PYROLYSIS
OF WASTE PLASTIC FISH BAGS TO USEABLE FUEL OIL

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MEMORIAL UNIVERSITY
MAY 2018

2016-17 HARRIS CENTRE - MMSB WASTE
MANAGEMENT APPLIED RESEARCH FUND

THE HARRIS CENTRE
Memorial University

Pyrolysis of waste plastic fish bags (polyethylene and polypropylene) to useable fuel oil

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Acknowledgements: The authors wish to thank the MMSB Harris Centre fund, Newfoundland Aquaculture Industries Association, and Abritech for their financial and technical support for this project.

Executive Summary

The objective of this study is to determine the feasibility of pyrolysis of waste plastic fish feed bags to heating oil. Pyrolysis is a thermal treatment without oxygen and produces three products (gas, oil, and solid), the yields depend on the feedstock and operating conditions. The fish feed bags are polyethylene (PE) or polypropylene (PP) and are typically contaminated with a small amount of residual fish feed. This limits the treatment and disposal options. Thermal decomposition of the bags to their original oil base could potentially produce a fuel for use in heating and possibly power for the plant. Unused and used bags were pyrolyzed and compared to determine the impact of the fish feed on the oil and the residual solids and gas evolved during the process. The temperature for the pyrolysis temperature is a function of the feed material. For waste plastic the temperature can range between 400−550 °C depending on the type of plastic. In this work a series of pyrolysis experiments were performed where key factors that would impact the oil quality produced, were varied including; temperature of pyrolysis (400−550 °C) type of bag (PE, PP, and mixtures of the two), mass of residual fish feed retained in bag (0-40% by mass of feedstock) and gas residence time. Based on these experiments the optimum operating conditions were obtained. A temperature of 500°C produced the maximum wax/oil yields, 69-75wt% of feedstock with a solids (residue) between 6-7 wt%, and gas between 23-25 wt%, depending on the feedstock. The melting point of wax/oil samples varied between 53-62°C. The melting point of the wax/oil samples decreased slightly with increasing amounts of fish feed. The increase in wax/oil yield is likely a result that the FF pyrolysis products are predominantly lipids, this would both add to the overall oil content and possibly decrease the uncondensable gas content through co-pyrolysis. The heating values of the wax/oil samples varied from 42.8- 45.7 MJ/kg, The pure fish feed heating value was 25.47 MJ/kg,. The heating values of all waxes are comparable to standard fuels, 44-46 MJ/kg petrol/gasoline, 43 MJ/kg for diesel, and from 43-44 MJ/kg for fuel oil. Although, the wax/oil samples are solid (wax) at temperatures below 50^{o}C, heating to above 60^{o}C produces a liquid oil with a high heating value. The gas produced in

the pyrolysis, largely methane and ethane, could be used as a fuel gas. Based on 100 metric tonnes of waste bags per year this translates to 2.8 MJ/yr from the oil and 1.38 MJ/yr from the gas.

Contents

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1. Introduction

Plastics are polymers consisting of long chains of monomers or smaller component units and are produced chemically from petroleum. Plastics can be grouped into five major classes; polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), and polyethylene terephthalate (PET) [1]. The increased demand and production of plastics has led to the accumulation of large amounts of waste materials due to their slow/limited chemical and/or biodegradation [2]. The growth of the use of plastics for more than 50 years has resulted in the global production of plastics of approximately 135 million tonnes in 2013 and increases at an annual growth rate of approximately 4% [3]. Recycling of plastic waste accounts for on 10% of waste plastic. Landfill disposal is problematic due to possible contamination of the plastics and decreasing landfill availability. Other options for waste plastic management include incineration, however, incineration is problematic due to toxic emissions. Further, recycling, landfills, incineration etc. represent costs with respect disposal not only with respect to transport and handling but also in the energy that could be recovered from the plastic [3].

Pyrolysis (thermally treating without oxygen) uses high temperatures, produces a liquid and gaseous fuel, and does not require additional chemicals. The pyrolysis process of waste plastics can be potentially used to convert plastic-to-fuel (PTF) for the sustainable management of plastic waste along with the production of liquid oil as a source of energy and gases as value-added products [5-9]. Pyrolysis including thermal and catalytic processes involves heating the material to moderate temperatures (300–900 °C) in the absence of oxygen; however, typical pyrolysis temperatures for plastic waste are approximately 450–550 °C [10]. The organic components of the material thermally decompose, generating liquid (oil), wax and gaseous products, which can be useful as fuels and/or sources of useful feedstock chemicals. In the absence of catalyst with thermal pyrolysis, plastics convert into waxes instead of liquids. The yield of the oils can be improved by using a catalyst during pyrolytic conversion.

Several processes have been used in both thermal and catalytic pyrolysis of waste plastics, such as the use of a tube furnace [11], a batch reactor [12-14], fixed beds [15-17], fluidized bed [18-20] and/or spouted bed [21-24]. Pyrolysis in a fluidized bed reactor is the more widely studied technology on a laboratory and pilot plant scale. The plastic pyrolysis in fluidized bed reactors were carried out normally at a temperature as low as 290–850 °C for both thermal and catalytic processes.

Park et al. [11] investigated the product yields of liquid, solid and gas obtained from pyrolysis experiments on refuse plastic fuel (RPF) using a tube furnace at 400 °C, 600 °C, and 800 °C in a nitrogen atmosphere. They reported that the product yields of solids, liquids and gases from the pyrolysis of RPF at 400 °C were 50% liquids, 15% solids and 35% gases; at 600 °C 53% liquids, 10% solids and 37% gases and at 800 °C, 41% liquids, 6% solids and 53% gases. Sakata et al. [12] investigated the thermal and catalytic pyrolysis to fuel oil by batch operation of plastic polymers polyethylene (PE) at 430°C and polypropylene (PP) at 380°C. The yields of liquid oils obtained from catalytic pyrolysis were lower compared to the thermal pyrolysis for some catalysts. The liquid yields from HDPE was 69 wt% and from

PP was 80 wt% using thermal pyrolysis. With the catalysts, such as silica–alumina (SA-1) and zeolite ZSM-5, the liquid yields for both HDPE and reduced to 49–67 wt% and 47–78 wt%, respectively.

Luo et al. [20] compared the yields obtained from HDPE and PP using silica–alumina catalytic degradation with a fluidized bed reactor. The authors reported that the liquid produced by PP was 87 wt% while HDPE produced slightly lower 85 wt% liquid compositions at 500 °C.

Several studies reported that waxes are the main products obtained in the thermal pyrolysis of polyolefins at moderate temperatures [24-25]. Waxes consist of linear and branched saturated and unsaturated hydrocarbons, depending on the type of plastics and thermal cracking conditions. Arabiourrutia et al. [24] reported a maximum wax yield of 80 wt% in the pyrolysis at 450 °C, of PE and 90 wt% in the pyrolysis of PP in a spouted bed reactor. The yield of waxes decreased with increased temperatures: 51% at 600 °C for PE and 50% at 600 °C for PP. At higher temperatures, more of the waxes are cracked into liquid or gaseous products. Predel et al. [25] reported that a maximum wax yield for pyrolysis of PE was 84 wt% at 510 °C of PE and 6 wt% for PP in a fluidized bed reactor. The yield of waxes is enhanced when the pyrolysis is carried out under mild conditions. As waxes are the primary products obtained by the thermal pyrolysis of polyolefins by polymer chain scission, the optimum conditions for their selective production are moderate temperatures (~500 °C) and short residence times in the reactor. These conditions minimize the cracking of waxes to secondary products, such as gases and light hydrocarbons.

Approximately 45 metric tonnes of polyethylene and 50 metric tonnes of polypropylene bags will be generated as waste in aquaculture operations in NL in 2016. There have been no studies on the pyrolysis of waste plastic fish bags, specifically when the bags are contaminated with fish feed (lipids, moisture, feed particles). These contaminants may have limited or no impact on the pyrolysis of the bags to of oils or waxes, or may enhance the wax/oil fuel quality and increase solid product formation. In this study we investigated the pyrolysis of fresh plastics (polyethylene and polypropylene) with fish feed for the production yields of oils and waxes and resulting fuel quality. The pyrolysis experiments were conducted at 450-550°C in a lab-scale tube furnace reactor.

2. Experimental Section

2.1 Samples

The fish feed and the plastic fish bags (polyethylene and polypropylene) was received from Newfoundland Aquaculture Industry Association (NAIA).

2.2. Pyrolysis condition and analysis and pyrolysis products

Pyrolysis experiments were conducted to understand the thermal degradation of polyethylene (PE), polypropylene (PP) and their combined co-cracking using different ratios of PE and/or PP with fish feed, at 450-550 °C temperatures under nitrogen (flow rate between 50 to 200 mL/min) with a lab-scale tube furnace (Figure 1). DOE (Design-Expert 9.0.0) was used for the optimization of the number of pyrolysis experiments. Thermal gravimetric analysis (TGA) was used to measure the weight change of the feedstock as a function of temperature and time. The wax/oil samples were characterized for composition, heating values (HV) and melting points. As the lab reactor processes less than 5 grams of sample there was not enough wax/oil to test for viscosity. Differential scanning calorimetry (DSC) was used to determine the melting points of the pyrolysis products (wax/oil). The chemical composition of the wax/oil products were characterized by GC-MS. An oxygen bomb calorimeter (Model 1314 Plain Jacket Bomb Calorimeter, Parr Instrument Company, Moline, Illinois, USA) was used to determine the heating values of the wax products.

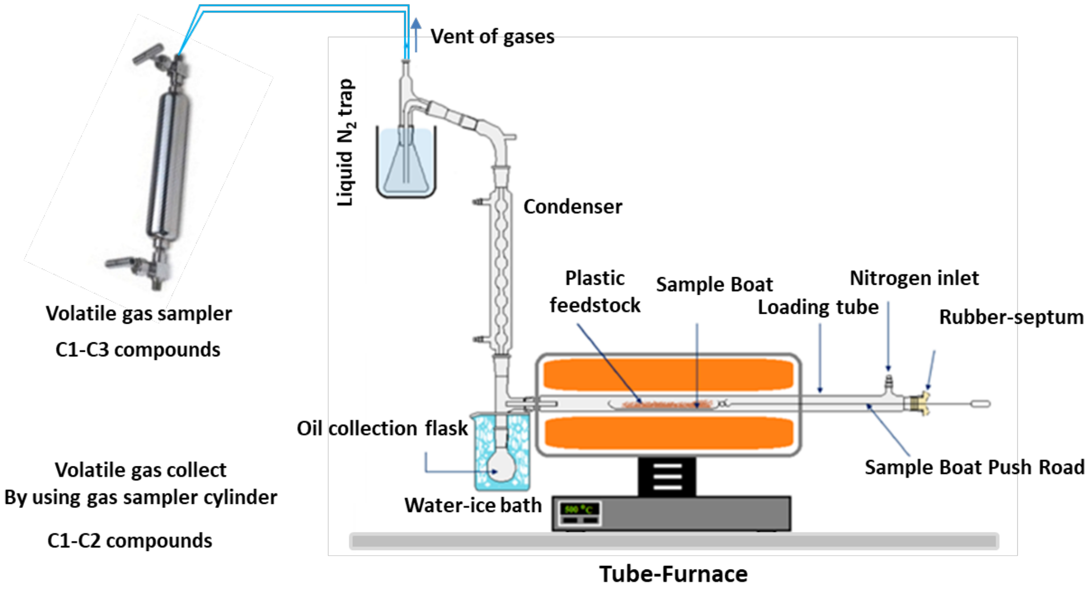


Figure 1. Schematic diagram of pyrolysis of plastic fish bags.

3. Results and discussion

3.1. Chemical properties of Plastics:

Thermogravimetric analysis (TGA) is as a technique to measure the chemical properties of the plastic compound based on four factors, moisture content, fixed carbon, volatile matter and ash content. Volatile matter and ash content are the major factors that influence the liquid oil yields from the pyrolysis process. High volatility indicates high liquid oil production while high ash content indicates increased gaseous yield and solid reside formation. Approximately 20–25 mg of each plastic (PE or PP) sample was weighed into a platinum pan and subjected to thermogravimetric analysis (TGA, model Q500, TA Instruments). Samples were heated in a nitrogen atmosphere (50 mL/min) from room temperature to 550°C at a rate of 20°C/min. The flow gas was then switched to air (50 mL/min) and the temperature held at 550°C for 5 min to combust the sample to ash. A representative TGA result showing weight change data for PE or PP plotted against temperature is shown in Figure 2. The ash content was calculated as the mass percent remaining after heating in air at 550°C. Moisture was calculated as the TGA mass percent lost between ambient temperature and 150 °C. Volatile matter was calculated as the TGA mass percent lost between 150°C and 500°C. Fixed carbon was calculated using the equation: 100% - % volatile carbon - % ash - % moisture.

Table 1 summarizes the proximate analysis of three different samples.

Table 1. Thermogravimetric analysis (TGA) of plastics.

Plastics	Moisture (%)	Volatiles (%)	Fixed Carbon (%)	Ash (%)
Polyethylene (PE, 100%)	0.1	85.7	10.3	3.9
Polypropylene (PP, 100%)	0.1	93.9	2.3	3.7
PE:PP (50:50)	0.1	86.9	9.5	3.5

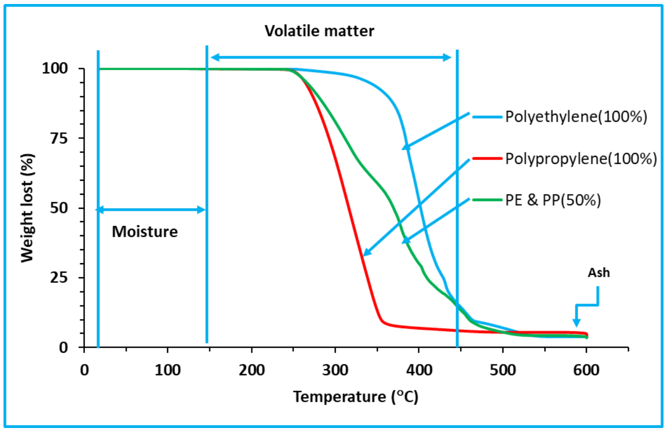


Figure 2. TGA curve of polyethylene(PE), polypropylene(PP) and PE/PP(50%).

The volatile matter for all plastics is very high while the ash content is low. These characteristics indicate that waste fish bag plastics (PE and PP) have high potential to produce large amounts of waxes/oils using a pyrolysis process.

3.2. Pyrolysis of fresh polyethylene (PE), polypropylene(PP), and PE, PP with ratios of fish feed (FF)

Pyrolysis experiments were conducted using three different temperatures: 450 °C, 500 °C and 550 °C, under N_2 (flow rate between 50 to 200 mL/min) with a lab-scale tube furnace. Unused PE and PP bag samples were tested with and without residual FF. Approximately 1.0 g of each plastic sample was loaded in a sample boat and pyrolysis. The pyrolysis results are summarized in Table 2-4.

Table 2: DOE results for pyrolysis of polyethylene(PE) and polypropylene(PP):

Run #	Plastics (%)	Temp. (°C)	Nitrogen flow (mL/min)	Yields (%)		
				Wax/oil	Residue	Gas*
1	PE (100)	450	50	68.5	20.9	10.7
2	PE (100)	450	200	67.2	20.1	12.7
3	**PE (100)**	**500**	**50**	**72.4**	**7.1**	**20.5**
4	PE (100)	500	125	71.6	6.8	21.6
5	PE (100)	550	50	66.3	6.7	27.0
6	PE (100)	550	200	65.6	6.4	28.1
7	PE/PP (50/50)	450	50	66.9	15.1	18.1
8	PE/PP (50/50)	450	200	67.7	20.2	11.3
9	**PE/PP (50/50)**	**500**	**50**	**69.1**	**6.0**	**25.0**
10	PE/PP (50/50)	500	125	68.4	5.6	26.0
11	PE/PP (50/50)	550	50	59.9	5.9	34.2
12	PE/PP (50/50)	550	200	58.8	5.7	35.8
13	PE/PP (75/25)	500	125	68.7	6.3	25.1
14	PE/PP (75/25)	450	125	68.1	20.1	11.8
15	**PE/PP (75/25)**	**500**	**50**	**70.4**	**6.8**	**22.8**
16	PE/PP (75/25)	500	125	69.9	6.7	23.3
17	PE/PP (75/25)	550	125	63.1	4.3	31.6

Note:

- *Amount of gas was calculated by 100% - % wax/oil - % residue.
- Residence time 10 minutes for sample boat stay inside the furnace.

Three variables, including temperature (450−550 °C), ratios of fresh polyethylene or polypropylene (25-100%), and N_2 gas flow rate (50−200 mL/min) were varied to investigate the wax/oil product yields produced from the pyrolysis. In this study, three center-point replicate experiments were performed, for a total of 17 experiments. The plastics (free of FF) pyrolysis results are summarized in Table 2 and the residues are shown in Figure 3.

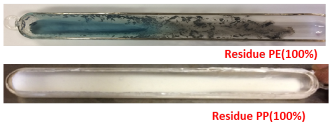


Figure 3. Solid residues after pyrolysis of polyethylene (PE) and polypropylene (PP) with fish feed (FF) at at 450 °C and 50 mL/min N_2 flow.

Based on these experiments, the results in Table 2 show that the optimum condition found for the pyrolysis temperature was 500 °C and N_2 flow rate 50 mL/min. The maximum wax/oil yields, 69-72% (wt), solids (residue) between 6-7 wt%, and gas between 23-25 wt%, depending on the feedstock at 500°C. Based on these results a series of pyrolysis PE and PP with residual FF (0-20% by mass of plastic) experiments were performed at 500°C, N_2 flow rate (50 mL/min) to determine the impact the oil quality. The results are summarized in Tables 3-4 and the residues are shown in Figures 4-5.

Table 3. Pyrolysis conditions and results for polyethylene (PE) with fish feed (FF).

Run #	PE with FF (%)	Temperature (°C)	Nitrogen flow (mL/min)	Yields (%)		
				Wax/oil	Residue	Gas*
1	PE (100)	500	50	72.4	5.5	22.2
2	PE/FF (95/5)	500	50	72.7	6.0	21.3
3	PE/FF (90/10)	500	50	73.2	6.6	20.2
4	PE/FF (85/15)	500	50	73.8	7.5	18.7
5	PE/FF (80/20)	500	50	74.1	8.2	17.6
6	PE/FF (70/30)	500	50	75.0	9.6	15.5
7	PE/FF (60/40)	500	50	75.4	11.8	12.9
8	FF (100)	500	50	63.5	26.0	10.5

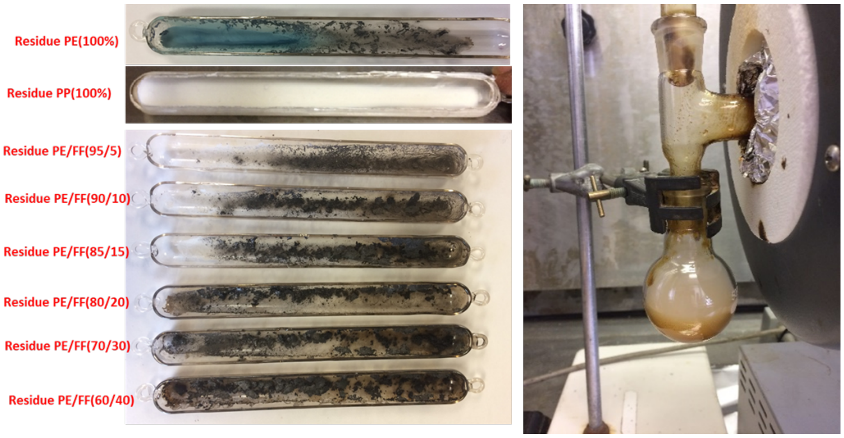


Figure 4. *Left:* Residues and *right* the product (wax/oil) after pyrolysis of polyethylene (PE) with fish feed (FF) at at 500 °C and 50 mL/min N_2 flow.in the furnace tube apparatus.

Table 4. Pyrolysis conditions and results for polypropylene (PP) with fish feed (FF):

Run #	PP with FF (%)	Temperature (°C)	Nitrogen flow (mL/min)	Yields (%)		
				Wax/oil	Residue	Gas*
1	PP (100)	500	50	63.9	4.6	31.5
2	PP/FF (95/5)	500	50	64.6	5.3	30.1
3	PP/FF (90/10)	500	50	66.1	6.9	27.0
4	PP/FF (85/15)	500	50	67.1	7.4	25.5
5	PP/FF (80/20)	500	50	68.2	8.1	23.7
6	PP/FF (70/30)	500	50	69.1	9.6	21.4
7	PP/FF (60/40)	500	50	70.1	12.0	17.9

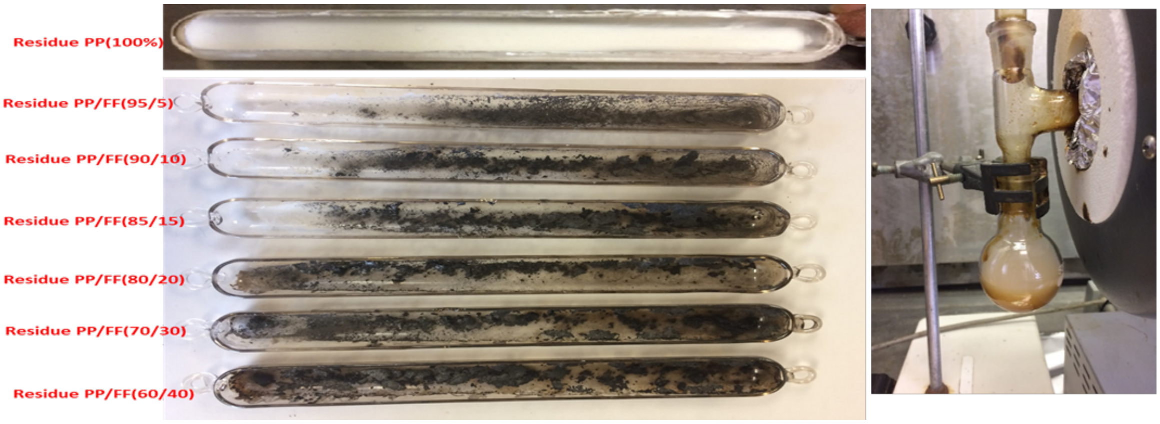


Figure 5. *Left:* Residues and *right* the product (wax/oil) after pyrolysis of polypropylene (PP) with fish feed (FF) at at 500 °C and 50 mL/min N_2 flow in the furnace tube apparatus.

The oil/wax and residue yields increased linearly with the increasing FF, while the gas decreased linearly. The increase in oil/wax is small (4% for PP and 8% for PE) relative to the increase in residual (over double the value for both PE and PP). This is reflected in the higher overall residual solid when pure FF is pyrolyzed compared to PE or PP. The decrease in gas is proportionally the same for both PE and PP with FF, increasing by approximately 45% for the highest FF (40 wt%). It should be noted, the residual FF is more likely to be below 10wt% of the bags and therefore the overall impact is minimal with respect to yields.

3.3. Chemical composition of the wax/oil was analysis by GC-MS.

The wax/oil products were characterized by gas chromatography with mass spectrometry (GC-MS) equipped with a vertical micro-furnace pyrolyzer [26]. Approximately 0.250 mg of sample was weighed in a pyrolysis cup which was then introduced into a quartz tube vertical micro-furnace PY-2020D (Frontier laboratories Ltd., Yoriyama, Japan) pyrolyzer coupled to a HP 5890 II gas chromatograph/HP 5971A mass-selective detector (MSD) (Hewlett Packard, Palo Alto, CA, USA) with a ChemStation Data system. The MSD was operated under the following conditions: interface temperature, 280 ºC; electron ionization energy, 70 eV; and scan range, 30–550 m/z. The GC injector and pyrolysis microfurnace temperatures were set at 270 ºC. The carrier gas was helium with a constant flow of 2 mL/min. A Zebron DB-1701 capillary column (30 m × 0.32 mm, 1.00 μm film thickness) was used. The GC oven was programmed to hold at 60 ºC for 4 min, ramp at 6 ºC/min to 260 ºC and hold for 4 min. The identification of compounds was based on the National Institute of Standards and Technology (NIST) mass spectrum library and mass spectra found in the literature. The identified compounds in the wax/oil products are summarized in Tables 5-6 and are labeled in Figure 6.

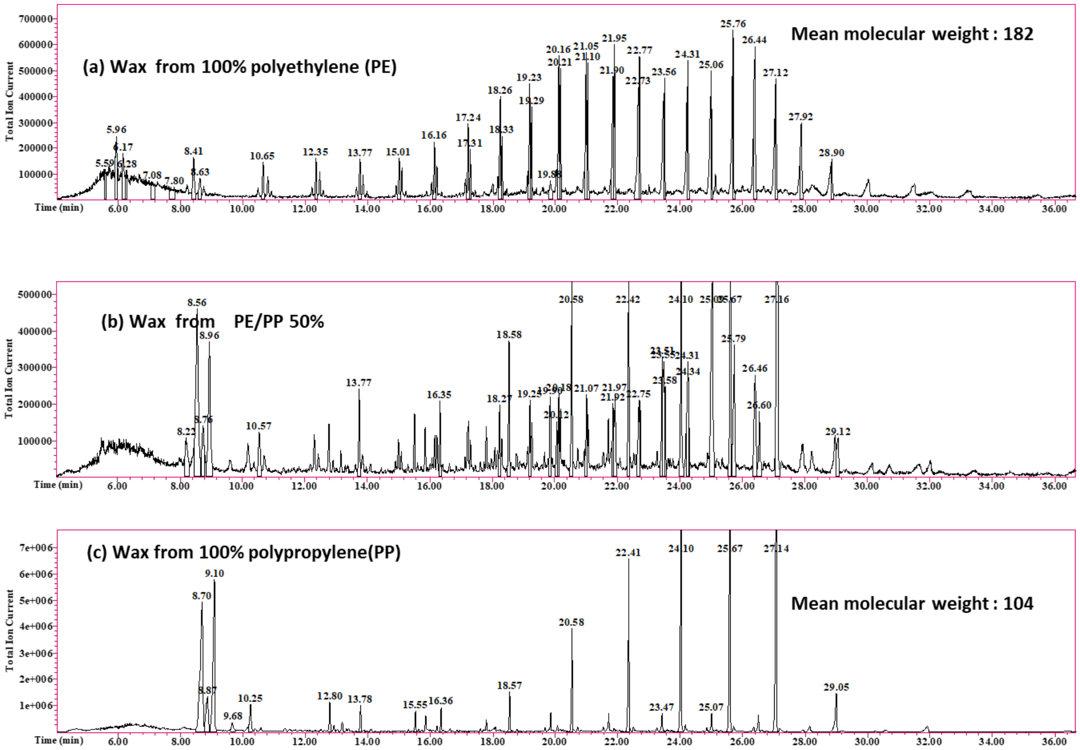


Figure 6. GC-MS chromatograms of wax/oil from pyrolysis of polyethylene (PE), polypropylene(PP) and 50 % mixture of polyethylene (PE) and polypropylene(PP).

Table 5. Identified compounds present in the PE wax/oil by GC-MS.

Peak #	Compound	Relative Area (%)	Molecular weight
1 (C4)	1-Butene (C4)	2.12	58
2 (C4)	n-Butane (C4)	1.86	56
3 (C5)	1-Pentene (C5)	1.76	72
4 (C5)	n-Petane (C5)	1.1	70
5 (C6)	1-Hexene (C6)	1.28	86
6 (C6)	n-Hexane (C6)	0.8	84
7 (C7)	1-Heptene (C7)	1.15	100
8 (C7)	n-Heptane (C7)	0.81	98
9 (C8)	1-Octene (C8)	1.1	114
10 (C8)	n-Octane (C8)	0.67	112
11 (C9)	1-Nonene (C9)	1.12	128
12 (C9)	n-Nonane (C9)	0.72	126
13 (C10)	1-Decene (C10)	1.48	142
14 (C10)	n-Decane (10)	0.82	140
15 (C11)	1-Undecene (C11)	1.95	156
16 (C11)	n-Undecane (C11)	1.03	154
17 (C12)	1-Dodecene (C12)	2.39	170
18 (C12)	n-Dodecane (C12)	1.52	160
19 (C13)	1-Tridecene (C13)	3.04	184
20 (C13)	n-Tridecane (C13)	1.96	182
21 (C14)	1-Tetradecene (C140	4.06	198
22 (C14)	n-Tetradecane (C14)	2.56	196
23 (C15)	1-Pentradecene (C15)	4.39	212
24 (C15)	n-Pentradecane (C15)	3.14	210
25 (C16)	1-Hexadecene (C16)	4.18	226
26 (C16)	n-Hexadecane (C16)	3.33	224
27 (C17)	1-Heptadecene (C17)	4.63	240
28 (C17)	n-Heptadecane (C17)	3.35	238
29 (C18)	1-Octadecene (C18)	1.29	254
30 (C18)	n-Octadecane (C18)	3.07	252
31 (C19)	1-Nonadecene (C19)	1.15	268
32 (C19)	n-Nonadecane (C19)	3.88	266
33 (C20)	1-Eicosene (C20)	2.7	282
34 (C20)	Icosane (C20)	2.72	280
35 (C21)	1-Heneicosene (C21)	3.84	296
36 (C21)	1-Heneicosane (C21)	3.39	294
37 (C22)	1-Docosene (C22)	0.42	310
38 (C22)	n-Docosane (C22)	5.53	308
39 (C23)	1-Tricosene (C23)	2.61	324
40 (C23)	n-Tricosane (C23)	3.2	322
41 (C24)	1-Tetracosene (C24)	0.68	338
42 (C24)	n-Tetracosane (C24)	2.96	336
43 (C25)	1-Pentacosene (C25)	1.36	352

44 (C25)	n-Petacosane (C25)	0.17	350
45 (C26)	1-Hexacosene (C26)	0.43	366
46 (C26)	n-Hexacosane (C26)	0.59	364
47 (C27)	1-Heptacosene (C27)	0.46	380
48 (C27)	n-Heptacosane (C27)	0.63	378
49 (C28)	1-Octacosene (C28)	0.32	294
50 (C28)	n-Octacosane (C28)	0.3	292

Table 6. Identified compounds present in the PP wax/oil by GC-MS.

Peak #	**Compound**	**Relative Area (%)**	**MW**
1	2-Methyl-1-pentene	11.011	84
2	3-Methyl-1-pentene	2.65	84
3	4-Methyl-1-pentene	7.959	84
4	2-Methyl-2-pentene	0.614	84
5	2-methylhex-1-ene	1.396	98
6	3-methylhex-1-ene	0.883	98
7	4-methylhex-1-ene	0.756	98
8	5-methylhex-1-ene	0.61	98
9	2,3-dimethylpent-1-ene	0.528	98
10	3,4-dimethylpent-1-ene	0.673	98
11	2,4-dimethylpent-1-ene	1.092	98
12	2,4-dimethylpent-2-ene	0.504	98
13	2,3-dimethylpent-2-ene	2.707	98
14	3,4-dimethylpent-2-ene	0.559	98
15	6-methylhept-1-ene	4.69	112
16	5-methylhept-1-ene	0.675	112
17	4-methylhept-1-ene	9.376	112
18	2,3-Dimethylhex-1-ene	0.705	112
19	2,2-Dimethylhex-1-ene	15.367	126
20	2,2-Dimethyl-2-heptene	0.598	126
21	2,2-Dimethyl-3-heptene	11.917	126
22	2,3-Dimethylhex-2-ene	1.867	126

The mean molecular weight 182 g/mole for wax/oil from polyethylene and 104 g/mole from polypropylene. Figure 7 outlines the identified compounds in the pure fish feed and comparisons with pure PP and 10% FF+90% PP.

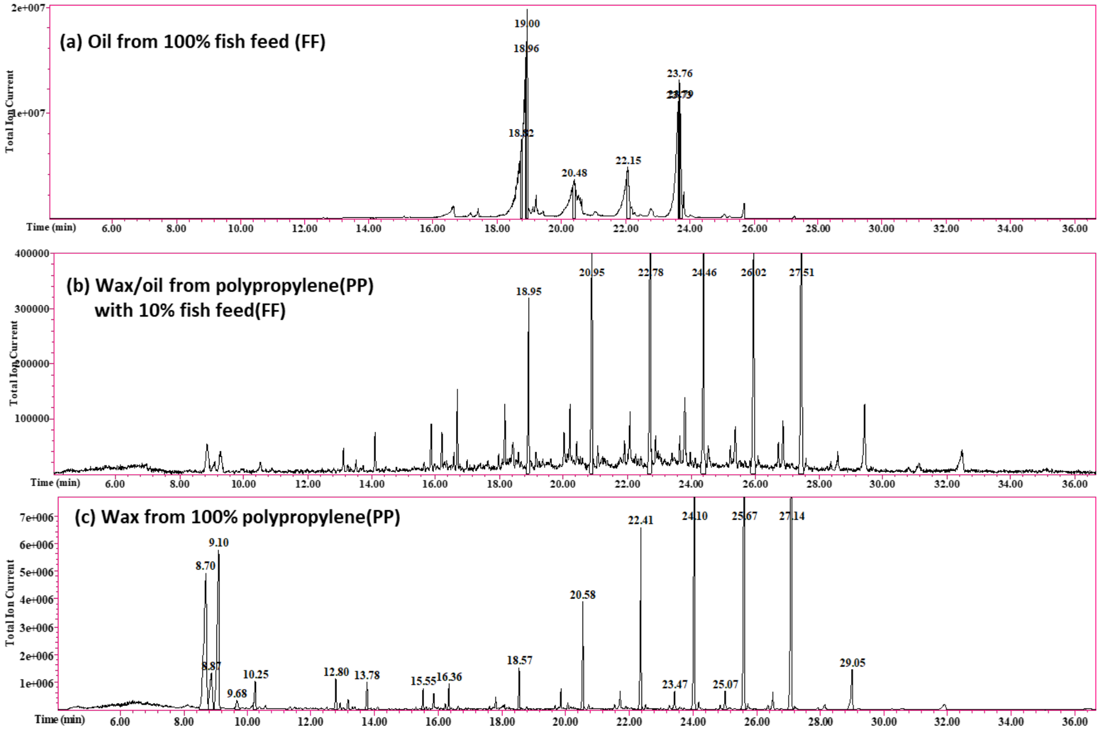


Figure 7. GC-MS chromatograms of wax/oil for (a) fish feed (pure), polypropylene (PP 90%) and fish feed (FF 10%) and (c) polypropylene (PP 100%).

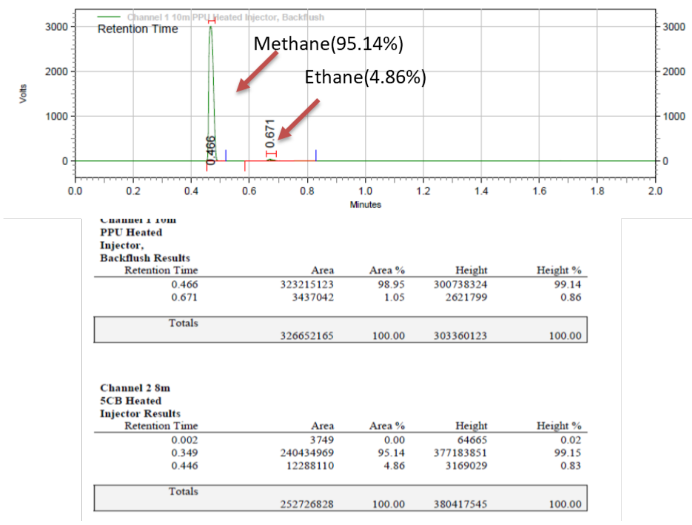
The major pyrolysis products of the fish feed are lipid based (Figure 7 a). A GC-MS analysis indicate of the identified compounds, the lipids are fatty acids (predominantly hexanoic acid and nonanoic acid at approximately 80 wt% with heptanoic and octanoic making up less than 20 wt%).

Gasoline is predominantly made up of hydrocarbons in the C5-C13 range and diesel from C5-c23 ref. If we compare our "best" yield, at 500^{o}C, In the pure PE oils the gasoline fraction is approximately 20 wt% of the identified compounds while the diesel fraction covers 88wt % of the identified compounds. It should be noted, approximately ½ or these compounds are identified as olefins (unsaturated hydrocarbons). For PP all the oil lies in the gasoline range, however in this case all the compounds identified were methylated olefins. This could have an impact on combustion. Further, the "identified" compounds are function of the analytical method, as such this composition does not represent a true compositional analysis of the wax/oil, but rather an indication of the various fractions.

3.4. Chemical composition of the volatile gas:

The volatile gas for the pyrolysis of PE was analyzed by Agilent 490 Micro GC- Natural Gas Analyzer B Version. The Agilent 490 Micro GC- Natural Gas Analyzer B is a dual cabinet micro GC equipped with two channels: Channel (1): PoraPLOT U channel with a backflush option and Channel (2): CP-Sil 5 CB channel.

The volatile gas was collected by using gas sampler cylinder as shown in Figure 1. The identified compounds in the volatile gas are labeled in Figure 8. The volatile hydrocarbon gases, mostly methane (95 wt%) and ethane (5wt%) produced along with the waxes.



Channel 1 10m PPU Heated Injector, Backflush Results

Retention Time	Area	Area %	Height	Height %
0.466	323215123	98.95	300738324	99.14
0.671	3437042	1.05	2621799	0.86
Totals	326652165	100.00	303360123	100.00

Channel 2 8m 5CB Heated Injector Results

Retention Time	Area	Area %	Height	Height %
0.002	3749	0.00	64665	0.02
0.349	240434969	95.14	377183851	99.15
0.446	12288110	4.86	3169029	0.83
Totals	252726828	100.00	380417545	100.00

Bomb Cylinder

Figure 8. Micro GC chromatogram of volatile gas from pyrolysis of polyethylene (PE).

The heating value of the gas is high (~13 GJ/kg or 9.5 GJ/m^3) and could be used as a fuel gas to run the pyrolysis process or in combined heat and power system.

3.5. Melting point of waxes/oils.

The melting points of the waxes were analyzed by Differential Scanning Calorimetry (Mettler-Toledo DSC1). The wax/oil samples were weighed precisely and transferred into a DSC aluminum smelting bowl and capped. The bowl was set into the DSC apparatus and the sealed pans were then heated (25–80 °C at 5 °C/min) under 20 mL/min purge gas and 50 mL/min shield gas (nitrogen gas) ambience. DSC curves of the waxes/oil samples from the pyrolysis of PE and PP with fish feed(FF) are shown in Figures 9 and 10. The melting points of the following wax/oil samples: PE (100%), PE/FF (90/10%), PE/FF(80/20%), PP(100%), PP/FF (90/10%) and PP/FF(80/20%) are 62.2 °C, 62.2 °C, 52.96 °C, 64.10 °C, 62.12 °C and 60.92 °C, respectively. The melting point of the wax/oil samples decrease with increase of fish feed ratios from the pyrolysis of the PE and PP. The melting point lowered from 62 °C to 53 °C and 64 °C to 51 °C for PE and PP with addition of 20% fish feed likely due to the lipid components derived from the fish feed pyrolysis. Given that it is unlikely the residual fish feed constitutes 20 wt % of the bag this likely not a significant factor but does demonstrate the fish feed has no negative impact on melting point, or any of the fuel properties outlined above.

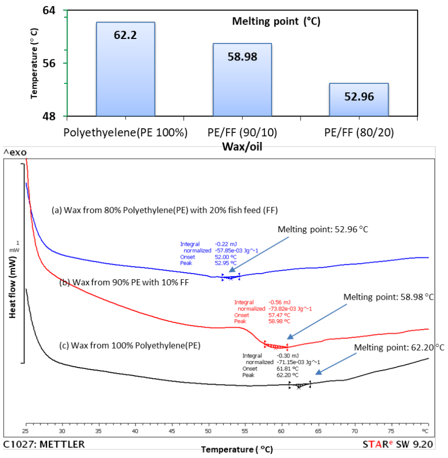


Figure 9. DSC curves of the wax/oil samples: (a) wax/oil from polyethylene/fish feed (80/20 %), (b) wax/oil from polyethylene/fish feed (90/10 %) and (c) wax/oil from polyethylene 100%.

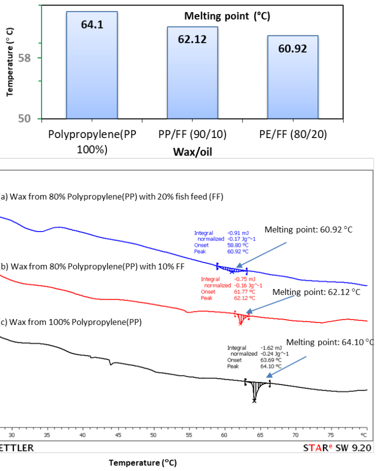


Figure 10. DSC curves of the wax/oil samples: (a) wax/oil from polypropylene/fish feed (80/20 %), (b) wax/oil from polypropylene/fish feed (90/10 %) and (c) wax/oil from polypropylene 100%.

3.6. Higher heating value (HHV):

An oxygen bomb calorimeter (Model 1314 Plain Jacket Bomb Calorimeter, Parr Instrument Company, Moline, Illinois, USA) was used to determine the higher heating value (HHV) of the wax/oil samples. The higher heating values of the wax/oil samples PE (100%), PE/FF (90/10%), PP (100%) and PP/FF (90/10%)

are 45.73 kJ/g, 43.83 kJ/g, 44.64 kJ/g, and 42.79 kJ/g, respectively (Table 7). The pure fish feed heating value was 25.47 MJ/kg,

Table 7. Higher heating value (HHV) of the wax/oil samples.

Parameters	**HHV(kJ/g)**
Wax/ oil from 100% Polyethylene (PE)	45.73
Wax/ oil from 100% Polypropylene (PP)	44.64
Wax/ oil from 90% Polyethylene (PE) and 10% fish feed(FF)	43.81
Wax/ oil from 90% Polypropylene (PP) and 10% fish feed(FF)	42.79
Oil from 100% fish feed(FF)	25.47

The heating values of all waxes are close to those of the standard fuels, 44-46 MJ/kg petrol/gasoline, 43 MJ/kg for diesel, and from 43-44 MJ/kg for fuel oil. [27]. Although, the wax/oil samples are highly viscous and require preheating before use, they could be used as a heating oil or bunker fuel due to their higher HHVs. Again, the FF has no detrimental impact on the HV even at very high concentrations.

3.7. Preliminary metal analysis of plastic fish bags residues

In order to ensure the residues did not represent a disposal issue, the metal concentrations in the plastic residues were considered for analysis. In the method digestion (EPA method 3050B, acid digestion of residues) is required. The resulting solution is then analyzed by inductively-coupled plasma optical emission spectrometry (ICP-OES). In the acid digestion step several different acids can be used, from mild to very strong (e.g. hydrofluoric acid or HF). The residue proved difficult to completely digest by acids (all acids suggested by method except HF) available for use in the CREAIT lab. A review of the literature showed that for this type of residue (plastic based) HF is recommended and due to safety issues we cannot use this particular acid in the room where the analysis takes place. Therefore we were not able to accurately analyze for metals in the samples. However, given the low probability of metals in the plastic bags or the fish feed this residue is not likely to be a disposal problem. This could be verified by contacting the fish bag manufacturer and fish feed produced.

4. Conclusion and future recommendation:

The pyrolysis of PE and PP fish feed bags produces a waxy liquid product with a heating value on par with diesel and heating oil (44-46 MJ/kg). At the optimum conditions determined in the lab scale semi-batch reactor, 500°C and N_2 flow rate of 50 mL/min, yields of oil/wax vary from 72 wt% (of feedstock) for pure PE bags, 69wt% for a 50:50 mixture of PE/PP and ~70wt% for pure PP bags. The melting point of the wax/oil varied rom 62°C for the PE to 64°C for PP, indicating the oil should be heated or kept above 60°C for use as a fuel. The gas produced varies from 20 wt% for pure PE to a maximum 25 wt% (50:50 PE/PP). The gas is predominantly methane (~95%) and ethane (~5%). The gas represents a valuable fuel gas that could be used to provide energy for the pyrolysis unit, or in combined heat and power. The residue varies from as low as 6 wt% for 50:50 mixture to 7.1 wt% for pure PE.

Based on the analyses contamination of the feed bags with fish feed has little impact on the HV of the plastic bags. The FF has a HV of approximately 25 MJ/kg, and decreased the HV of the bags to between 43-44 MJ/kg when at 10wt% of the total pyrolysed mass, again this is likely much higher than the actual FF contamination in the bags. The FF had little impact on the melting points at 10 wt% of feedstock, but at 20 wt% decreased the melting point by 4-10°C.

Overall the pyrolysis of these bags produces an oil and gas with high heating values. The FF does not negatively impact the quality of the oil based on the analyses done here. It should be noted the lab scale size of this system sets limitations on the tests that can be done, such as viscosity, density, flash point, solids content, and ASTM distillation analyses, due to amount of oil and residue generated. As such, in any scaled up or pilot scale system we recommend:

- Full fuel standard analysis including but not limited to viscosity as function of temperature (to determine cold flow properties), pour point, density, total acid number (for corrosion purposes given the fatty acids in the pyrolyzed fish feed), flash point (should be low due to the viscous nature of the oil), and other required parameters.
- Analysis of the residue for metals. Again although it is unlikely there are measureable heavy metals this should be verified either through vendor information or analyses.
- Feasibility of use of produced gas to provide heat or power.
- Heating of the produced oil/wax prior to use as a fuel.

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