C. (Song, Xue, Chen, He, & Dai, 2014) Besides, gasification requires temperature of biodiesel reaction requires temperature of 700K to 100K. (H. Liu et al., 2014) On the other hand, HTC requires temperature lower than 300^{o}C and do not require drying of sample.

2.2 BRIEF HISTORY

The hydrothermal carbonization process (HTC) was first described by Friedrich Bergius in 1913, however due to the rising importance of oil, its industrial application was not developed.("Hydrothermal Carbonization of Biomass Technology,") The topic only starts getting interest from researchers around the year 2005 and 2006. In 2005, Japanese researchers had tried to convert methane fermentation sludge into hydrochar using hydrothermal carbonisation.(Sato, Mochidzuki, Sakoda, & Sato, 2005) On the other hand, in 2006, catalyst of iron oxide nanoparticles were being tested in the trial of converting starch and rice carbohydrates into biochar.(Cui, Antonietti, & Yu, 2006)

Since then, more researchers started to look into the hydrothermal carbonisation process. In 2009, the possibility of microwave heating technique to be integrated into hydrothermal carbonisation process had been tested. (Guiotoku, Rambo, Hansel, Magalhães, & Hotza, 2009) Besides, more and more organic wastes are being tested consequently which includes Palm Empty fruit bunch (EFB), microalgae, maize silage, sugarcane bagasse, waste whey and sewage sludge. Some plants such as loblolly pine are also used to conduct the experiment. From here we can know that most researches are conducted on solid biomass instead of sludgy liquid waste except sewage sludge.

The timeline and development of hydrothermal carbonisation can be summarised by the table 3. It involves the discovery of microwave- assisted heating method and a series of possible material for the HTC process. Some had tried different additives in their researches.

TABLE 2.1. Timeline of Hydrothermal Carbonisation related researches

Year	**Research Focus**	**References**
2005	Methane Fermentation Sludge	(Sato et al., 2005)
2006	Starch and Rice Carbohydrates	(Cui et al., 2006)
2009	Microwave-Assisted Method	(Guiotoku et al., 2009)
2010	Palm Empty Fruit Bunches	(Inoue, 2010)
2010	Microalgae	(Heilmann et al., 2010)
2011	Maize Silage	(Mumme et al., 2011)
2012	Sugarcane bagasse with microwave heating	(Chen, Ye, & Sheen, 2012)
2013	Waste Whey	(Escala et al., 2013)
2013	Loblolly pine	(Uddin, Reza, Lynam, & Coronella, 2013)
2014	Sewage Sludge	(Zhao, Shen, Ge, & Yoshikawa, 2014)
2014	Prosopis africana shell with Microwave-assisted	(Elaigwu, Rocher, Kyriakou, & Greenway, 2014)
2014	Woody Biomass and Agro-Residue	(Liu, Quek, & Balasubramanian, 2014)
2014	Urban Food Waste	(Parshetti, Chowdhury, & Balasubramanian, 2014)

2.3 RELEVANT RESEARCHES AND THEORY

Hydrochar produced by hydrothermal carbonisation is more often being tested and examined as a solid fuel where common analysis for fuel such as heating value analysis and ash content analysis are being conducted. However, hydrochar has also potential to become an adsorbance. According to (Parshetti, Chowdhury, & Balasubramanian, 2014), hydrochar derived from food waste exhibit positive results in removing dye from large volume of aqueous solution.

According to Kang, Li, Fan, & Chang (2012), black liquor from paper making industry can be used to produce hydrochar. This research highlighted the application of formaldehyde as a catalyst. The effect of reaction temperature towards properties such as yield, high heating value, carbon recovery efficiency and ash content is also studied in this research. It is proven in this research that presence of formaldehyde and temperature of 265^{o}C give positive results towards the properties. Figure 3 shows the result of the research.

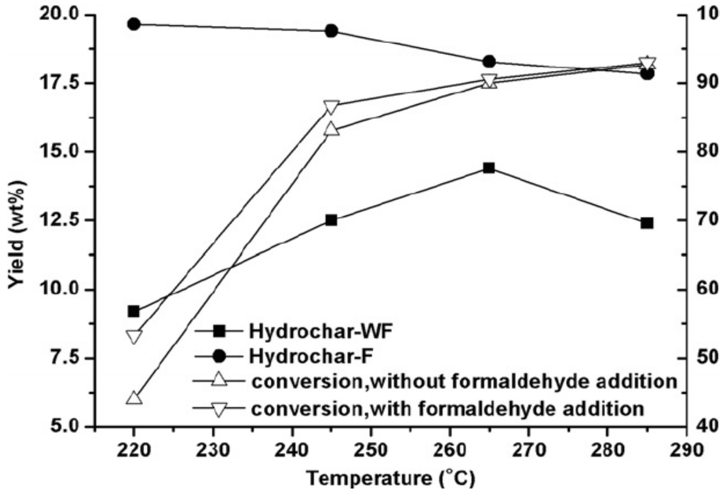


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FIGURE 2.2 Yield of hydrochar with and without Formaldehyde

As stated by Danso-Boateng et al. (2013), faecal biomass can also be used to generate hydrochar using HTC process. The research focuses on the effect of moisture content towards the hydrochar quality. It also compares the significance of temperature and reaction time towards the quality of hydrochar. The research outcomes include temperature is a more significant factor compare to reaction time. Higher initial moisture content resulted in lower hydrochar yield while the extent of carbonisation was more evident in feedstock with lower moisture content. Figure 4 and 5 show the result.

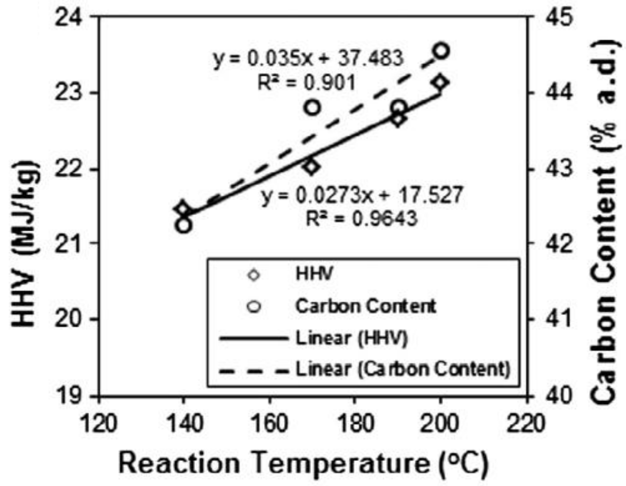


FIGURE 2.3 Effect of temperature (Faecal Biomass)

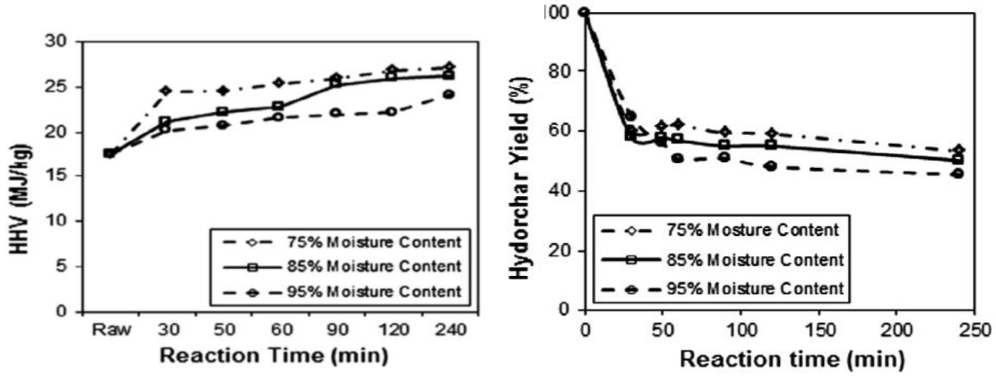


FIGURE 2.4 Effect of Humidity

Based on research conducted by Oliveira, Blöhse, & Ramke (2013), different types of agricultural residues are tested for the potential use as solid fuel of their HTC products. Chemical analysis also had been done on the process water to verify its possibility of further usage. The outcome of the research showed that mixture of agricultural residue gave better quality of hydrochar and the produced hydrochar is comparable to brown coal. The process water has potential to be used in biogas plants. The research also suggested further study on the use of hydrochar as soil amendment or scrubbing material.

In addition, an interesting research is also conducted by Poerschmann et al., (2013). The research focuses on investigating the suitability of Olive Mill Wastewater (OMW) as the material for hydrothermal carbonisation through chemical analysis on the HTC product. The research concludes that the yield of hydrochar is low using OMW. However, there is useful substrate for biogas generation in the aqueous phase.

Referring to research conducted by Mumme et al. (2011), digested maize silage is used to produce hydrochar using hydrothermal carbonisation. The research focuses on the effect of temperature towards carbon content and hydrochar yield. The research concludes that higher temperature increased the carbon content but reduces the yield of hydrochar. It is showed in figure 6.

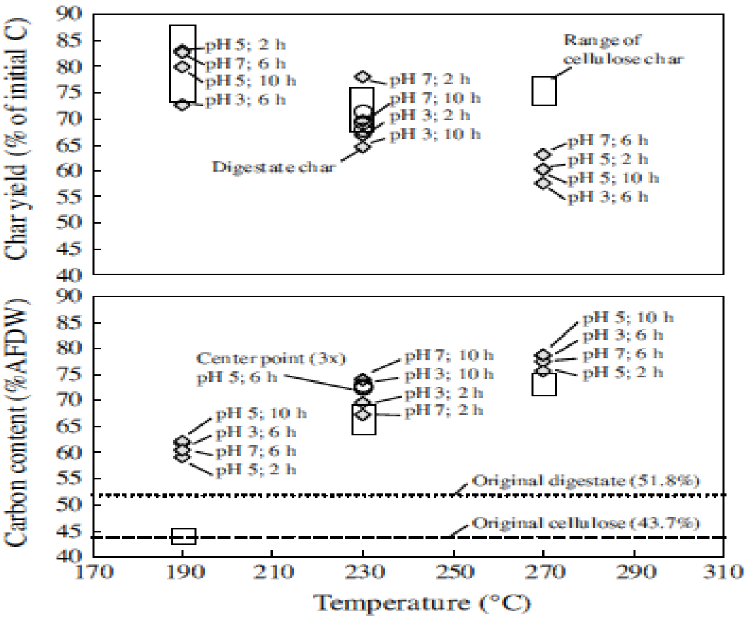
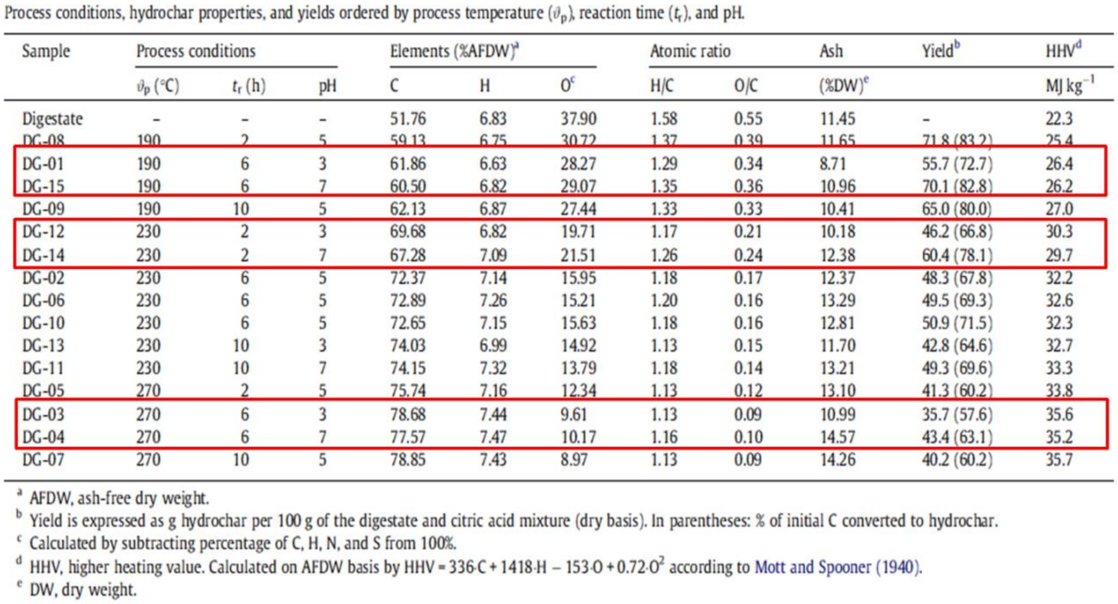


FIGURE 2.5 Effect of temperature (Maize Silage)

In addition, the research also showed briefly the effect of pH value to the reaction. With the same process condition, lower pH value increases heating value and carbon content while decreases ash content and yield as shown in table 4.

TABLE 2.2 Effect of pH Value



Process conditions, hydrochar properties, and yields ordered by process temperature (ϑ_p), reaction time (t_r), and pH.

Sample	Process conditions			Elements (%AFDW)[a]			Atomic ratio		Ash	Yield[b]	HHV[d]
	ϑ_p (°C)	t_r (h)	pH	C	H	O[c]	H/C	O/C	(%DW)[e]		MJ kg^{-1}
Digestate	–	–	–	51.76	6.83	37.90	1.58	0.55	11.45	–	22.3
DG-08	190	2	5	59.13	6.75	30.72	1.37	0.39	11.65	71.8 (83.2)	25.4
DG-01	190	6	3	61.86	6.63	28.27	1.29	0.34	8.71	55.7 (72.7)	26.4
DG-15	190	6	7	60.50	6.82	29.07	1.35	0.36	10.96	70.1 (82.8)	26.2
DG-09	190	10	5	62.13	6.87	27.44	1.33	0.33	10.41	65.0 (80.0)	27.0
DG-12	230	2	3	69.68	6.82	19.71	1.17	0.21	10.18	46.2 (66.8)	30.3
DG-14	230	2	7	67.28	7.09	21.51	1.26	0.24	12.38	60.4 (78.1)	29.7
DG-02	230	6	5	72.37	7.14	15.95	1.18	0.17	12.37	48.3 (67.8)	32.2
DG-06	230	6	5	72.89	7.26	15.21	1.20	0.16	13.29	49.5 (69.3)	32.6
DG-10	230	6	5	72.65	7.15	15.63	1.18	0.16	12.81	50.9 (71.5)	32.3
DG-13	230	10	3	74.03	6.99	14.92	1.13	0.15	11.70	42.8 (64.6)	32.7
DG-11	230	10	7	74.15	7.32	13.79	1.18	0.14	13.21	49.3 (69.6)	33.3
DG-05	270	2	5	75.74	7.16	12.34	1.13	0.12	13.10	41.3 (60.2)	33.8
DG-03	270	6	3	78.68	7.44	9.61	1.13	0.09	10.99	35.7 (57.6)	35.6
DG-04	270	6	7	77.57	7.47	10.17	1.16	0.10	14.57	43.4 (63.1)	35.2
DG-07	270	10	5	78.85	7.43	8.97	1.13	0.09	14.26	40.2 (60.2)	35.7

[a] AFDW, ash-free dry weight.

[b] Yield is expressed as g hydrochar per 100 g of the digestate and citric acid mixture (dry basis). In parentheses: % of initial C converted to hydrochar.

[c] Calculated by subtracting percentage of C, H, N, and S from 100%.

[d] HHV, higher heating value. Calculated on AFDW basis by $HHV = 336 \cdot C + 1418 \cdot H - 153 \cdot O + 0.72 \cdot O^2$ according to Mott and Spooner (1940).

[e] DW, dry weight.

Table 5 summaries the outcomes of the researches that had been selected as the references for this project. It shows all the operating parameters and conclusions of the experiments.

Table 5 showed the research summaries for the journals referred for this project.

TABLE 2.3 Research summaries

Material	**Catalyst**	**Temperature**	**Duration**	**Moisture Content**	**Conclusion**	**References**
Black Liquor from paper making industry	2.8 wt.% Formaldehyde	220^{o}C, 245^{o}C, 265^{o}C, 285^{o}C	8hr	25 g of dried BLS and 100 mL of water,	265^{o}C, with Formaldehyde works better	(Kang, Li, Fan, & Chang, 2012)
Faecal Biomass, synthetic faeces	NA	140^{o}C, 170^{o}C, 190^{o}C, 200^{o}C	0, 30, 50, 60, 90, 120, 240 min	75%, 85%, 95%	Higher temperature and higher moisture gives lower Heating value and yield	(Danso-Boateng et al., 2013)
Agriculture residue	NA	>180^{o}C	4hr	75%	Biochar comparable to brown coal. Process water have potential for biogas plants	(Oliveira, Blöhse, & Ramke, 2013)
Olive Mill Wastewater	100 mg L^{-1} Citric Acid	180^{o}C, 220^{o}C	14hr	NA	Low biochar generation but aqueous phase have potential for biogas production	(Poerschmann et al., 2013)
Maize Silage	Citric Acid (pH 3,5,7)	190^{o}C, 230^{o}C, 270^{o}C,	2hr, 6hr, 10hr	302 g digestate was diluted with 198 g of water	Higher temperatures and lower pH Increased the hydrochar's carbon content but reduced its yield and surface area.	(Mumme et al., 2011)
Urban food Waste	NA	250^{o}C, 350^{o}C	20 min	75%	250^{o}C HTC of food waste is efficient adsorbent for removal of AO and R6G from water	(Parshetti et al., 2014)

In addition, from most of the literature review, there are two ways to conduct the experiment which are using autoclave or steel batch reactors.

TABLE 2.4 Research Methods summaries

Material	Methods	References
Black Liquor from paper making industry	Autoclave	(Kang et al., 2012)
Faecal Biomass, synthetic faeces	Steel Batch Reactor in Oil Bath	(Danso-Boateng et al., 2013)
Agriculture residue	Autoclave	(Oliveira et al., 2013)
Olive Mill Wastewater	Autoclave	(Poerschmann et al., 2013)
Maize Silage	Stirred pressure reactor with an external resistance heater	(Mumme et al., 2011)
Woody Biomass and Agro-Residue	Autoclave	(Liu, Quek, & Balasubramanian, 2014)
Microcrystalline cellulose	Gas-tight stainless steel tubular reactors in Oven	(Lu et al., 2014)
Organic Pollutants	Autoclave	(Weiner, Baskyr, Poerschmann, & Kopinke, 2013)
Urban Food Waste	Parr stirred pressure batch reactor with heater	(Parshetti et al., 2014)
Beech (Fagus) wood chips	High temperature entrained flow reactor with Steam heating	(Tremel, Stemann, Herrmann, Erlach, & Spliethoff, 2012)

There was little or no research conducted to convert POME to biochar using HTC process. Information can only obtained by referring to the experiment conducted with other materials. The most similar researches would be the research conducted on Olive mill wastewater and black liquor which we sludgy liquid waste. All the experiments are conducted at the temperature of lower than 300^{o}C. Formaldehyde or citric acid is added in some experiments. Formaldehyde is a common polymerisation agent. It may increase the yield of hydrochar.

Thus, based on the literature review, the operating parameters for this project are selected. Temperature of 230 ^{o}C, 270^{o}C or 290^{o}C, formaldehyde concentration of 0wt%, 2.5 wt.% or 5.0 wt.% and humidity of 65%, 80% and 95% is selected for the subsequence project.

CHAPTER 3

METHODOLOGY/PROJECT WORK

3.1 EXPERIMENT PROCEDURE

The following flowchart shows the general process flow of the project.

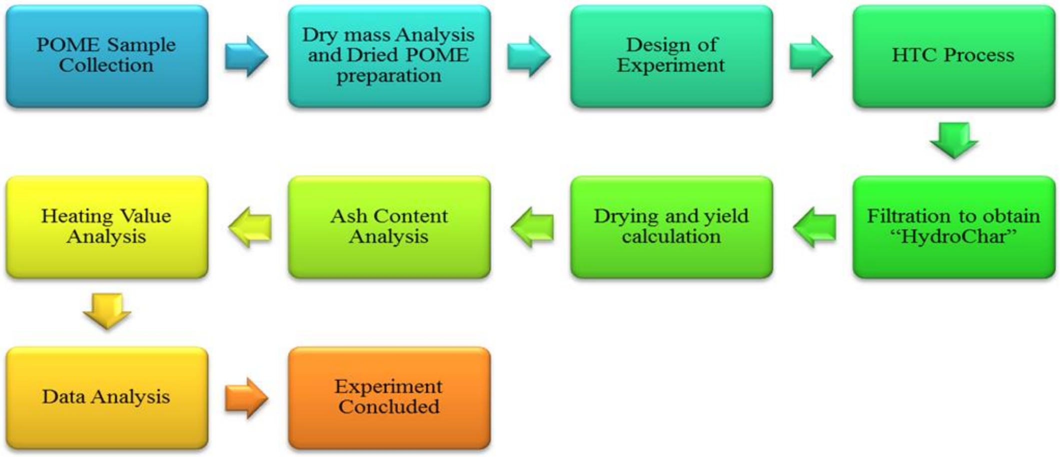


FIGURE 3.1 Project Flow chart

4.1.1 Sample Collection

Palm Oil Mill Effluent (POME) is collected from Nasaruddin Palm Oil Mill in Bota Perak. The POME sample is collected at the sampling point right after all the separation processes for palm oil extraction. The sample is collected at this point as the experiment aims to verify the possibility of additional process on POME before any treatment process is done.

FIGURE 3.2 Raw POME from Palm Oil Mill

4.1.2 Dry Matter Analysis on Raw POME and Sample Preparation

Dry matter analysis is used to know the original humidity in the feed material POME while preparing the dried solid sample for further HTC process. The steps are as follow:

1. Aluminium dish is weighted.

FIGURE 3.3 Aluminium dishes

2. Approximately 50g of sample is weighted with the dish.
3. The sample is dried in the oven at 75^0C.

FIGURE 3.4 Laboratory Oven

4. The weigh is monitored every 3 hours until no changes in weigh are observed.
5. The final weigh is recorded.
6. Dry matter Percentage is calculated from the reading. The equation used is

$$\% \, Dry\ matter = \frac{Dried\ Mass - Dish\ Mass}{Initial\ Mass - Dish\ Mass} \times 100\% \quad \text{------ (Equation 1)}$$

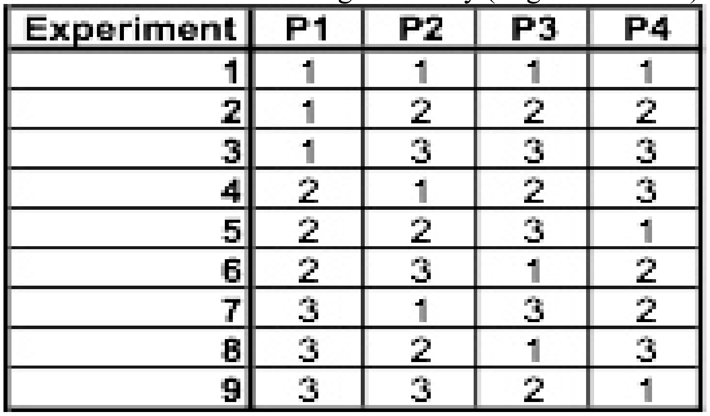
7. The experiment is repeated 4 times to obtain average dry matter percentage of the sample.
8. Dried Pome is grinded in mortar and pestle.
9. Dried POME is used for further reaction or analysis later in the experiment.

*Note: The sample is dried to strictly monitor the water and solid content for the purpose of controlling the variable. Drying is not required for the actual process.

4.1.3 Design of Experiment

1. Taguchi method is used to design the experiment.(Fraley et al., 2007)
2. With 3 variables with 3 levels, L9 Orthogonal Array is selected.

TABLE 3.1 L’16 Orthogonal Array (Taguchi Method)



Experiment	P1	P2	P3	P4
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

3. Constructing the table:

TABLE 3.2 Experiment designed using Taguchi method.

Run	**Temperature (^{O}C)**	**Formaldehyde (wt.%)**	**Humidity, %**	**Yield**	**Heating Value**	**Ash Content**	**Carbon Content**
1	230	0	65				
2	230	2.5	80				
3	230	5	95				
4	270	0	95				
5	270	2.5	65				
6	270	5	80				
7	290	0	80				
8	290	2.5	95				
9	290	5	65				

*By using Taguchi Method, only 9 experiments is required compared to 27 experiments if the experiment is designed using factorial method.

3.1.1 HTC process

Dried sample together with premeasured amount of water will go through HTC process using a 1L lab-scale autoclave. The steps are as follow:

1. 0wt%, 2.5 wt.% or 5.0 wt.% of Formaldehyde is prepared.
2. Amount of dried POME is weighed to match the pre-set ratio of formaldehyde solutions.
3. The dried Formaldehyde solution to POME ratio (65%wt, 80%wt and 95%wt) is prepared. The value is represented by % humidity.
4. The mixture is added into the autoclave.

FIGURE 3.5 Autoclave

5. Stirrer is set to 500 rpm. Pressure is increased automatically due to temperature settings.

FIGURE 3.6 Autoclave Control Panel

6. A temperature of 230 ^{o}C, 270^{o}C or 290^{o}C will be applied for 8 hrs.
7. The reactions are repeated with different changing Formaldehyde concentration, moisture content and temperature.

3.1.2 Reaction Product Sample Preparation and Product Yield Measurement

1. The HTC-slurry is allowed to pass through a Whatman Filter Paper.
2. The filtrate is collected in a sample bottle for further analysis.
3. The residue (Solid hydro-char) is dried at 75^{o}C for 24 hours in the oven.
4. The dried solid is weighed to determine the yield.
5. The dried solid is grinded with mortar and pestle and collected in sampling bottle for further testing.
6. % yield is calculated from the readings. The equation used is

$$\%\, yield = \frac{Final\ hydrochar\ Mass}{Initial\ POME\ Mass} \times 100\% \qquad \text{------- (Equation 2)}$$

3.1.3 Ash Content Analysis

ASTM Method D3174, standard testing method for ash content in coal sample is selected as a reference as this analysis. (Lindahl, n.d.) The reason is the aim of this process is to obtain solid fuel that is comparable to actual coal.

1. The crucible with lid is weighed. The value is recorded.
2. Approximately 1g of sample is weighed in the crucible.
3. The final weight of crucible + lid+ sample is recorded.
4. The crucible is put into a cold furnace.
5. The furnace is heated up gradually to 450-500^{o}C in one hour.
6. The Furnace temperature reached 700-750^{o}C at the end of second hour.
7. The furnace is allowed to cool down.
8. The crucible is weighed again and the final weight is recorded.
9. Ash Content is calculated from the readings. The equation used is

$$\%\, ash = \frac{Final\ Total\ Mass - Crucible\ Mass}{Initial\ Total\ Mass - Crucible\ Mass} \times 100\% \qquad \text{--------(Equation 3)}$$

10. The experiment is repeated 3 times for each sample. Average is calculated.
11. The data is recorded in the table

TABLE 3.3 Ash Content Analysis

Sample	Trials	Crucible weight (g)	Crucible + sample (g)	Final weight (g)	% Ash Content	Average (% Ash)
POME	1					
	2					
	3					
Solid 1	1					
	2					
	3					
Solid 2	1					
	2					
	3					
Solid 3	1					
	2					
	3					
Solid 4	1					
	2					
	3					
Solid 5	1					
	2					
	3					
Solid 6	1					
	2					
	3					
Solid 7	1					
	2					
	3					
Solid 8	1					
	2					
	3					
Solid 9	1					
	2					
	3					

3.1.4 Heating Value Analysis

Bomb-calorie meter is selected to conduct the heating value analysis.

FIGURE 3.7 Bomb calorie meter

1. Approximately 0.5g of sample is measured in a sample cell.
2. The ignition wire is applied and checked in the sample cell.
3. Sample cell is inserted into the bomb calorie meter.
4. The sample is ignited and change in temperature of the inner vessel overtime is recorded.
5. The result of experiment is waited to be displayed in the screen.
6. The result is recorded in the table.

TABLE 3.4 Heating Value Analysis

Sample	Weight (g)	Energy (J/g)
POME		
Solid 1		
Solid 2		
Solid 3		
Solid 4		
Solid 5		
Solid 6		
Solid 7		
Solid 8		
Solid 9		

3.1.5 Carbone, Hydrogen, Nitrogen (CHN) Content Analysis

The analyses are done on the samples in order to know the quality of the solid product. CHN analysis provides information about carbon content, hydrogen content, nitrogen content and sulphur content in a solid sample. It is a very important analysis for fuel characterisation. However, Carbon content is the major focus for this experiment.

1. Approximately 0.2 g of sample is measured and wrapped in an aluminium foil.
2. Sample is put on the sampling rack on CHN Analyser.
3. The Sample is dropped into the furnace of CHN analyser.
4. Result is waited to be displayed on the screen.
5. Result is recorded and tabulated.

3.1.6 Data analysis

Data analysis is done to interpret the table generated using Taguchi method. Average value for each parameter can be compared while Signal-to-noise ratio analysis will be done on the data. Average values of each parameters comparison show their relationship to the targeted performance characteristic while Signal-to-noise ratio analysis indicates the significant of each parameter to the process.

1. Calculations:

$SN_i = -10\log(\sum_{u=1}^{N_i} \frac{y_u^2}{N_i})$ --- For minimizing performance Characteristic

$SN_i = -10\log(\frac{1}{N_i}\sum_{u=1}^{N_i} \frac{1}{y_u^2})$-- For maximizing performance Characteristic

$Where$ ------- (Equation 4 & 5)

$y_u =$ Performance characteristics. eg: Ash content, heating value, yield etc

$u =$ Trial number;

$N_i =$ number of trial for experiment i;

(Fraley et al., 2007)

2. Table 12 shows the classification of performance characteristics:

TABLE 3.5 Classification of performance characteristics.

Minimizing	Maximizing
Ash Content	Heating Value Yield Carbon Content

3. Average values of each parameters and average SN value is calculated for each factor and level.
4. Table 13 shows the tabulation of average values of each parameters.

TABLE 3.6 Average Values tabulation.

Level	**Temperature (^{o}C)**	**Formaldehyde (wt.%)**	**Humidity, %**
1	$T_{avg,230}$	$Wt\%_{avg,0}$	$H\%_{avg,65}$
2	$T_{avg,270}$	$Wt\%_{avg,2.5}$	$H\%_{avg,80}$
3	$T_{avg,290}$	$Wt\%_{avg,5}$	$H\%_{avg,95}$

5. Table 14 shows the tabulation for SN ratio analysis
6. The average SN values are compared. The larger the R value the larger the effect the variable has on the process.

TABLE 3.7 SN ratio analysis

Level	**Temperature (^{o}C)**	**Formaldehyde (wt.%)**	**Humidity, %**
1	$SN_{T,230}$	$SN_{wt\%,0}$	$SN_{H\%,65}$
2	$SN_{T,270}$	$SN_{wt\%,2.5}$	$SN_{H\%,80}$
3	$SN_{T,290}$	$SN_{wt\%,5}$	$SN_{H\%,95}$
Δ	R_T	$R_{wt\%}$	$R_{H\%}$
Rank	…	…	…

*$R = SN_{max} - SN_{min}$ ---------- (Equation 6)

3.1.7 Simple error analysis

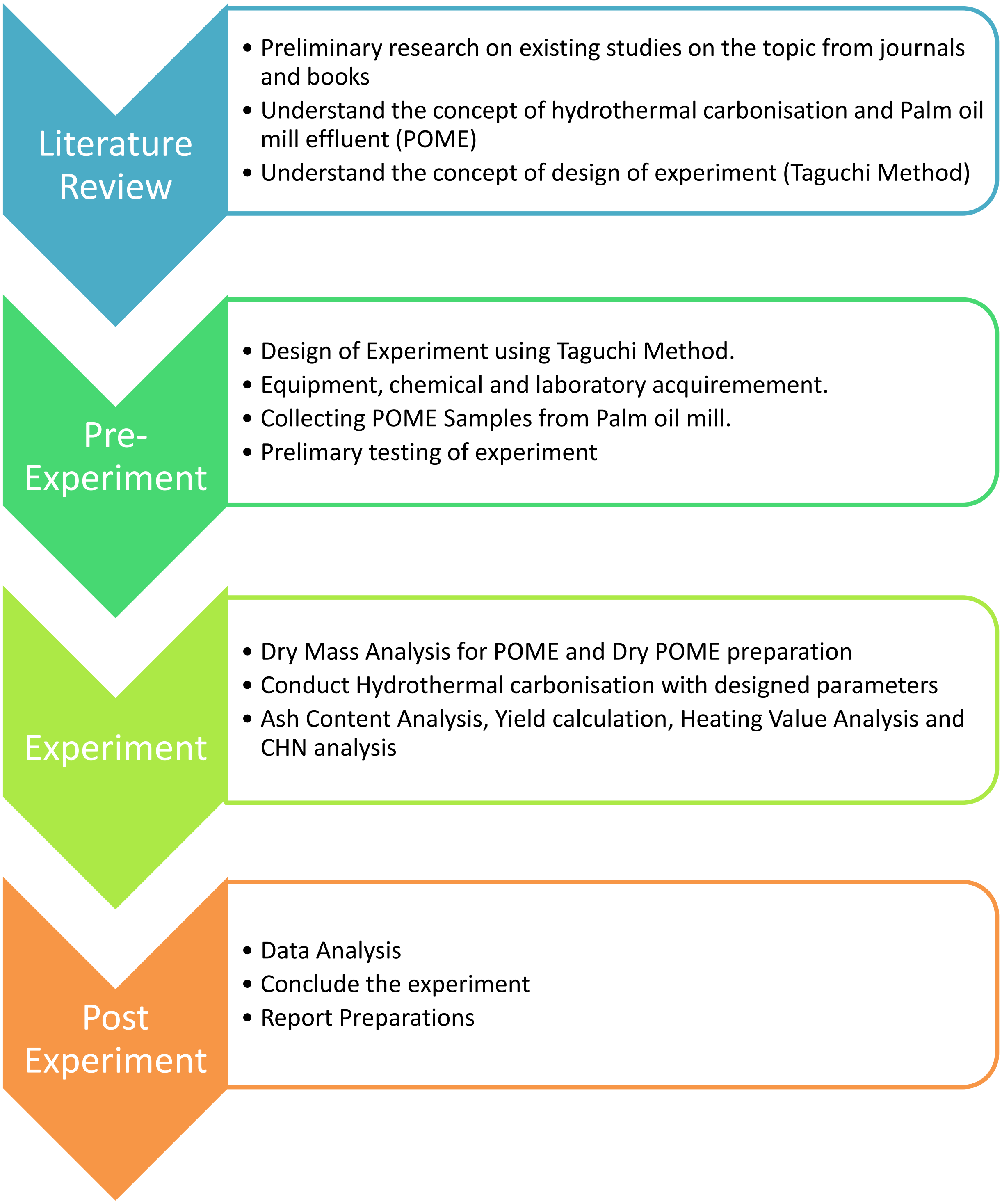
With limited amount of time and resources, simple error analysis is done to signify the accuracy of project data.

1. Second trial of HTC process is done based on parameter settings for solid 4.
2. The Sample undergoes yield mass calculation, Ash Content Analysis, Heating Value analysis and CHNS analysis.
3. Two trials are compared and the error for each parameters will be calculated using the equation

$$\% \, error = \frac{|Trial\ 1\ value - Trial\ 2\ value|}{Mean\ Value} \times 100\%$$ ----------(Equation 7)

4. The data is recorded.

3.2 Project Activities



Literature Review

- Preliminary research on existing studies on the topic from journals and books
- Understand the concept of hydrothermal carbonisation and Palm oil mill effluent (POME)
- Understand the concept of design of experiment (Taguchi Method)

Pre-Experiment

- Design of Experiment using Taguchi Method.
- Equipment, chemical and laboratory acquirement.
- Collecting POME Samples from Palm oil mill.
- Prelimary testing of experiment

Experiment

- Dry Mass Analysis for POME and Dry POME preparation
- Conduct Hydrothermal carbonisation with designed parameters
- Ash Content Analysis, Yield calculation, Heating Value Analysis and CHN analysis

Post Experiment

- Data Analysis
- Conclude the experiment
- Report Preparations

FIGURE 3.8. Project Activities

3.3 Project Key Milestones and Project Timeline

	No	Detail/ Activities	1	2	3	4	5	6	7	8	9	10	11	12	13	14
FYP 1	1	Selection of Project Topic	🟦	🟦												
	2	Preliminary background research		🟦	🟦	🟦	🟦	🟦	🟦	🟦						
	3	Requesting Laboratory and Chemicals				🟦	🟦	🟦								
	4	Submission of Extended Proposal						☒								
	5	Proposal Defence								☒						
	6	Design of Experiment using Taguchi Method								🟦	🟦	🟦				
	7	Collecting POME Samples from Palm oil mill									🟦	🟦				
	8	Prelimary testing of experiment										🟦	🟦	🟦	🟦	🟦
	9	Submission of Interim Report														☒
FYP 2	1	Conduct Hydrothermal carbonisation	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦						
	2	Conduct Heating Value Analysis				🟦	🟦	🟦	🟦	🟦						
	3	Conduct Ash Content Analysis				🟦	🟦	🟦	🟦	🟦						
	4	Conduct CHNS Analysis							🟦	🟦	🟦					
	5	Data Analysis									🟦	🟦				
	6	Selected best Operating Parameters										☒				
	7	Conclude Experiment										☒				
	8	Report Preparations										🟦	🟦	🟦		
	9	Submission of technical paper												☒		
	10	Viva													☒	
	11	Final Submission of Project														☒

☒ Suggested Milestone

🟦 Process

FIGURE 3.9 Project Key Milestones and Project Timeline

CHAPTER 4

RESULT AND DISCUSSION

4.1 POME Dry Mass Analysis

Results:

TABLE 4.1 POME Dry mass analysis result

Trials	Sample weight (g)	% Dry Mass
1	5.0086	11.9694
2	5.0122	11.9309
3	5.0057	11.9524
4	5.0244	11.9677
5	5.0016	11.9522
	Average	11.9545

*Calculations are in appendix A

Discussion:

POME is proven to be one type of high solid content waste water. High solid contain makes it harder to treat and more harmful to environment if release without treatment. However, high solid content makes it a possible good source to undergo hydrothermal carbonisation. The high moisture contain compare to other type of solid biomass makes it hard to be utilised. However, this characteristic suits the requirement of hydrothermal carbonisation which presence of water is required.

4.2 Physical Characteristics of hydrochar

Some observations are done on the hydrochar produces in the experiment. It is also proven that produced hydrochar hold the characteristic of combustible fuel. It can be ignited by flame.

FIGURE 4.1 Ignited Hydrochar

Results:

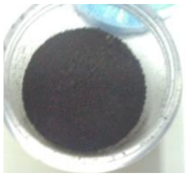
Sample	Appearance	Observations	Sample	Appearance	Observations
POME		• Non-greasy • Light brown	**SOLID 5**		• Very Greasy • Black
SOLID 1		• Non-greasy • Black	**SOLID 6**		• Greasy • Black
SOLID 2		• Non-greasy • Dark-brown	**SOLID 7**		• Very Greasy • Black
SOLID 3		• Non-greasy • Slightly Dark-brown	**SOLID 8**		• Greasy • Black
SOLID 4		• Slightly Greasy • Black	**SOLID 9**		• Slightly Greasy • Black

TABLE 4.2 Observation of the products

Discussion:

All samples are darker than raw POME. These changes in appearance signify the solid had undergoes certain degree of carbonisation. Logically, the higher the carbon contents in the sample, the darker the sample. Increasing temperature shows darker sample which signify higher degree of carbonisation. In addition, Lower concentration of Formaldehyde and lower humidity gives darker samples. However, this can only be observed easily in low reaction temperature. (230^{o}C samples). On the other hand, higher temperature gives greasier sample which signify more heavy hydrocarbons are broken down to form slightly oily content. Lower Formaldehyde concentrations give greasier product. Formaldehyde as a polymerisation agent hold the hydrocarbons together instead of breaking into lighter hydrocarbon which contribute to the greasiness of the product.

4.3 Hydrochar Yield

The significance of this analysis is the amount of output product can be known based on the operating conditions.

Results:

TABLE 4.3 Yield results

Run	Temperature (^{O}C)	Formaldehyde (wt.%)	Humidity, %	POME Weight (g)	Hydrochar weight (g)	% yield
1	230	0	65	100.0011	61.2704	61.2697
2	230	2.5	80	50.0236	35.0088	69.6887
3	230	5	95	13.0015	7.3633	56.6342
4	270	0	95	13.0023	4.8128	37.1499
5	270	2.5	65	50.0233	26.5560	53.0873
6	270	5	80	50.0126	29.4080	58.8012
7	290	0	80	50.0155	12.6868	25.3657
8	290	2.5	95	25.0023	14.9363	59.7397
9	290	5	65	50.0032	30.2316	60.4593

TABLE 4.4 Average value analysis for yield

Yield, %			
Level	**Temperature**	**Formaldehyde**	**Humidity**
1	62.53	41.26	58.27
2	49.67946667	60.84	51.29
3	48.52	58.63	51.17

TABLE 4.5. SN ratio Analysis for yield

Yield, %			
Level	**Temperature**	**Formaldehyde**	**Humidity**
1	35.89	31.74	35.29
2	33.76	35.63	33.45
3	33.08	35.36	34.00
Δ	2.81	3.62	1.85
Rank	2	1	3

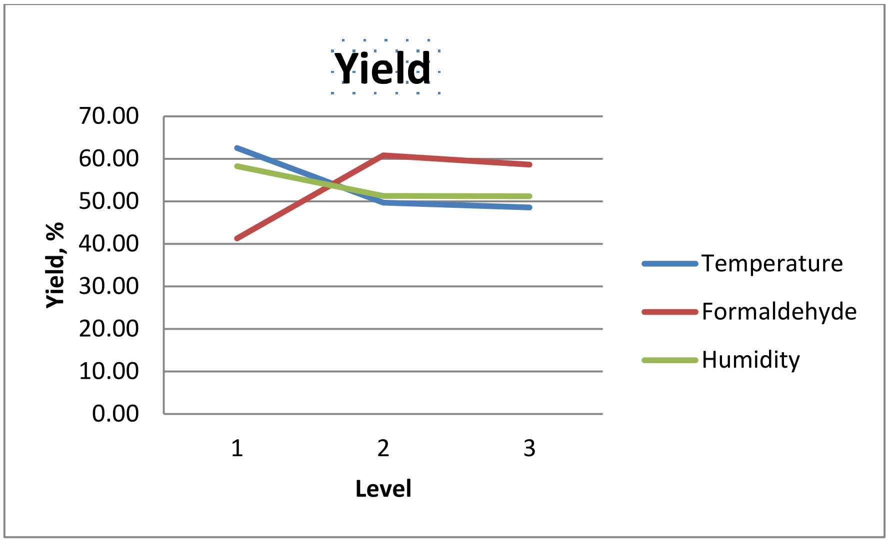


FIGURE 4.2 Average Values plotting of Yield

Discussion:

Level 1, 2 and 3 indicates the increasing settings of each parameter. (Temperature: 230°C, 270°C, 290°C; Formaldehyde concentration: 0%wt, 2.5%wt, 5.0% wt; Feed Humidity: 65wt% H_2O, 80wt% H_2O, 95wt% H_2O) From the signal to noise ratio analysis, it is proven that formaldehyde concentration has then highest effect on yield while temperature has slightly lower effect on yield. Humidity does not affect yield significantly compare to these two parameters. From the average value analysis, yield is lower when temperature is higher. The reason is because more solid hydrocarbons are broken down into liquid or gas in high temperature. Furthermore, high humidity or solution to POME ratio shows lower yield. The reason is more mineral ions are dissolved into the water from the solid where mass transfer from solid phase to liquid phase occurred. High formaldehyde show higher yield as formaldehyde is a polymerisation agent which prevents the solid hydrocarbons from breaking down. However, higher yield does not means that the parameters are the best as quality and fuel potential for the product is also important. From the average value analysis, we can see that the yield between level 2 and level 3 for all three parameters are near. Hence, in terms of economical effectiveness, it is suggested that temperature and formaldehyde should operate at level 2 which is 270°C and 2.5%wt respectively. Humidity is not significant in contributing effects on yield.

4.4 Ash Content analysis

Ash content is one of the important characteristic for any fuel. Lower ash content means lesser possibility of furnace tubing erosion due to ash and also ash coating that inhibit heat transfer across furnace tube in case of utility application.

Results:

TABLE 4.6 Ash Content

Sample	**Temperature (^{O}C)**	**Formaldehyde (wt.%)**	**Humidity, %**	**% Ash Content**
POME	-	-	-	10.8235
SOLID 1	230	0	65	10.8693
SOLID 2	230	2.5	80	9.1282
SOLID 3	230	5	95	4.5096
SOLID 4	270	0	95	5.9145
SOLID 5	270	2.5	65	5.7906
SOLID 6	270	5	80	3.8038
SOLID 7	290	0	80	5.9514
SOLID 8	290	2.5	95	3.9141
SOLID 9	290	5	65	3.6301

*Calculations can be found in appendix B

TABLE 4.7 Average Value Analysis for Ash Content

Ash Content, %			
Level	Temperature	Formaldehyde	Humidity
1	8.17	7.58	6.76
2	5.17	6.28	6.29
3	4.50	3.98	4.78

TABLE 4.8 SN ratio Analysis for Ash content

Ash Content, %			
Level	**Temperature**	**Formaldehyde**	**Humidity**
1	-17.67	-17.22	-15.73
2	-14.10	-15.44	-15.43
3	-12.85	-11.96	-13.46
Δ	3.57	5.26	2.27
Rank	2	1	3

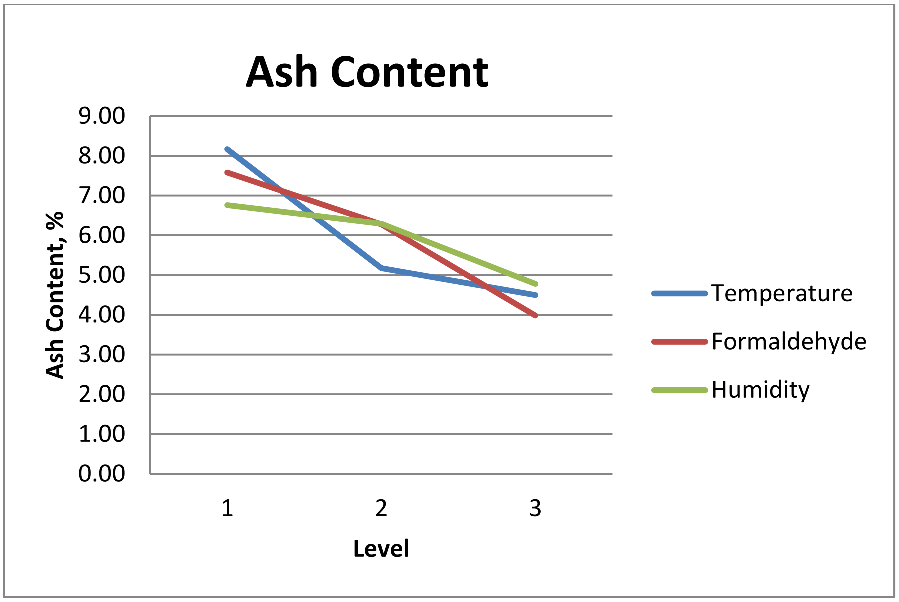


FIGURE 4.3 Average Values plotting of Ash Content

Discussion:

Generally, most hydrochar except experiment 1 have lower ash content than POME. It proves that hydrothermal carbonisation reduces ash content in the biomass. The data proved that higher temperature promotes lower ash content. The reason would most probably be the mineral in the POME which contribute to the ash content dissolve more into water in higher temperature and the consequence high pressure. On the other hand, there is positive effect in reducing the ash content for increasing formaldehyde concentration.. Next, higher humidity or solution to POME ratio creates lower ash content products. The reason is more mineral ions which contribute to ash content are more soluble with higher amount of water (lower concentration of ions in water). For the signal to noise ratio analysis, it is proven that formaldehyde concentration is the biggest contributor in reducing ash content. The second is temperature while humidity or solution to solid ratio has the least significance effect. In conclusion, in terms of reducing ash content, the best operating condition would be level 3 for every parameter.

4.5 Heating value Analysis

Heating value analysis is conducted to know the energy content in the sample as a fuel.

Results:

TABLE 4.9. Heating Value results

Sample	**Temperature (^{O}C)**	**Formaldehyde (wt.%)**	**Humidity, %**	**Heating value (J/g)**
POME	-	-	-	23544
SOLID 1	230	0	65	28118
SOLID 2	230	2.5	80	28270
SOLID 3	230	5	95	30075
SOLID 4	270	0	95	31707
SOLID 5	270	2.5	65	32235
SOLID 6	270	5	80	32779
SOLID 7	290	0	80	32018
SOLID 8	290	2.5	95	31867
SOLID 9	290	5	65	32988

TABLE 4.10 Average Value Analysis for Heating Value

Heating Value, kJ/kg			
level	**Temperature**	**Formaldehyde**	**Humidity**
1	28821	30614.33	31113.67
2	32240	30790.67	31022.33
3	32291	31947.33	31216.33

TABLE 4.11 SN ratio Analysis for Heating Value

Heating Value, kJ/kg			
Level	**Temperature**	**Formaldehyde**	**Humidity**
1	89.19	89.70	89.84
2	90.17	89.75	89.82
3	90.18	90.08	89.88
Δ	0.98	0.38	0.02
Rank	1	2	3

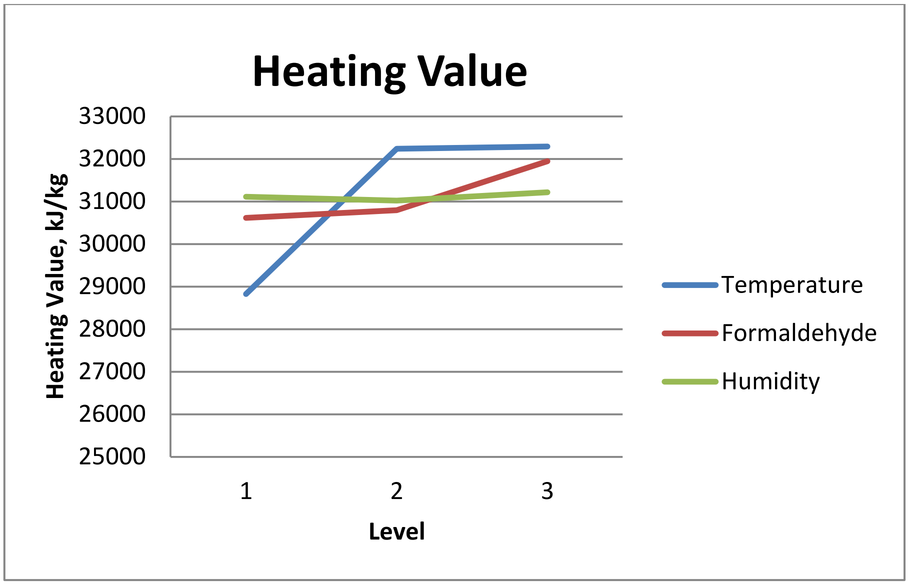


FIGURE 4.4 Average Values plotting of Ash Content

<u>Discussion:</u>

First, all hydrochar have higher heating value than POME which signify the hydrothermal process is successful to increase energy density of biomass. From the average values analysis, higher temperature produces higher heating value hydrochar. High degree of carbonisation in hydrochar under higher temperature causes higher carbon content and hence higher energy density. Slight increase in heating value is observed when formaldehyde is added. On the other hand, increasing humidity also gives positive result in increasing heating value. Based on signal and noise ratio analysis, temperature has the most significant effect on increasing heating value. Booth effect of formaldehyde and humidity are not significant. Humidity has the lowest significance in increasing heating value. From the analysis of result, we can conclude that temperature at level 2 is preferable as the effect of increasing temperature to level 3 is not significant. Furthermore, effect of formaldehyde concentration and humidity is not significant.

4.6 Carbon content from CHN analysis

Carbon, Hydrogen , nitrogen analyser is used to verify the carbon content in the hydrochar produced in the experiments.

TABLE 4.12 CHN Analysis results

Sample	**Temperature (^{O}C)**	**Formaldehyde (wt.%)**	**Humidity, %**	**C %**	**H%**	**N%**
POME	-	-	-	50.865	7.919	1.448
SOLID 1	230	0	65	60.114	8.523	1.286
SOLID 2	230	2.5	80	60.662	8.680	1.152
SOLID 3	230	5	95	65.764	8.802	0.468
SOLID 4	270	0	95	68.300	9.460	0.841
SOLID 5	270	2.5	65	69.068	9.187	1.077
SOLID 6	270	5	80	68.390	9.135	0.807
SOLID 7	290	0	80	66.371	8.968	0.956
SOLID 8	290	2.5	95	69.616	9.094	0.574
SOLID 9	290	5	65	70.190	9.254	0.773

TABLE 4.13 Average Value Analysis for Carbon content

Carbon Content %			
Level	Temperature	Formaldehyde	Humidity
1	62.18	64.93	66.46
2	68.5860	66.45	65.14
3	68.73	68.11	67.89

TABLE 4.14 SN ratio Analysis for Carbon Content

Carbon Content, %			
Level	**Temperature**	**Formaldehyde**	**Humidity**
1	89.19	89.70	89.84
2	90.17	89.75	89.82
3	90.18	90.08	89.88
Δ	0.98	0.38	0.02
Rank	1	2	3

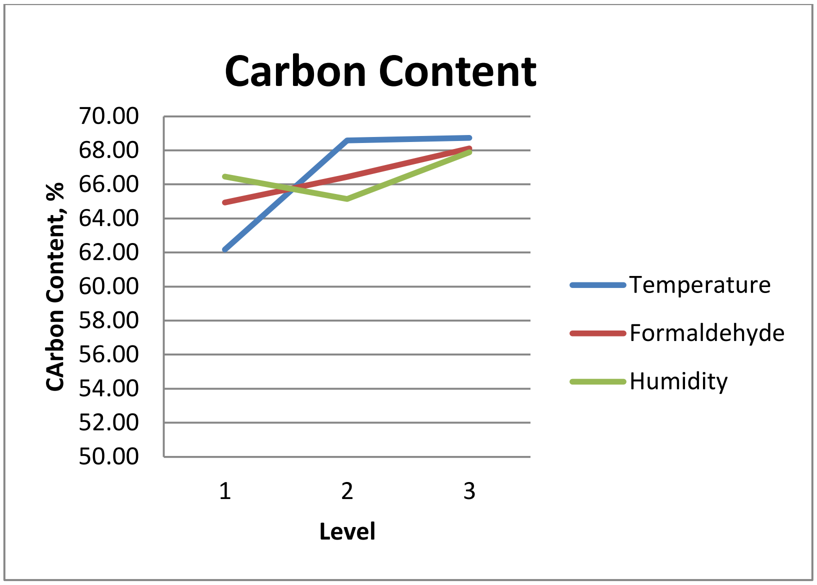


FIGURE 4.5 Average Values plotting of Ash Content

Discussion:

First, all hydrochar have higher carbon content, higher hydrogen content, lower nitrogen content compare POME which signify the hydrothermal process is successful to increase energy density and carbon content of biomass. From the average values analysis, higher temperature produces higher carbon content hydrochar. High degree of carbonisation in hydrochar under higher temperature causes higher carbon content. Slight increase in carbon content is observed when formaldehyde is added. On the other hand, increasing humidity also gives positive result in increasing heating value (level 3 is higher than level 1). However, the pattern is not obvious and clearly explains the characteristic. This is due to the low significance of humidity had affected by the temperature and formaldehyde concentration. Based on signal and noise analysis, temperature has the most significant effect on increasing carbon content. Formaldehyde concentration is the second significant factor. Humidity has the lowest significance in increasing carbon content. From the analysis of result, we can conclude that temperature at level 2 is preferable as the effect of increasing carbon content to level 3 is not significant. Furthermore, effect of formaldehyde concentration and humidity is relatively not significant.

4.7 Selection of best operating parameter

Most of result analysis suggest that both temperature and formaldehyde concentration is sufficient to provide good result using level 2 settings except for ash content. Most of the parameter work best using level 3 settings but the improvement is not significant. Hence, method 5 is selected. The comparison of solid 5 with medium volatile bituminous coal is provided in table below:

TABLE 4.15 CHN Analysis results

Sample	**Heating Value, J/g**	**Ash Content, %**	**Carbon Content %**	**Reference**
Bituminous Coal	30108-30971	13.03-13.18	73.39-74.23	(Vaysman & Lu, 2012)
SOLID 5	32235	5.7906	69.0680	-

Solid 5 has better heating value but lesser carbon content compared to medium volatile bituminous coal. However, it is approximately 2 times lower in ash content. Ash content is the main culprit of pipeline erosion and ash accumulation in hot utility system. Ash accumulation can affect heat transfer efficiency and also causes surface overheating and boiler tube meltdown.

Solid 5 was prepared with humidity or solution: solid ratio of 65wt% water. The increment in humidity is proven to be giving positive results for increasing heating value, reducing ash content and increasing carbon content although the effect is not significance. Hence, it is suggested that POME can be used directly before it leaves the processing mill. This reduces the cost for water feeding or POME drying. In fact, the humidity or solution : solid ratio of 88.05% (11.95% dry matter) will gives better result.

In conclusion, the selected operating conditions are 270^{o}C, 2.5 wt% Formaldehyde concentration and 88.05% humidity which is the original obtained POME.

4.8 Error Analysis

With limited amount of time and resources, simple error analysis is done to signify the accuracy of project data.

Results of solid 4:

TABLE 4.16 Solid 4 Results

Trial	**Yield, %**	**Ash Content, %**	**Heating Value, J/g**	**Carbon content %**
1	37.1499	5.9145	31707	68.30
2	36.5520	6.0253	31605	67.86
|Difference|	0.5979	0.1108	102	0.44
Mean	36.8510	5.9699	31656	68.08
% Error	1.62	1.86	0.32	0.65

Discussion:

All the errors are small. Hence, solid 4 experimental data is valid.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

As a conclusion, this project is very relevant to current situation of Malaysia as the waste product of one of the largest industries in Malaysia is selected. Through the literature review, it is believed that hydrothermal carbonisation is the effective way to upgrade high moisture content biomass waste products into useful product. In addition, lower energy consumption compare to other thermal conversion process. To study the hydrothermal carbonisation process itself, the effect of temperature, effect of additives (formaldehyde) concentration and also solid:water ratio (humidity content) towards the reaction are suggested to study through the suggested methodology.

The Project had verified that HTC process has potential to upgrade POME into solid fuel. It is supported by the positive result by ash analysis, heating value analysis and CHN analysis. Preliminary observation and possible explanations are made. Product of HTC process produces solid with fuel characteristics.

The result of the experiment shows that HTC process has high potential to upgrade POME to higher value product. Increasing temperature and humidity reduces yield and ash content but increases heating value and carbon content. Increasing formaldehyde concentration gives positive results to all the parameters. The effect of temperature and formaldehyde concentration is more dominant in HTC process. The suggested operating conditions for HTC process are 270^{o}C, 2.5 wt% Formaldehyde concentrations and 88.05% humidity which is the originally obtained POME.

As for recommendation, the project can be further developed by investigating the potential of hydrochar generated by hydrothermal carbonisation of POME as the adsorbance for dye polluted waste water. Besides, potential of aqueous phase waste water as sources of chemical productions can be verified. This project is focusing on observing the pattern of changing each parameter instead of a focus, detail and specific testing parameter. It is recommended that detail investigation can be done on each parameter separately with detail error analysis. It is also possible to further explore possible additives to the process.

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APPENDICES

A :

DRY MASS CALCULATION

Trials	Dish weight (g)	Dish + sample (g)	Final weight (g)	% Dry Mass
1	0.5559	5.5645	1.1554	11.9694
2	0.5534	5.5656	1.1514	11.9309
3	0.5559	5.5616	1.1542	11.9524
4	1.5015	6.5359	2.1040	11.9677
5	1.4646	6.4662	2.0624	11.9522
			Average	11.9545

B: ASH CONTENT CALCULATION

Sample	Trials	Crucible weight (g)	Crucible + sample (g)	Final weight (g)	% Ash Content	Average (% Ash)
POME	1	51.2316	53.4579	51.4792	11.1216	10.8235
	2	81.0454	82.9763	81.2549	10.8499	
	3	77.7082	79.2093	77.8658	10.4990	
Solid 1	1	51.2399	52.5051	51.3778	10.8995	10.8693
	2	78.1285	79.4274	78.2702	10.9092	
	3	81.6750	82.8825	81.8054	10.7992	
Solid 2	1	51.2344	53.2571	51.4206	9.2055	9.1282
	2	78.4032	80.7187	78.6140	9.1039	
	3	78.1222	80.1552	78.3067	9.0753	
Solid 3	1	82.0802	83.6016	82.1484	4.4827	4.5096
	2	85.3433	86.4687	85.3939	4.4962	
	3	87.1903	87.7002	87.2135	4.5499	
Solid 4	1	51.2428	52.0124	51.2889	5.9901	5.9145
	2	87.1935	88.0458	87.2416	5.6436	
	3	85.3464	85.6983	85.3679	6.1097	
Solid 5	1	74.9479	77.0945	75.0730	5.8278	5.7906
	2	81.5939	84.3078	81.7518	5.8182	
	3	82.0839	84.6635	82.2316	5.7257	
Solid 6	1	51.2397	52.3184	51.2929	4.9319	3.8038
	2	85.8853	86.9687	85.9194	3.1475	
	3	81.0528	82.0882	81.0873	3.3320	
Solid 7	1	82.0851	83.4164	82.1682	6.2420	5.9514
	2	84.4215	85.5889	84.4910	5.9534	
	3	77.7748	79.1850	77.8546	5.6588	
Solid 8	1	51.2327	52.3350	51.2883	5.0440	3.9141
	2	87.8755	88.9162	87.9103	3.3439	
	3	85.1815	86.3919	85.2221	3.3543	
Solid 9	1	85.6015	86.8419	85.6456	3.5553	3.6301
	2	78.4122	79.6543	78.4565	3.5665	
	3	87.3467	88.7213	87.3985	3.7684	

B: SIGNAL TO RATIO CALCULATION

Run	Temperature ('C)	Formaldehyde (wt.%)	Humidity, %	Yield, %	Heating Value, J/g	Ash %	Carbon%	SN yield	SN hv	SNac	SN c%
POME	-	-	-	-	23544	10.8235	50.8650				
1	230.0	0.0	65.0	61.2697	28118	10.8693	60.1140	35.7449	88.9797	-20.7240	35.5795
2	230.0	2.5	80.0	69.6887	28270	9.1282	60.6620	36.8632	89.0265	-19.2077	35.6583
3	230.0	5.0	95.0	56.6342	30075	4.5096	65.7640	35.0616	89.5641	-13.0828	36.3598
4	270.0	0.0	95.0	37.1499	31707	5.9145	68.3000	31.3992	90.0231	-15.4383	36.6884
5	270.0	2.5	65.0	53.0873	32235	5.7906	69.0680	34.4998	90.1666	-15.2544	36.7855
6	270.0	5.0	80.0	58.8012	32779	3.8038	68.3900	35.3877	90.3119	-11.6044	36.6999
7	290.0	0.0	80.0	25.3657	32018	5.9514	66.3710	28.0849	90.1079	-15.4924	36.4396
8	290.0	2.5	95.0	59.7397	31867	3.9141	69.6160	35.5253	90.0668	-11.8525	36.8542
9	290.0	5.0	65.0	60.4593	32988	3.6301	70.1900	35.6293	90.3671	-11.1983	36.9255

Material Safety Data Sheet (MSDS): Formaldehyde

Section 1: Product Identification

Product name:	FORMALDEHYDE
Chemical formula:	N/A
Synonyms:	Methylene oxide, AC-4553, AC-4554, 41860, 41883
Supplier:	Chemicals LTD 123 Anywhere St. Ottawa, ON K5R 8N9
Material uses:	For laboratory use only.

Section 2: Hazardous Ingredients

Name	**CAS #**	**%**	**TLV**
1. Formaldehyde	50-00-0	30 – 40	Exposure limits: 0.3 ppm (0.37mg/m3)
2. Methanol	67-56-1	5 – 15	Exposure limits: 200 ppm (262mg/m3)
3. Water	7732-18-5	Balance	N/A

Section 3: Physical Data

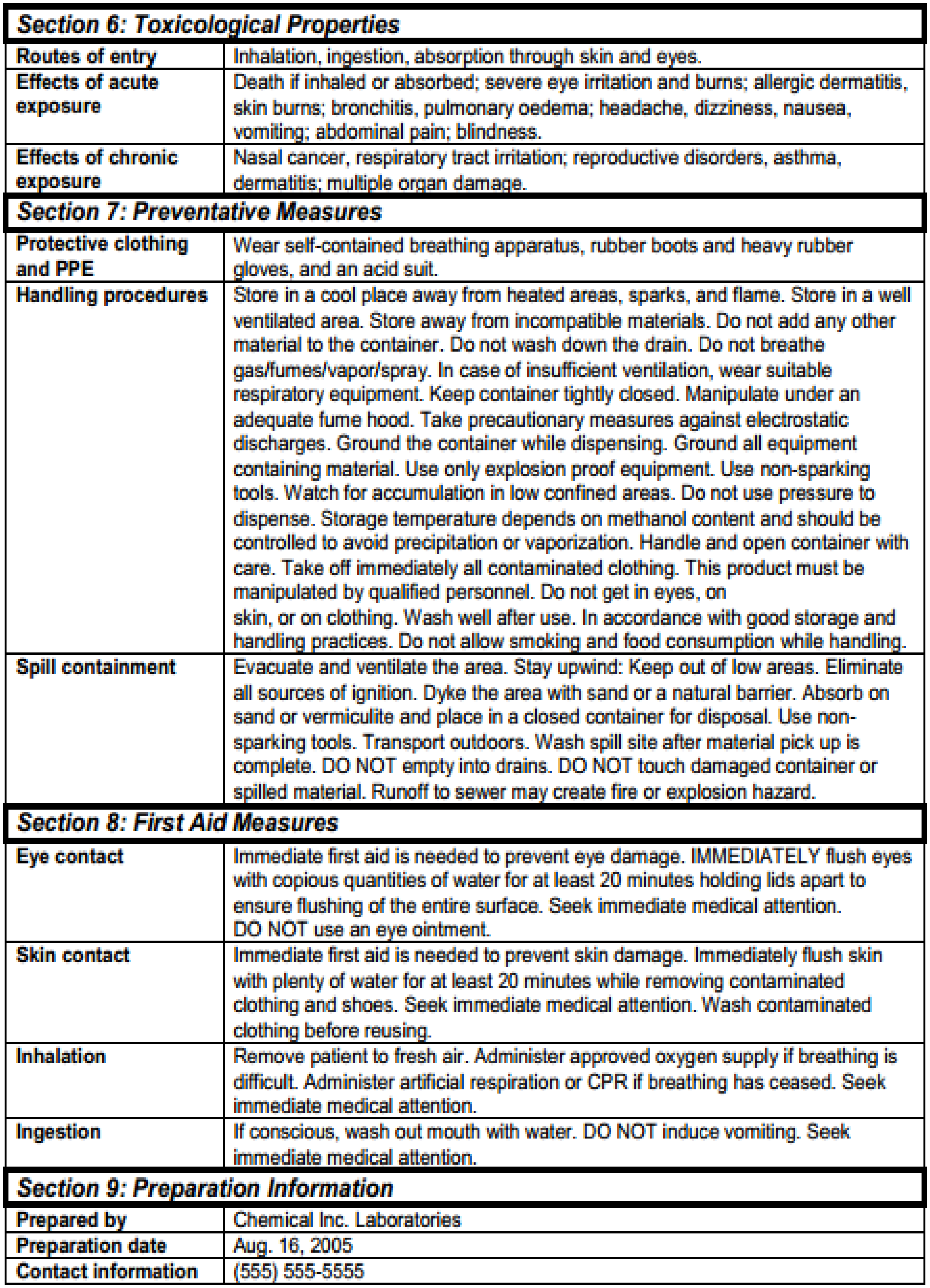
Physical state	Clear, colourless liquid with strong formaldehyde odour.
pH	2.8 – 4.0 (25 degrees Celsius) (37% solution)
Odour threshold	0.8 – 1ppm
Percent volatile	100%(V/V)
Freezing point	Insoluble polymer gradually forms.
Boiling point	90 - 100
Specific gravity	1.08 to 1.0975 (Water = 1)
Vapour pressure	~40 mm of Hg (@ 39°C)
Vapour density	0.62 to 1.04 (Air = 1)
Evaporation rate	2.1(n-Butyl acetate = 1) (Methanol).
Solubility	Miscible in water.

Section 4: Fire and Explosion Data

Flash point	50 – 78 degrees Celsius
Flammability	Lower: 7%; Upper: 73%
Fire extinguishing procedures	Use DRY chemical, carbon dioxide, alcohol-resistant foam or water spray. Cool containing vessels with flooding quantities of water until well after fire is out.

Section 5: Reactivity Data

Stability	Stable. Conditions to avoid: heat, sparks and flame, temperatures below 20°C.
Incompatibility	May react violently with: acids, alkalis, anhydrides, isocyanates, urea, phenol, oxidizing agents, oxides, organic oxides, reducing agents, ammonia, aniline, magnesium carbonate, performic acid, alkali metals, amines, hydrogen peroxide, nitromethane, nitrogen dioxide, perchloric acid, perchloric acid-aniline mixtures, bases, monomers, water reactive materials, magnesium carbonate hydroxide.



Section 6: Toxicological Properties

Routes of entry	Inhalation, ingestion, absorption through skin and eyes.
Effects of acute exposure	Death if inhaled or absorbed; severe eye irritation and burns; allergic dermatitis, skin burns; bronchitis, pulmonary oedema; headache, dizziness, nausea, vomiting; abdominal pain; blindness.
Effects of chronic exposure	Nasal cancer, respiratory tract irritation; reproductive disorders, asthma, dermatitis; multiple organ damage.

Section 7: Preventative Measures

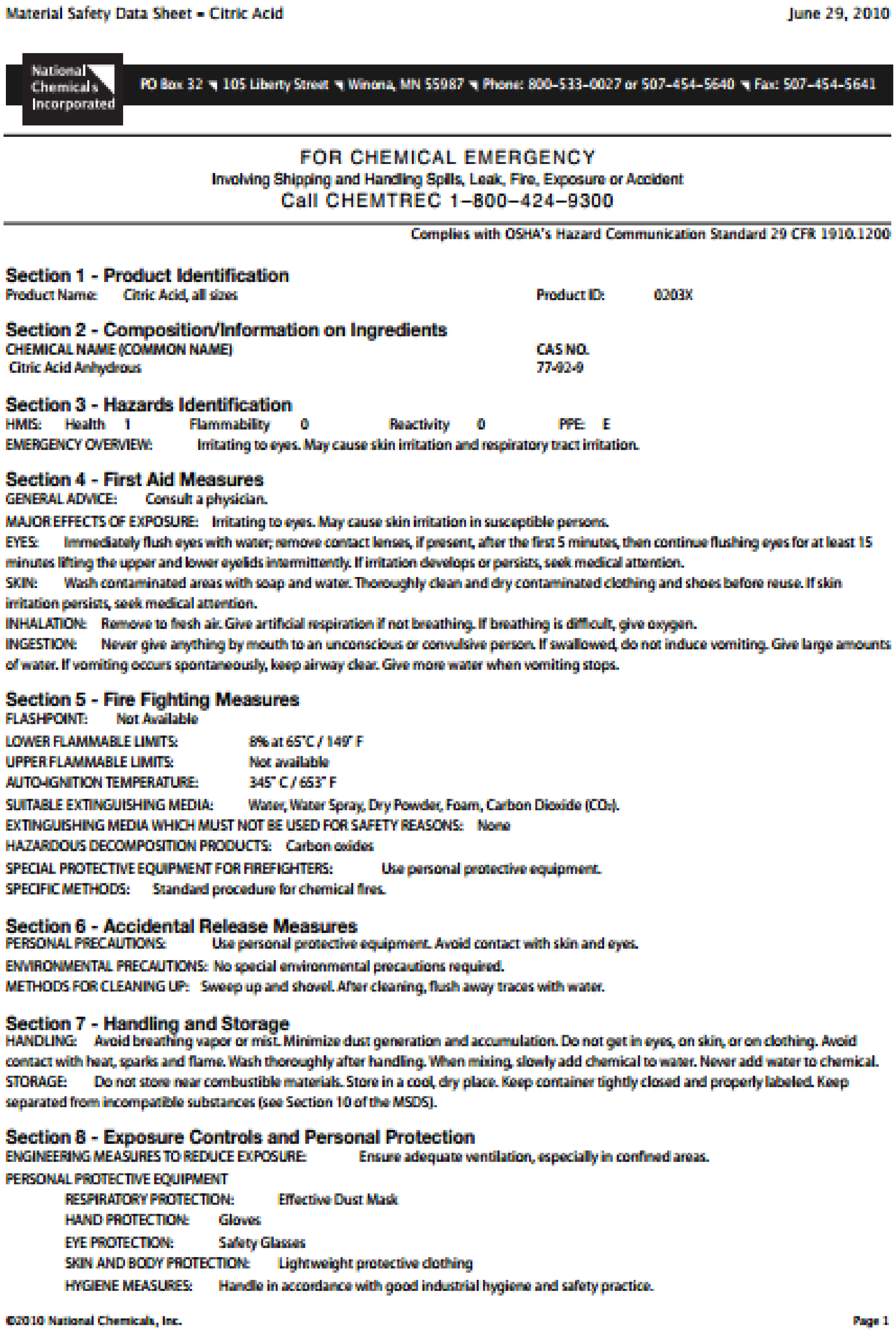
Protective clothing and PPE	Wear self-contained breathing apparatus, rubber boots and heavy rubber gloves, and an acid suit.
Handling procedures	Store in a cool place away from heated areas, sparks, and flame. Store in a well ventilated area. Store away from incompatible materials. Do not add any other material to the container. Do not wash down the drain. Do not breathe gas/fumes/vapor/spray. In case of insufficient ventilation, wear suitable respiratory equipment. Keep container tightly closed. Manipulate under an adequate fume hood. Take precautionary measures against electrostatic discharges. Ground the container while dispensing. Ground all equipment containing material. Use only explosion proof equipment. Use non-sparking tools. Watch for accumulation in low confined areas. Do not use pressure to dispense. Storage temperature depends on methanol content and should be controlled to avoid precipitation or vaporization. Handle and open container with care. Take off immediately all contaminated clothing. This product must be manipulated by qualified personnel. Do not get in eyes, on skin, or on clothing. Wash well after use. In accordance with good storage and handling practices. Do not allow smoking and food consumption while handling.
Spill containment	Evacuate and ventilate the area. Stay upwind: Keep out of low areas. Eliminate all sources of ignition. Dyke the area with sand or a natural barrier. Absorb on sand or vermiculite and place in a closed container for disposal. Use non-sparking tools. Transport outdoors. Wash spill site after material pick up is complete. DO NOT empty into drains. DO NOT touch damaged container or spilled material. Runoff to sewer may create fire or explosion hazard.

Section 8: First Aid Measures

Eye contact	Immediate first aid is needed to prevent eye damage. IMMEDIATELY flush eyes with copious quantities of water for at least 20 minutes holding lids apart to ensure flushing of the entire surface. Seek immediate medical attention. DO NOT use an eye ointment.
Skin contact	Immediate first aid is needed to prevent skin damage. Immediately flush skin with plenty of water for at least 20 minutes while removing contaminated clothing and shoes. Seek immediate medical attention. Wash contaminated clothing before reusing.
Inhalation	Remove patient to fresh air. Administer approved oxygen supply if breathing is difficult. Administer artificial respiration or CPR if breathing has ceased. Seek immediate medical attention.
Ingestion	If conscious, wash out mouth with water. DO NOT induce vomiting. Seek immediate medical attention.

Section 9: Preparation Information

Prepared by	Chemical Inc. Laboratories
Preparation date	Aug. 16, 2005
Contact information	(555) 555-5555



National Chemicals Incorporated
PO Box 32 ◥ 105 Liberty Street ◥ Winona, MN 55987 ◥ Phone: 800-533-0027 or 507-454-5640 ◥ Fax: 507-454-5641

FOR CHEMICAL EMERGENCY
Involving Shipping and Handling Spills, Leak, Fire, Exposure or Accident
Call CHEMTREC 1-800-424-9300

Complies with OSHA's Hazard Communication Standard 29 CFR 1910.1200

Section 1 - Product Identification

Product Name: Citric Acid, all sizes
Product ID: 0203X

Section 2 - Composition/Information on Ingredients

CHEMICAL NAME (COMMON NAME)	CAS NO.
Citric Acid Anhydrous	77-92-9

Section 3 - Hazards Identification

HMIS: Health 1 Flammability 0 Reactivity 0 PPE: E

EMERGENCY OVERVIEW: Irritating to eyes. May cause skin irritation and respiratory tract irritation.

Section 4 - First Aid Measures

GENERAL ADVICE: Consult a physician.

MAJOR EFFECTS OF EXPOSURE: Irritating to eyes. May cause skin irritation in susceptible persons.

EYES: Immediately flush eyes with water; remove contact lenses, if present, after the first 5 minutes, then continue flushing eyes for at least 15 minutes lifting the upper and lower eyelids intermittently. If irritation develops or persists, seek medical attention.

SKIN: Wash contaminated areas with soap and water. Thoroughly clean and dry contaminated clothing and shoes before reuse. If skin irritation persists, seek medical attention.

INHALATION: Remove to fresh air. Give artificial respiration if not breathing. If breathing is difficult, give oxygen.

INGESTION: Never give anything by mouth to an unconscious or convulsive person. If swallowed, do not induce vomiting. Give large amounts of water. If vomiting occurs spontaneously, keep airway clear. Give more water when vomiting stops.

Section 5 - Fire Fighting Measures

FLASHPOINT: Not Available
LOWER FLAMMABLE LIMITS: 8% at 65°C / 149° F
UPPER FLAMMABLE LIMITS: Not available
AUTO-IGNITION TEMPERATURE: 345° C / 653° F
SUITABLE EXTINGUISHING MEDIA: Water, Water Spray, Dry Powder, Foam, Carbon Dioxide (CO_2).
EXTINGUISHING MEDIA WHICH MUST NOT BE USED FOR SAFETY REASONS: None
HAZARDOUS DECOMPOSITION PRODUCTS: Carbon oxides
SPECIAL PROTECTIVE EQUIPMENT FOR FIREFIGHTERS: Use personal protective equipment.
SPECIFIC METHODS: Standard procedure for chemical fires.

Section 6 - Accidental Release Measures

PERSONAL PRECAUTIONS: Use personal protective equipment. Avoid contact with skin and eyes.
ENVIRONMENTAL PRECAUTIONS: No special environmental precautions required.
METHODS FOR CLEANING UP: Sweep up and shovel. After cleaning, flush away traces with water.

Section 7 - Handling and Storage

HANDLING: Avoid breathing vapor or mist. Minimize dust generation and accumulation. Do not get in eyes, on skin, or on clothing. Avoid contact with heat, sparks and flame. Wash thoroughly after handling. When mixing, slowly add chemical to water. Never add water to chemical.

STORAGE: Do not store near combustible materials. Store in a cool, dry place. Keep container tightly closed and properly labeled. Keep separated from incompatible substances (see Section 10 of the MSDS).

Section 8 - Exposure Controls and Personal Protection

ENGINEERING MEASURES TO REDUCE EXPOSURE: Ensure adequate ventilation, especially in confined areas.

PERSONAL PROTECTIVE EQUIPMENT
  RESPIRATORY PROTECTION: Effective Dust Mask
  HAND PROTECTION: Gloves
  EYE PROTECTION: Safety Glasses
  SKIN AND BODY PROTECTION: Lightweight protective clothing
  HYGIENE MEASURES: Handle in accordance with good industrial hygiene and safety practice.

Section 9 - Physical and Chemical Properties

FORM:	white powder/crystalline	ODOR:	odorless
pH SOLUTION (5%):	1.80 (25°C/77° F)	WATER SOLUBILITY:	61.8 % (w/w)
VAPOR PRESSURE:	Practically zero at room temperatures	VAPOR DENSITY:	No data available
MELTING POINT:	153°C/ 307° F	BOILING POINT:	No data available
DECOMPOSITION TEMPERATURE:	> 170°C / > 338° F	RELATIVE DENSITY:	1.665 g/cm3
AUTO-IGNITION TEMPERATURE:	345°C/ 653° F		

Section 10 - Stability and Reactivity

STABILITY: Stable

CONDITIONS TO AVOID: Avoid dust formation. Take precautionary measures against static discharges.

MATERIALS TO AVOID: Incompatible with strong bases and oxidizing agents.

HAZARDOUS DECOMPOSITION: No decomposition if stored normally. Thermal decomposition can lead to release of irritating gases and vapors.

CORROSION: May corrode metals. 316 Stainless steel recommended material for handling.

Section 11 - Toxicological Information

ACUTE TOXICITY: LD50/p.o./rat = 11.700 mg/kg (1) LD50/i.p./rat = 883 mg/kg (2) LD50/p.o./mouse = 5.040 mg/kg (1)
LD50/i.v./mouse = 42 mg/kg (17) LD50/i.p./mouse = 961 mg/kg (2)

LOCAL EFFECTS: Irritating to eyes. May cause skin irritation and respiratory tract irritation.

CHRONIC TOXICITY: None.

CARCINOGENIC: This product does not contain any substances that are considered by ACGIH, OSHA or NTP to be human carcinogens.

REPRODUCTIVE TOXICITY: No data available

TERATOGENICITY: No data available

MUTAGENIC CHARACTERISTIC: negative

Section 12 - Ecological Information

MOBILITY: Completely Soluble

PERSISTENCE / DEGRADABILITY CHEMICAL OXYGEN DEMAND (COD): 750 (50 mg 02 /g)

BIOCHEMICAL OXYGEN DEMAND WITHIN 5 DAYS (BOD5): 625 (50 mg 02 /g)

DIN 38412 PART 25 (DIN EN ISO 9888): Readily biodegradable (98 % after 2 days)*

ECOLOGICAL TOXICITY: DIN 38412 Part 15 (DIN EN ISO 7346) TOXICITY TO FISH: 440 - 706 mg/L
DIN 38412 Part 5 TOXICITY TO BACTERIA: >10.000 mg/L

BIOACCUMULATION: None

Section 13 - Disposal Considerations

WASTE FROM RESIDUES/UNUSED PRODUCTS: Where possible recycling is preferred to disposal or incineration. Can be disposed in landfill or incinerated, when in compliance with local regulations.

CONTAMINATED PACKAGING: Empty containers should be taken for local recycling, recovery or waste disposal.

Section 14 - Transport Information

Not classified as dangerous according to TDG (Transportation of Dangerous Goods) and DOT (Department of Transportation).

Section 15 - Regulations

WHMIS - Class E

IDL: Citric Acid (CAS-No. 77-92-9) is listed in the Ingredient Disclosure List

DSL: Citric Acid (CAS-No. 77-92-9) is listed in Domestic Substance List

TSCA: Citric Acid (CAS-No. 77-92-9) is listed on the TSCA Inventory

TSCA 8(D): Citric Acid (CAS-No.77-92-9) exempted from regulations.

ACCORDING TO EUROPEAN COMMUNITY DIRECTIVE 67/548/EEC, AS AMENDED, THE PRODUCT SHALL BE LABELED:

SYMBOL(S): Xi - Irritant RISK -PHRASE(S): R36 - Irritating to eyes.
SAFETY -PHRASE(S): S26 - In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

Section 16 - Other Information

SUPERSEDES DATE: July 21, 2008

The information and recommendations in this Material Safety Data Sheet are based upon data believed to be correct and does not relate to its use in combination with any other material or process. Since use conditions vary, we assume no liability for failure to follow product use direction and safety precautions. As data, standards and regulations change; NO WARRANTY, EXPRESS OR IMPLIED, IS MADE AS TO THE COMPLETENESS OR CONTINUING ACCURACY OF THIS INFORMATION.