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Thermochemical recycling of mixed plastic wastes through pyrolysis and steam cracking – Assessment of centralized vs. Decentralized approaches[☆]

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ABSTRACT

Thermochemical recycling of medical plastic waste (MPW) was evaluated experimentally and through development of mass & energy balances. Fluidized bed (FB) steam cracking of MPW at a centralized petrochemical site was compared to thermal and catalytic pyrolysis of MPW to intermediate WAX (thermal) and POil (catalytic) feedstocks at a decentralized site, followed by FB steam cracking of WAX and POil at a centralized petrochemical site. Pyrolysis and FB steam cracking experiments were performed in lab-scale reactors. Steam cracking yields of primary products (light olefins, C2-3 alkynes, BTXs) were highest for MPW, followed by WAX, and POil feedstocks. Higher steam cracking temperature increased the primary product yields for the MPW feedstock but showed a less significant effect in WAX and POil cases. For all cases, higher cracking temperature increased chain scission and hydrogen abstraction, resulting in rising yields of ethylene, methane, and hydrogen, and lower yields of longer chain aliphatic hydrocarbons. Material, carbon, and energy balances, developed from experimental results, showed that excess heat from incineration of pyrolysis and steam cracking byproducts can meet the energy demands of the pyrolysis and steam cracking processes. The balances also showed that direct FB steam cracking of MPW can achieve high product yields and high rates of fossil carbon recycling. However, steam cracking of WAX feedstock, the product of pyrolysis pre-treatment, can achieve moderate product yields and fossil carbon recycling while realizing several practical advantages: easier transport, reduced need for feedstock preparation, and removal of ash and heteroatoms for improved steam cracker operability.

1. Introduction & Background

Due to their complexity, many polymer-rich waste streams have no clear conventional recycling options, even though the input materials were of high quality and chemical value [1]. Globally, approx. 79 % of plastics are landfilled, 12 % are incinerated, and only 9 % of plastics are recycled via mechanical recycling [2]. The low rate of plastics recycling stems from the difficulties in collection, decontamination, and separation of plastics from waste streams and the downgrade in the quality of the resulting recycled plastics products. The other plastic waste handling methods, landfilling and incineration, do not allow circular reuse of plastics. Landfilled plastics break down over long periods of time and have been found to release harmful chemicals, as well as to contribute to soil and water contamination with microplastics [3]. Incineration of plastic waste for energy recovery contributes to carbon emissions as well

as emissions of harmful NO_x, SO_x, and PAH compounds.

Thermochemical recycling is a broad term referring to processes that are capable of thermally decomposing plastics to their monomer building blocks or to other useful chemicals [4]. Thermochemical recycling processes include pyrolysis, gasification, and fluidized bed (FB) steam cracking, among other technologies. In pyrolysis, plastic waste is thermally decomposed at temperatures in the range of 400–800 °C to produce pyrolysis oil, with char and pyrolysis gas as byproducts[5]. Pyrolysis oil is most often further processed to fuels [6,7]. The use of these fuels results in CO₂ emissions and does not allow a circular material flow, where waste plastics are ideally converted to virgin plastics. To enable circularity, recent research has aimed at producing plastic-waste-derived pyrolysis oil that can substitute naphtha — the primary fossil feedstock for the conventional steam cracking process that produces light olefins for use in polymer synthesis [5]. However, the

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use of pyrolysis oils in conventional naphtha crackers faces several significant challenges. Plastic-waste-derived pyrolysis oils typically contain longer carbon chains, higher olefin content, and significant amounts of heteroatoms (such as oxygen, nitrogen, sulphur, chlorine) that cause excessive coking within tubular steam crackers [8,9]. Thus, pyrolysis oils often require significant pre-treatment to produce a naphtha-like product with low heteroatom content [8,10,11].

In gasification, waste plastics are thermally decomposed at temperatures in the range of 700–1500 °C to produce syngas [5]. The syngas can then be used to produce synthetic naphtha via Fischer-Tropsch synthesis, or to produce methanol that can subsequently be converted to light olefins via the methanol-to-olefins process [12,13]. Although versatile, the gasification approach suffers from unfavorable economics that stem from the substantial energy demand of the gasification process and the need for hydrogen that is required in naphtha and methanol synthesis [1,10].

FB steam cracking of plastics and plastic wastes is carried out at temperatures in the range of 600–800 °C in a fluidized bed reactor that is fluidized with steam. Unlike pyrolysis and gasification, FB steam cracking directly converts plastics to an olefin-rich product gas, such that the olefin content can be recovered and used directly for polymer synthesis. FB steam cracking based on a dual interconnected fluidized bed configuration has been successfully demonstrated at the pilot scale by Wilk and Hofbauer [14] for production of light olefins and monoaromatics from polyolefin-rich feedstocks, and more recently at the semi-industrial scale by Thunman et al. [1]. The key advantage of the FB steam cracking process is its ability to convert highly heterogeneous and contaminant-rich solid waste-derived feedstocks directly to light olefins and aromatics. Thus, FB steam cracking is analogous to conventional steam cracking of naphtha and gaseous hydrocarbons but has the distinct advantage of being able to convert complex solid feedstocks, including waste-derived feedstocks [15]. Furthermore, FB steam cracking has the advantage of being scalable, as it is based on well-established fluidized bed technology. A detailed overview of the FB steam cracking process is available in [1].

Due to its scalability, FB steam cracking of waste plastics has the potential to replace conventional naphtha steam cracking as the major process of olefin production at major petrochemical sites. This would entail replacing naphtha crackers with FB crackers, establishing waste plastic feedstock sources and delivery, and adaptation of the downstream cracker effluent treatment/fractionation, and polymer synthesis processes. The goal of this type of implementation would be to replace fossil fuel with waste-derived feedstocks to establish a circular flow of plastics in our society [1]. Since major petrochemical sites tend to be centralized, the collection and transport of polymer-rich wastes to such sites can be challenging. Like all consumer waste, polymer-rich waste streams tend to be highly decentralized, but often have a localized collection and disposal/incineration. Diverting such waste streams to a centralized petrochemical site, in most cases, will require long-distance transport. Due to the low bulk density and the difficulty in handling heterogeneous solid waste feedstocks, long-distance transport of the waste feedstock in its original form may be uneconomical. Thus, waste pre-treatment to densify the feedstock and make it easier to handle should be considered as an option. Furthermore, even if the waste feedstock transport to the centralized FB steam cracking site is feasible, feedstock pre-treatment, such as pelletizing, will likely be required to make the feedstock easy to feed into an FB steam cracker, which would typically use either an extruder or a hopper and rotary valve system.

One example of a polymer-rich waste feedstock is medical plastic waste (MPW), which consists of disposable products from healthcare, diapers, and other disposable products which are often comprised of composites of various polymers and cellulose fibers. This study investigates how this type of feedstock can be pre-treated to make it transportable and easily utilized in an FB steam cracker, as well as how the pre-treatment affects the FB steam cracking product yields, associated process CO₂ emissions, and process energy requirements. The key

scenarios considered in this study are illustrated in Fig. 1.

Case 1 considers the transport, pelletizing, and subsequent FB steam cracking of the MPW pellets. This case simulates the physical and chemical feedstock transformations that would occur in a centralized scenario, where feedstock preparation and conversion occur at the centralized petrochemical site. Case 2 considers the use of low-temperature pyrolysis as a means for thermochemical pre-processing of the MPW feedstock. In this pre-processing step the MPW feedstock would be converted to pyrolysis products (char, wax/oil, gas), and the major hydrocarbon fraction (wax/oil) would be separated. The pyrolysis pre-treatment step would be carried out at the de-centralized locations where these waste streams are currently collected and utilized in municipal waste incinerators. The pyrolysis char and gas byproducts would be combusted for energy recovery at the de-centralized incinerator site or combusted to provide the heat input into the pyrolysis process. The separated wax/oil product would be transported to the centralized petrochemical site where it would be used as the feedstock for the FB steam cracking process. In this process scheme, the pyrolysis pre-treatment process would essentially be used to convert most of the useful hydrocarbon content of the original MPW feedstock to an intermediate product which is easier to handle and transport to the FB steam cracking site, vs. transporting the original MPW feedstock.

The evaluation of the above-mentioned approaches consisted of identification and characterization of potential waste streams, selection and preparation of a representative feedstock, followed by experimental evaluation of feedstock conversion in lab-scale pyrolysis and FB steam cracking reactors. Conversion product characterization was performed to close the mass and carbon balances. Comparison of the two cases, as well as an additional case representing MPW feedstock incineration, was carried out through mass and energy balance calculations. The alternative processes were then evaluated and compared on the basis of valuable product yields, carbon recovery rates, and energy demand.

2. Methodology

2.1. Characterization of plastic waste

The waste stream considered in this study was medical product waste from the Västra Götaland region (VGR) region in southwestern Sweden. Through analysis of the region's yearly procurement, it was determined that approx. 1300 tonnes/year of plastic-rich medical waste is generated in the region. To produce a representative medical waste feedstock, Mölnlycke Health Care, a local supplier of medical products, provided several product samples that would be typically used in VGR medical facilities. This product sample consisted of a trauma kit, which is a set of disposable medical products used by an operating team during a surgical procedure. The items in the product sample consisted primarily of thin and flexible textile-like items (surgical gowns, drapes, sheets, etc.) and a few items made of rigid plastic (syringes, plastic bowls, suction tube, etc.). To prepare a feedstock sample, the product sample was manually cut into segments of less than 10 cm x 10 cm and then milled in a Retsch SM-2000 knife mill. The milling was carried out in two stages, first milling the sample to <10 mm size and then re-milling the resulting material to <4 mm size. The textile-like and rigid plastic fractions were milled separately as this produced a more uniform particle size. After milling, the textile-like and rigid particles were blended to a homogeneous consistency. The shredded feedstock was then pelletized using a heated hand-operated pellet extruder (maintained at 150 °C) with a nozzle diameter of 8 mm. The extruded feedstock was broken down into pellets 2–3 cm in length. Fig. 2 shows the test feedstock and the feedstock preparation stages.

The resulting feedstock was characterized by several different means. First, the overall polymer composition of the product sample was established. Each item included in the provided product sample was itemized and weighed. The approximate material composition of each item, provided by Mölnlycke Health Care, was then used to estimate the

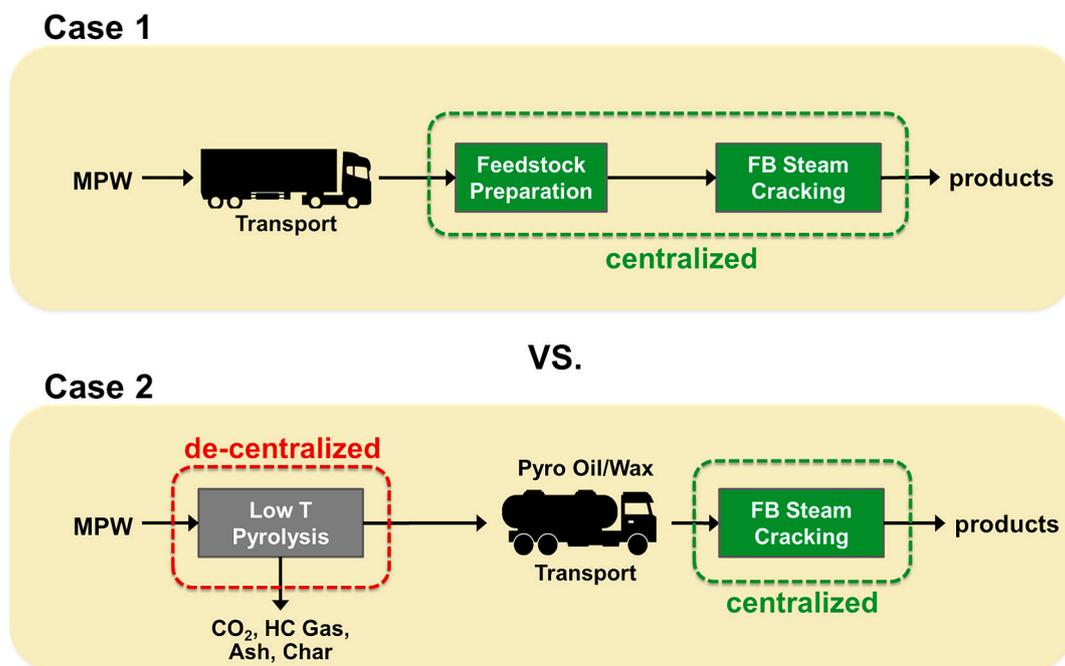


Fig. 1. Medical plastic waste pre-treatment and FB steam cracking cases.

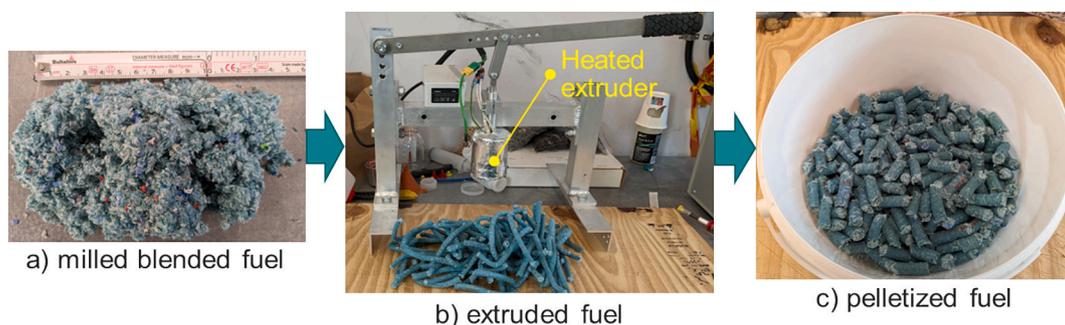


Fig. 2. Feedstock preparation: a) milled feedstock, b) extruded feedstock, c) pelletized feedstock.

overall compositional breakdown of the product sample. The resulting material breakdown estimate is presented in Table 1. It is important to note that this estimation is subject to possible errors in the material composition information provided by the medical product supplier. Also, the amount of PVC in the sample was back calculated from the Cl detected in the feedstock. To confirm the elemental composition of the actual product sample that was prepared for the experiments, the milled feedstock was analysed by Eurofins AB to determine the ultimate analysis that is presented in Table 2.

The material breakdown presented in Table 1 shows that MPW

Table 1
Material breakdown of MPW feedstock.

Component	wt. %
Polyethylene (PE)	26.3
Polypropylene (PP)	9.1
Polyester (PST)	21.5
Polyisoprene	4.3
Polyvinyl Chloride (PVC)	0.8
Polystyrene (PS)	1.5
Viscose	9.1
Wood fiber	23.0
Ethylene Vinyl Acetate (EVA)	1.5
Heating Value (MJ/kg)	29.5

Table 2
Ultimate analysis of MPW feedstock.

Component	Analysis value (w.t.% a.r.*)	Uncertainty (+/- % of analysis value)
Moisture	1.60	10
Ash	3.29	11
C	61.5	5
H	8.60	13
N	0.23	29
O	25.8	calculated**
S	0.20	26
Cl	0.44	25
Ca	0.82	12
Ti	0.39	24
F	0.05	n/a
Zn	0.04	26
Na	0.03	22
Al	0.02	26

*as received.

**calculated by weight difference.

feedstock is dominated by polyethylene and polyester polymers and contains a significant amount of wood fiber. Wood fiber is used as a substrate of the textile-like Spunlace® material used in medical gowns, sheets, and drapes. The ultimate analysis presented in Table 2 shows

that the test feedstock has a very low moisture content and a relatively low ash content, indicating that the polymers used in the products contain almost no fillers. The oxygen content of the feedstock is quite high and originates from the high polyester fraction and the high natural fiber content. The inorganic content of the feedstock is relatively low and is dominated by Ca and Ti, likely from pigments and additives. A notable amount of Cl is present in the feedstock, originating from the feedstock's PVC content.

The melting and decomposition behavior of the prepared feedstock was analyzed in a thermogravimetric analyzer (TGA). In the TGA, a 1 g feedstock sample was heated from 25 to 700 °C in an inert atmosphere at a rate of 5 °C/min. After stabilizing at 700 °C, the remaining sample was combusted in an O₂ atmosphere at 550 °C. The weight change of the sample was recorded vs. time and temperature. A representative weight loss curve and a curve for the rate of sample weight loss is presented in Figs. 3 and 4, respectively.

The TGA curves presented in Figs. 3 and 4 indicate three major release events occurring around 100, 300, and 450 °C. The first event corresponds to the release of a minor amount of water from the feedstock, while the latter two events are a result of decomposition of various polymers contained within the feedstock. The release at 300 °C is likely dominated by decomposition of cellulose, the major component of the natural fibers contained in the feedstock. Cellulose is known to decompose in the range of approx. 200–400 °C [16,17,]. The release event that occurs at 450 °C is dominated by decomposition of the polymers contained in the MPW feedstock.

2.2. Low-Temperature pyrolysis

To simulate thermochemical feedstock pre-treatment, the MPW feedstock was subjected to two types of pyrolysis: thermal and ex-situ catalytic. In each process, the MPW feedstock was thermally decomposed at approximately 500 °C in an inert environment to pyrolysis condensables (liquids and wax), solid residue and non-condensable gas. The lab-scale pyrolysis system used in these experiments is illustrated in Fig. 5. The system consists of a pyrolysis batch reactor, a condensable fraction recovery system, and gas analysis. For ex-situ catalytic pyrolysis, an additional catalytic reactor was added after the batch reactor to further crack the pyrolysis vapours.

The pyrolysis reactor has a volume of 7 dm³ and consists of a vessel with a mesh grate, where the MPW feedstock sample was placed. The reactor was placed inside an electrical kiln and the sample was heated in an inert atmosphere under a flow of nitrogen, controlled using a mass flow controller. The heat from the electrical kiln was controlled by

measuring the gas temperature inside the batch reactor. The reactor temperature was ramped up to 500 °C at a rate of approximately 5 °C/min. The nitrogen was pre-heated before entering the reactor. The solid product remained in the reactor while the produced pyrolysis vapours were condensed in the condensable fraction recovery system.

During the experiments, the produced pyrolysis vapours were continuously condensed and collected using two indirect condensers filled with coolant maintained at a temperature of –15 °C. Pyrolysis aerosols were mainly collected in a small glass wool aerosol filter before the second oil collector. The remaining aerosols were collected in a glass wool mist trap before the suction pump. Composition of the non-condensable gas was continuously analysed for CO, CO₂, H₂, N₂, O₂, CH₄ and C₂H₄ using a Varian 490 micro-GC with two thermal conductivity detectors (TCDs). Larger gaseous compounds were sampled using Tedlar® gas bags and analysed using a stationary GC system coupled to a flame ionization detector (GC-FID, Varian CP-3800).

Each pyrolysis experiment ended when no pyrolysis gas was detected in the online gas chromatograph. At that point, the oven was switched off and allowed to cool overnight under a low flow (0.5 L/min) of room temperature nitrogen. The morning after the experiment the system was dismantled, and the products were recovered and weighed. Product yields were determined by weighing the feedstock, condensables, and solid products, and via calculation of the weight of the pyrolysis gas components.

2.2.1. Thermal pyrolysis

The thermal pyrolysis experiment used 200 g of milled (non-pelletized) MPW feedstock, spiked with an additional amount of PVC (increased from 0.8 wt% PVC in the original feedstock, up to 5.8 wt%). The additional PVC was added to simulate an extremity in feedstock content variability that can occur in the supply of medical waste products. Due to the high content of chlorine, an absorbent (20 g of calcium oxide) was mixed with the sample, to capture chlorine by forming calcium chlorides. The experiment was performed at 500 °C for a period of 180 min using a nitrogen gas flow of 3 L/min through the reactor.

2.2.2. Ex-situ catalytic pyrolysis

The ex-situ catalytic pyrolysis experiment used 400 g of pelletized MPW feedstock. Pelletization was necessary to be able to fit more feedstock into the pyrolysis reactor to produce more condensable products, making sure that there is enough material for subsequent FB steam cracking experiments. For catalytic experiments the sample did not include additional PVC. 40 g of calcium oxide were added to this sample to capture chlorine. A catalytic reactor with a volume of 0.7 dm³

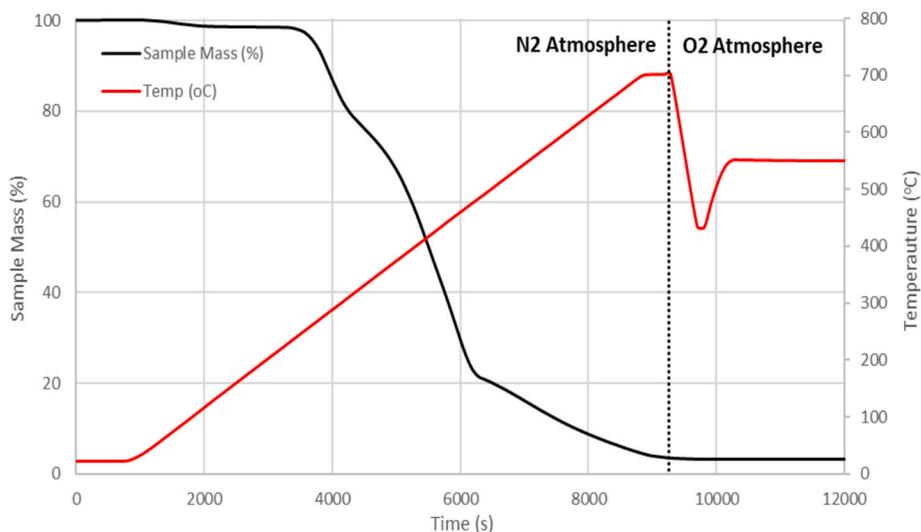


Fig. 3. Feedstock sample temperature and mass vs. time (TGA Analysis).

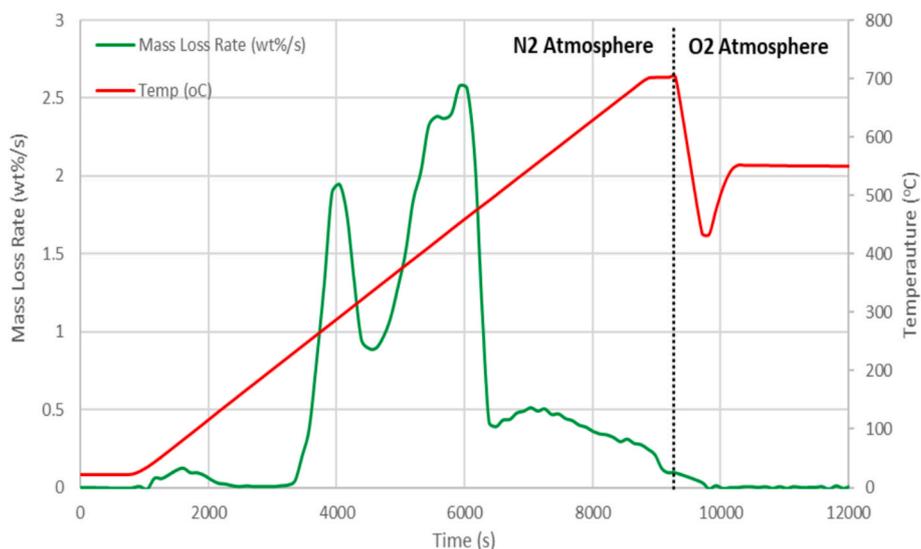


Fig. 4. Feedstock sample temperature and mass loss rate vs. time (TGA Analysis).

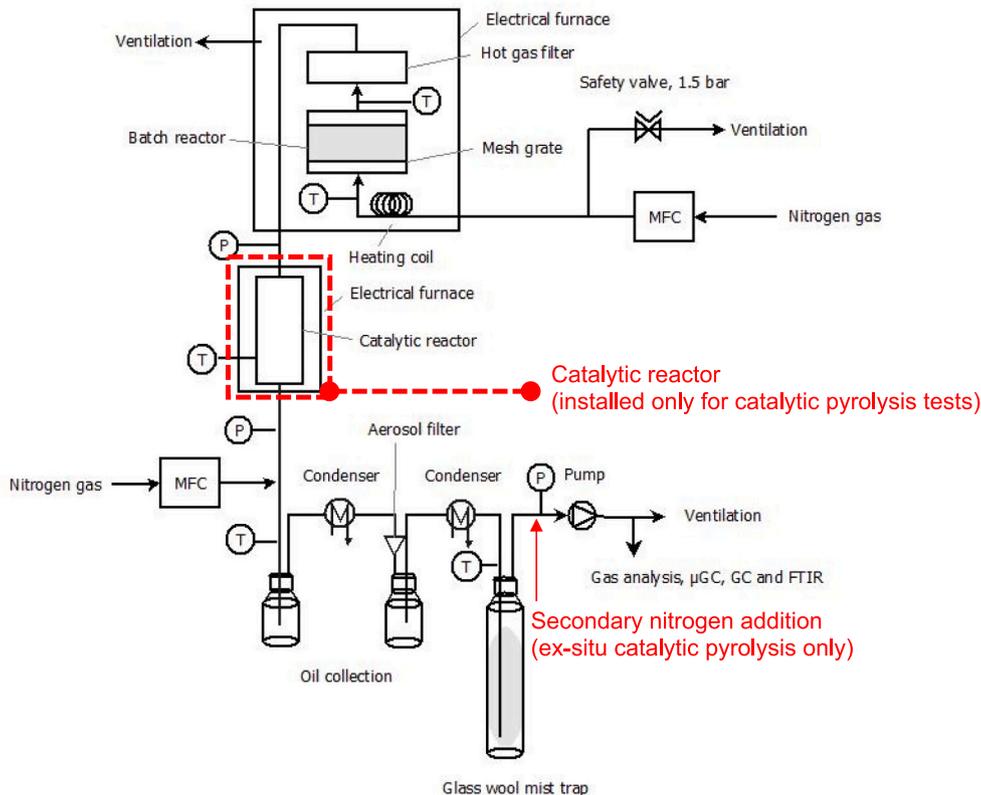


Fig. 5. Schematic sketch of the lab-scale pyrolysis set up.

was installed downstream of the pyrolysis reactor, allowing the pyrolysis vapours to pass through a bed of 133 g of TiO_2 catalyst. The catalytic reactor facilitated further cracking of the thermal pyrolysis vapours. TiO_2 catalyst was chosen for its relatively low cost and mild catalytic action. The low cost of catalyst is important in this application since the processing of waste-derived feedstocks would require frequent catalyst replacement. The mild catalytic action is important since the aim is to have just enough hydrocarbon chain cracking to produce a liquid product (as opposed to a waxy product which is more difficult to handle) while limiting excessive cracking so the product contains long chain

paraffins and a limited amount of cyclic compounds, such that higher yields of olefins can be achieved in subsequent FB steam cracking process. During the experiment, the pyrolysis reactor and the ex-situ catalytic reactor were maintained at 500 °C. A nitrogen flow of 0.5 l/min was added into the pyrolysis reactor, with an additional 2 L/min of nitrogen added after the glass wool mist trap (this additional flow was added to ensure enough gas for all gas analyses). The duration at the pyrolysis temperature 500 °C was approximately 240 min.

2.2.3. Pyrolysis product analysis

The chemical composition in the condensable pyrolysis products were analysed semi-quantitatively using GC/MS-FID. GC/MS-FID analysis was performed using a Shimadzu GCMS-QP2010 ultra gas chromatograph (GC) with a quadruple mass spectrometer (MS) and a flame ionization detector (FID), capable of detecting compounds up to C34 carbon chain length. The samples were diluted in dichloromethane in a 1:10 ratio. The compounds were identified using the mass spectrometer and semi-quantitatively determined using the FID detector.

2.3. Bubbling fluidized bed steam cracking reactor

The main product of thermal pyrolysis was pyrolysis wax (WAX), while for catalytic tests, pyrolysis oil (POil) was the major product. Steam cracking of the original pelletized MPW feedstock, as well as the WAX and POil products, was carried out in a lab-scale fluidized bed reactor. A schematic of the reactor is presented in Fig. 6.

The bubbling fluidized bed reactor is made from 253 MA high-temperature stainless steel. The reactor is tubular with an internal diameter of 8 cm, and a height of approximately 1.5 m. Fluidizing gas (air, nitrogen, steam) is introduced into the reactor via the wind box, which is separated from the main reactor section by a perforated metal fluidizer plate. The sand bed, which is filled on top of the perforated plate, is fluidized with the gases that flow through the small holes in the fluidizing plate. The reactor is mounted in an electrically heated oven that is used to control the reactor temperature in the range of 600–800 °C. The reactor is equipped with ports on two sides. The ports on one side are used for pressure and temperature measurements (T/P ports). On the other side, larger ports are used for product sampling and for liquid feedstock injection. The ports, as well as the wind box feed line extend to outside of the reactor oven. The reactor outlet is open-ended and is positioned beneath a fume hood. Feedstock was fed into the reactor in two ways. Liquid feedstock (POil) was introduced into the bed via a feedstock injection port through an air-cooled probe using a syringe pump. For the solid feedstocks (MPW pellets, WAX) there is no practical way to introduce these feedstocks into the reactor continuously. As such, these feedstocks were introduced into the reactor from the top opening of the reactor in small batches. MPW feedstock was introduced into the reactor in single pellets, weighting approx. 1–1.5 g each. WAX feedstock was introduced in small baggies (small wax-filled PE film bag), weighing approx. 1–1.5 g each.

2.3.1. Product sampling and analysis

During FB steam cracking experiments, the fuel conversion products are sampled from a heated sample port. The port is heated to 350 °C such that tars can be sampled without being condensed in the sampling port. Samples are taken with a suction pump for a 2 min in duration. During sampling the pumps draws the sample gas through two solid phase absorption columns (SPA). Each SPA column contains an amine which absorbs heavy polycyclic tar compounds. The remainder of the product compounds pass through the sample pump and are trapped in a Tedlar® sample bag. The composition of the gases trapped in the gas bag are analysed in a GC-TCD and a GC-VUV. The SPA columns are eluted with a dichloromethane-based solvent and are analysed in the GC-VUV. Combining the analyses from the GC-TCD and GC-VUV gives a complete overview of the product gas composition in the range of C1-C18 hydrocarbon species.

Throughout the experiments the permanent gases (CO, CO₂, CH₄, H₂, O₂) are continuously sampled and analysed. The gas sample is taken as a slip stream from the heated sampling port and are then scrubbed in contact with isopropanol to remove the tar fraction. This is necessary since the permanent gas analysers cannot tolerate tars. Permanent gas analysis is used primarily for online process monitoring purposes.

2.3.2. Steam cracking experimental test procedures

Solid Feedstock Experiments.

The experimental test procedure for solid feedstock tests is depicted in Fig. 7.

Initially the reactor is heated to the test temperature (700, 750, 800 °C) and is fluidized with nitrogen and steam. The experiments start when a small amount of solid feedstock (approx. 1 g) is dropped into the reactor. The sampling pump of the SPA and gas bag sampling system is started simultaneously with the feedstock introduction. The product gases are sampled for 2 min, during which time the feedstock is cracked, releasing gaseous products and tars, leaving char and ash in the reactor bed. At the two-minute mark, the sampling is stopped, and the reactor fluidizing gas is switched to nitrogen. Nitrogen atmosphere prevents char gasification. The sampling system is purged, and a new gas bag is installed on the sampling system. The fluidization gas is then switched to air, and the sampling pump is simultaneously turned on for a second 2-minute sampling period. During these 2 min, the char that is left from steam cracking undergoes burnout. This step converts the carbon in the char to CO₂. Thus, measuring the CO₂ trapped in the sample bag during this step can be used to determine the amount of char that was left in the

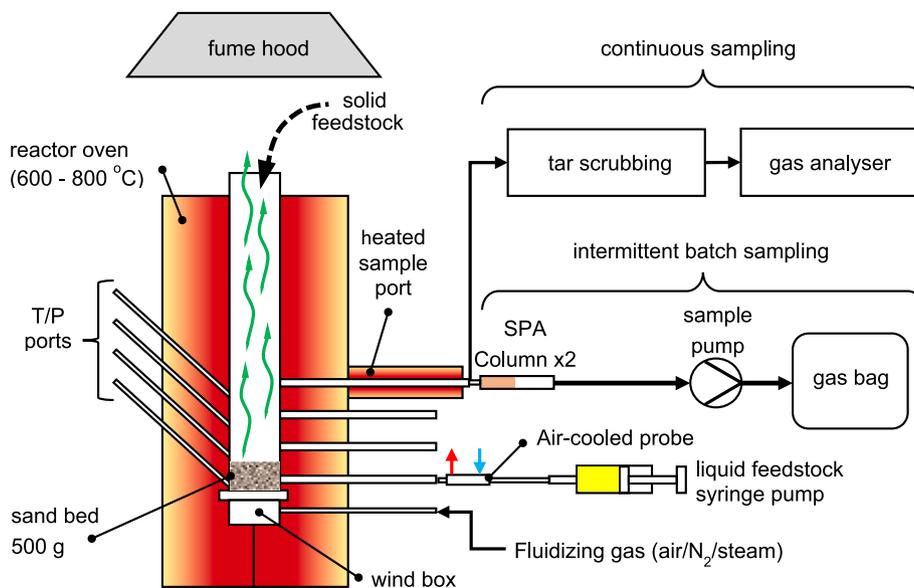


Fig. 6. Schematic of the bubbling fluidized bed steam cracking reactor.

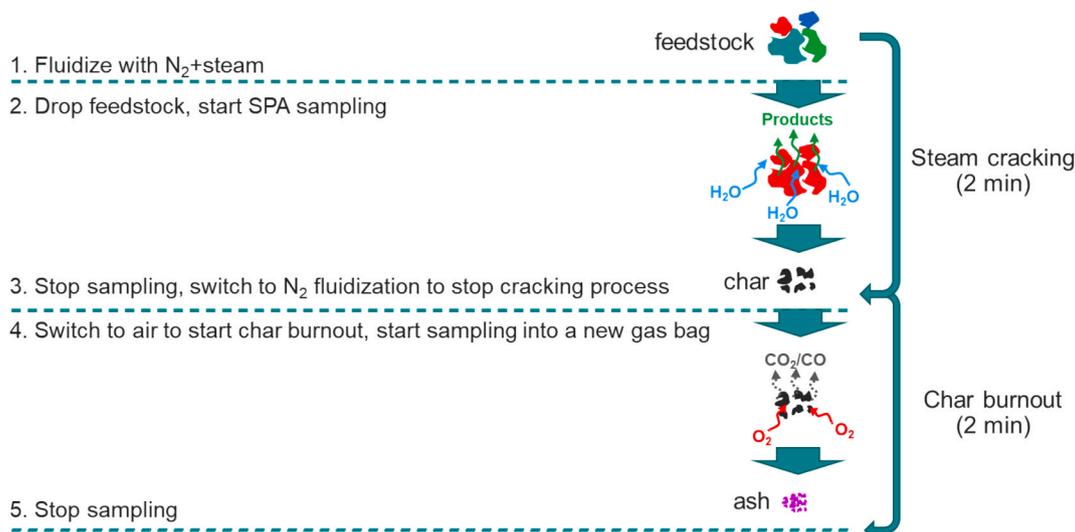


Fig. 7. Experimental procedure for solid feedstock steam cracking experiments.

bed after steam cracking.

The batch experiment methodology described above allows for a controlled study of the steam cracking process. The steam cracking product results obtained from such experiments have been shown to be largely transferrable to large-scale continuous steam cracking experiments, as can be seen from earlier works that have conducted experiments on similar feedstocks in the current reactor [18,19], and in a semi-industrial scale dual fluidized bed reactor [15]. In the continuous implementation of this process, the steam cracking reactions occur in a bubbling fluidized bed steam cracker reactor that is coupled to a fluidized bed combustor. The char left over from feedstock conversion is carried from the bubbling fluidized bed to the combustor, where char is burned along with additional fuel feed. The heat generated in this process is transferred to the sand bed material, which is recirculated back to the bubbling bed steam cracking reactor. The char burnout step in the procedure outlined in Fig. 7, simulates this process. More detailed description of the dual fluidized bed steam cracking process is available in [15].

Liquid Feedstock Experiments.

Steam cracking experiments with pyrolysis oil were conducted in continuous operation. To start the experiment, the reactor is brought to a desired operating temperature while fluidized with air and steam. The feedstock injection is then started using the automated syringe pump, injecting the feedstock at a rate of 2.5 ml/min. Once the feedstock injection starts, the system is allowed to stabilize to steady-state conditions (approx. 4 min) and then 3 repeat SPA and gas bag samples with a sampling duration of 1.5 min are taken to capture the tars and product gases. Once sampling was complete, the liquid injection is stopped and the reactor fluidization with switched to nitrogen. The sampling system is purged, and a new gas bag is installed on the sampling system. The fluidization gas is then switched to air, and the sampling pump is simultaneously turned on for a 6-minute sampling period. As in the solid feedstock experiments, this step is necessary to capture the CO₂ produced during the burnout of the char that remains in the bed after steam cracking.

3. Experimental results and discussion

3.1. Low-Temperature pyrolysis

MPW feedstock was pyrolyzed using thermal and ex-situ catalytic pyrolysis. The pyrolysis product mass fractions are presented in Fig. 8. The deviation (i.e., unaccounted mass) was approx. 10 wt%. In thermal pyrolysis, the main products were pyrolysis wax (WAX), followed by

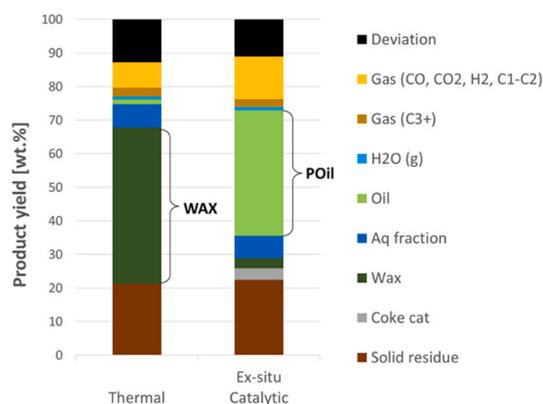


Fig. 8. Product distribution of thermal and catalytic pyrolysis.

solid residue, aqueous liquid fraction, light gases, higher gaseous hydrocarbons (C3 +) and a small amount of oil and water. In ex-situ catalytic pyrolysis, the main products were pyrolysis oil (POil), followed by solid residue, light gases, aqueous liquid fraction, coke on the catalyst, higher gaseous hydrocarbons, wax, and some remaining water in the gas phase. Pictures of the major WAX and POil fractions are shown in Fig. 9.



Fig. 9. Left – thermal pyrolysis wax (WAX), Right – catalytic pyrolysis oil (POil).

The major condensable product of thermal pyrolysis (WAX), and ex-situ pyrolysis (POil), constitute 47.9 wt% and 40.4 wt%, respectively, of the original MPW feedstock. From analysis of these fractions it was found that the WAX and POil fractions retain 66.7 and 57.6 % of the carbon from the original MPW feedstock, respectively. The POil product is a liquid at room temperature, which makes this fraction easily transportable by tanker truck or railcar in a scheme where the major pyrolysis product from a decentralized pyrolysis site must be transported to a centralized steam cracking site. The WAX product has a paste-like consistency at room temperature but melts into a liquid at approx. 50–60 °C. Thus, the WAX product is also transportable by means of a tanker truck or rail car that is equipped with a heating system. The WAX and POil products were analyzed with gas chromatography. The analysis results are shown in Fig. 10. The GC–MS/FID analysis showed that WAX and POil products consist mostly of olefins, paraffins and aromatics, some unclassified compounds, and small amounts of oxygenated compounds. The most notable difference is that POil contains a significantly higher proportion of aromatics than WAX. In terms of chain length, the POil appears to have shorter chain molecules. This indicates that the TiO₂ catalyst used in catalytic pyrolysis improved cracking but promoted formation of aromatic compounds. Another important observation is that no chlorinated compounds were detected in the WAX product, and only a trace amount chlorinated compounds were detected in the POil product. This indicates that most of the chlorine that originates from PVC was absorbed by reaction with CaO forming calcium chloride, or ended up in the aqueous product fraction as dissolved HCl. The presence of HCl in the aqueous fraction was confirmed by measuring a pH value in the range of 0 to 1 in the aqueous products.

3.2. Steam cracking experiments

Steam cracking experiments were carried out for MPW, WAX, and POil feedstocks at three steam cracking temperatures of 700, 750, and 800 °C. The product yields, expressed in percent of net carbon contained in the original MPW feedstock, are presented in Figs. 11–13, for steam cracking experiments for each of the feedstocks. Steam cracking of MPW simulates the process proposed in Case 1, where the original feedstock undergoes direct FB steam cracking at a centralized site. Thus, the sum of the products in Fig. 11 adds up to 100 %, showing how the carbon in the MPW feedstock is split between the generated products. Steam cracking of WAX and POil feedstocks simulates the second process step in Case 2, where only the main intermediate products, WAX from

thermal pyrolysis and POil from catalytic pyrolysis, undergo FB steam cracking. Since WAX and POil retain 66.7 and 57.6 %, respectively, of the original carbon from the pyrolyzed MPW feedstock, the steam cracking products of WAX and POil add up to those percentages of original MPW carbon. The remainder of the carbon in Figs. 12 and 13 is denoted as “carbon lost in thermal/catalytic pyrolysis byproducts” to illustrate the carbon that is incorporated into the pyrolysis byproducts (char, gas, coke, minor oil fraction in the thermal case, minor wax fraction in the catalytic case). The carbon in these byproducts is assumed to be released as CO₂ upon incineration of the pyrolysis byproducts at the decentralized pyrolysis site to provide heat input into the pyrolysis process.

Figs. 11–13 include the “unaccounted” term which represents the difference between the total carbon within each feedstock and the carbon that was found in the steam cracking product gas. Thus, the “unaccounted” term indicates the degree to which the carbon balance has been resolved. The unaccounted fraction is less than 15 % for the MPW and WAX feedstock results, indicating good carbon balance closure. For the POil test, shown in Fig. 13, 30–40% of the carbon present in the POil feedstock was not detected in the FB steam cracking product gas. The poor balance closure for the POil experiments coincides with the fact that POil was fed into the FB reactor system by means of continuous injection into the bed of the reactor. The flowrate of POil was set to 2.5 ml/min (2.14 g/min), as this was the lowest flowrate allowed by the syringe pump. In contrast, MPW pellets and WAX bags were added to the reactor by dropping a single 1–1.5 g pellet/bag into the reactor for each 2 min conversion period. Thus, for each 2 min conversion period the amount of POil feedstock added to the system was approximately three to four times higher than for the MPW and WAX cases. Since the fluidization steam and nitrogen flow rates were the same for all experiments, the higher feeding rate in POil experiments resulted in a lower steam-to-hydrocarbon ratio and a higher hydrocarbon partial pressure, which is known to lead to decreased primary product yields and increased carbonization [20,21]. Further to the effect of lower steam-to-hydrocarbon ratio, POil contains a high proportion of aromatics, which are known to be precursors for formation of coke and soot through cycloaddition and dehydrogenation reactions [21]. In the POil experiments, increased carbonization led to formation of soot which was evident from observations of black smoke reactor effluent. Soot was also found as a black deposit in the SPA columns that remained after eluting the SPA columns with dichloromethane. The dichloromethane solvent used to elute the SPA columns can dissolve a wide range of organic

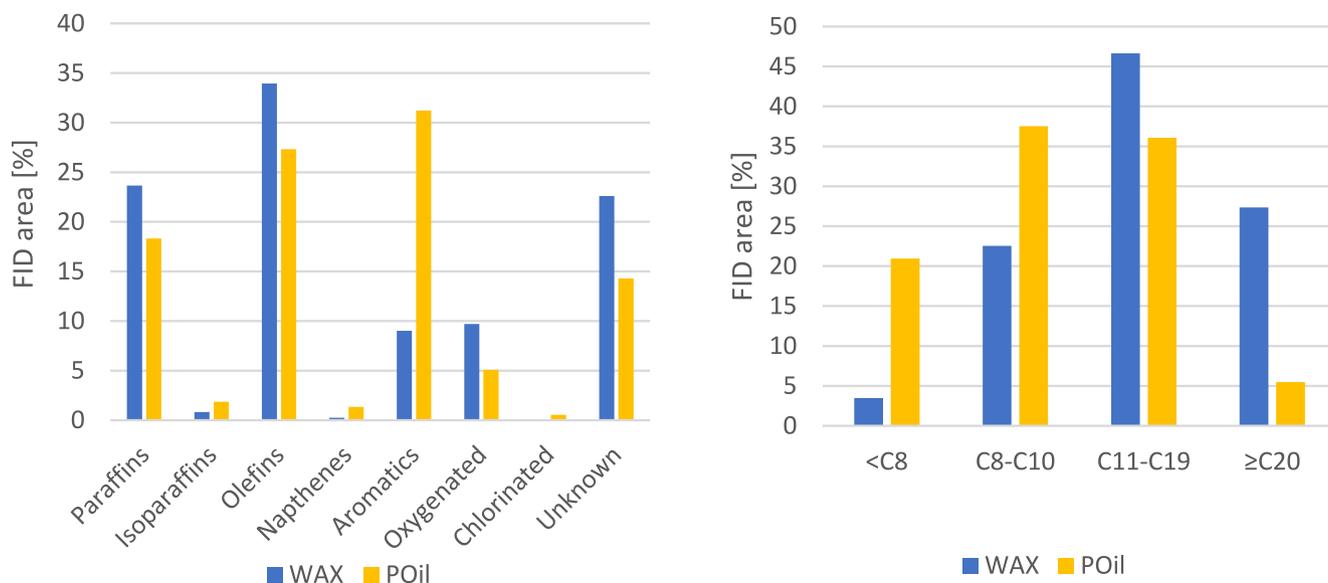


Fig. 10. Composition of WAX and POil pyrolysis products as determined by GC/MS-FID, categorized by PIONA classification (left) and carbon chain length(right).

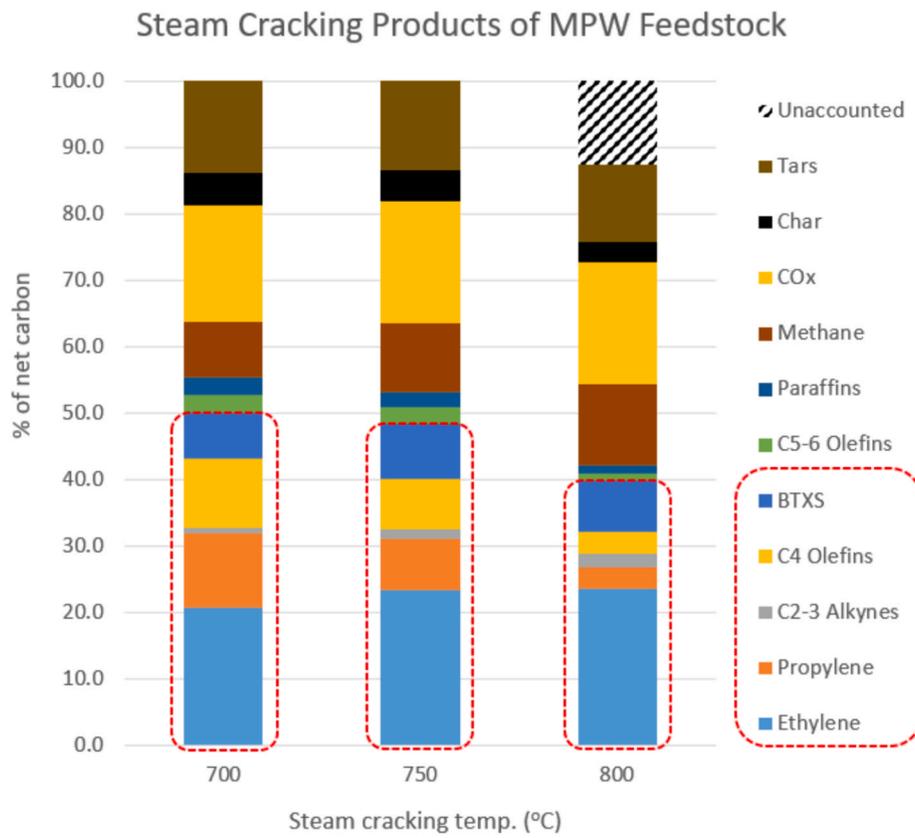


Fig. 11. Product distribution vs. temperature for FB steam cracking of MPW feedstock.

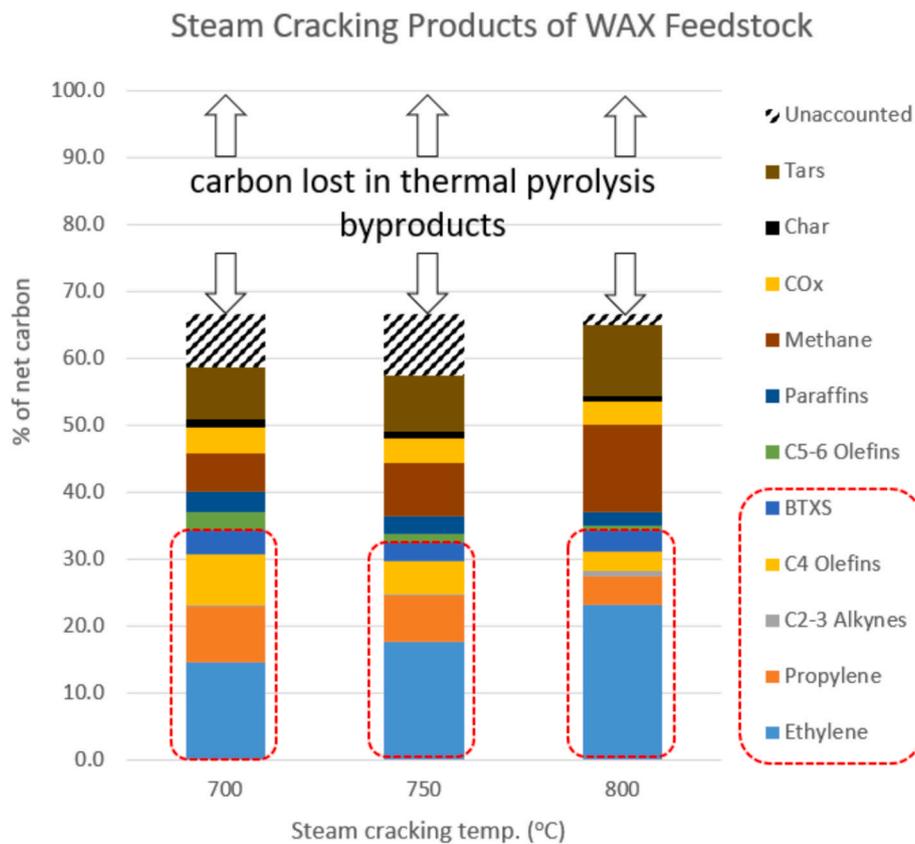


Fig. 12. Product distribution vs. temperature for FB steam cracking of WAX feedstock.

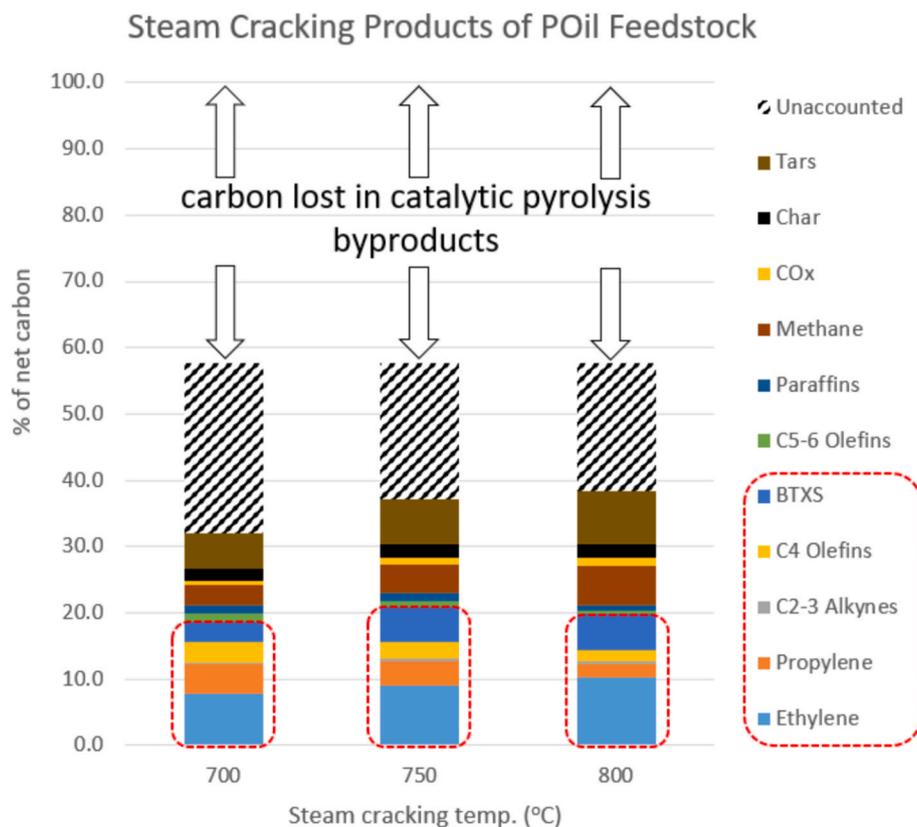


Fig. 13. Product distribution vs. temperature for FB steam cracking of POil feedstock.

compounds but is unable to dissolve soot. Unfortunately, the soot observed in the experiments could not be measured and quantified in the present experiments. Also, there was no possibility to repeat the POil experiments with optimized feeding parameters since the initially produced POil feedstock was used up in the presented experimental trials.

In Figs. 11-13, primary products, products which are considered as most valuable, are grouped, and outlined with a red dashed box. Ethylene, propylene, and C4 olefins, or collectively “light olefins” are valuable as they serve as a feedstock for production of new plastics. C2-3 alkynes are also considered valuable for plastic production as they can be hydrogenated to light olefins. Benzene, toluene, xylene (BTXs) are considered valuable for use in chemical production. In the industrial implementation of FB steam cracking, these valuable product species would be separated and recovered from the main steam cracking product stream. The remaining products have several utilization possibilities. The char and tar (mostly polyaromatic compounds) have little value in terms of upgrading as they are more difficult to handle than liquids or gases and would require a significant input of hydrogen and energy to be converted to useful products, such as light olefins. As such, char and tar would most likely be combusted. The recovered energy can be used to cover the energy demand of the FB steam cracking process. The remaining fractions (C5-6 Olefins, paraffins, methane and carbon oxides) can be either combusted for energy recovery or upgraded to useful products. C5-6 Olefins and paraffins can potentially be further cracked to yield more light olefins.

In comparing the steam cracking products distributions between the different feedstocks, there are several notable trends. Direct steam cracking of MPW feedstocks gives the highest yield of primary products, followed by the WAX and POil feedstocks. MPW feedstock steam cracking achieves the highest yields because the full polymer content is available for steam cracking. The poor yields of the POil feedstock are the result of significant carbonization and soot formation caused by POil’s high aromatic content and the lower steam-to-hydrocarbon ratio

experienced in the POil steam cracking experiments. Across the three tested temperatures, primary product yields decrease with temperature for the MPW feedstock. For the WAX and POil feedstocks, cracking temperature does not show a consistent or significant effect on the primary product yields. For all feedstocks, increased steam cracking temperature results in increasing yields of ethylene, C2-3 alkynes, and methane, and decreasing yields of propylene, C4 olefins, C5-6 olefins and paraffins. This suggests that higher steam cracking temperature results in intensified carbon chain scission and increased hydrogen abstraction, leading to the higher yields of alkenes and alkynes, as well as higher yields of molecular hydrogen, as shown in Fig. 14. This progressive dehydrogenation eventually results in formation of aromatics and tars (polyaromatics). This is somewhat supported by tar yields that rise with steam cracking temperature for the WAX and POil feedstocks.

The yields of CO and CO₂, collectively “carbon oxides” or “CO_x” are relatively constant across temperatures since they are limited by the availability of the oxygen in the feedstock. For the MPW feedstock, this corresponds to the oxygen that is contained in the polyester and the natural fibers of the medical waste sample. The CO_x yields for WAX and POil, however, are much lower due to the fact that a large proportion of the original oxygen is converted and released as carbon oxides in the thermal and catalytic pyrolysis stages. Thus, only a small amount of the original oxygen remains in the WAX and POil feedstock in the form of oxygenated compounds. In fact, the steam cracking CO_x yields for WAX and POil are proportional to the oxygenated compound levels presented in Fig. 10.

3.3. Material, Energy, and carbon balances

Two scenarios were evaluated to compare direct and indirect steam cracking of MPW feedstock:

Case 1: Direct steam cracking of MPW feedstock at 750 °C.

Case 2: Thermal pyrolysis of MPW feedstock at 500 °C to WAX,

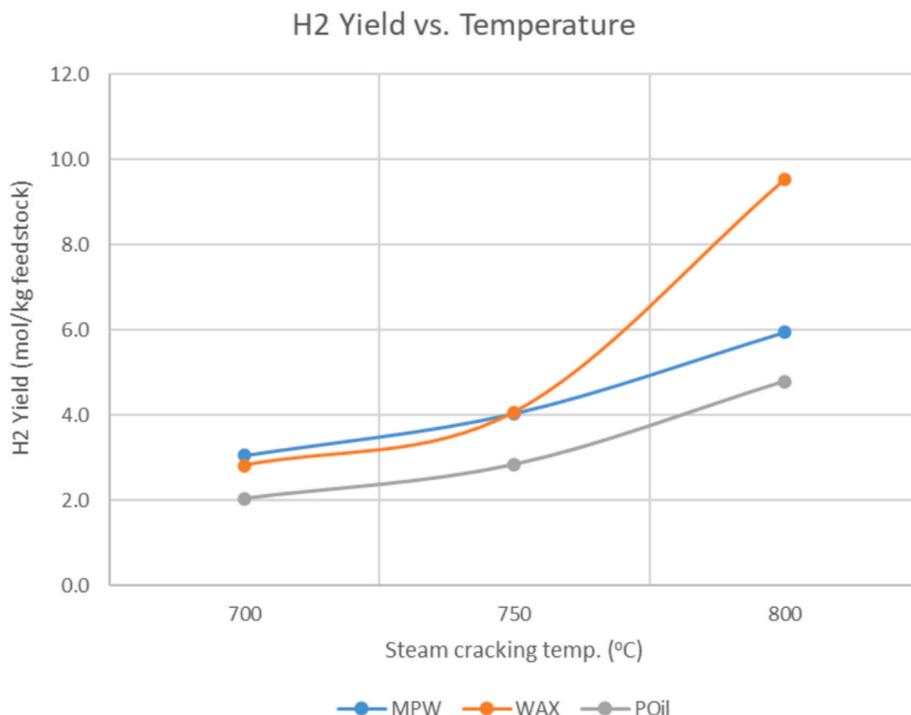


Fig. 14. Hydrogen yield vs. temperature for FB steam cracking MPW, WAX, and POil feedstocks.

followed by steam cracking of WAX at 750 °C.

Due to the poor carbon balance closure of the POil experiments, catalytic pyrolysis of MPW feedstock to POil was not considered in evaluating the material, energy, and carbon balances. For the two evaluated cases steam cracking temperature of 750 °C was selected as the basis for comparing the different cases. This temperature represents a good balance between the yields of primary products, ethylene, and tars. The mass, carbon, and energy balances developed for the above

cases are presented in Figs. 15 and 16. The balances are shown on the basis of 1 tonne of MPW feedstock. The material flows are represented in black, energy flows in red, and carbon distribution in green with percentage figures for each major material stream. The potential material and energy paths are shown in dotted black and red lines, respectively. Several assumptions were made for these balances:

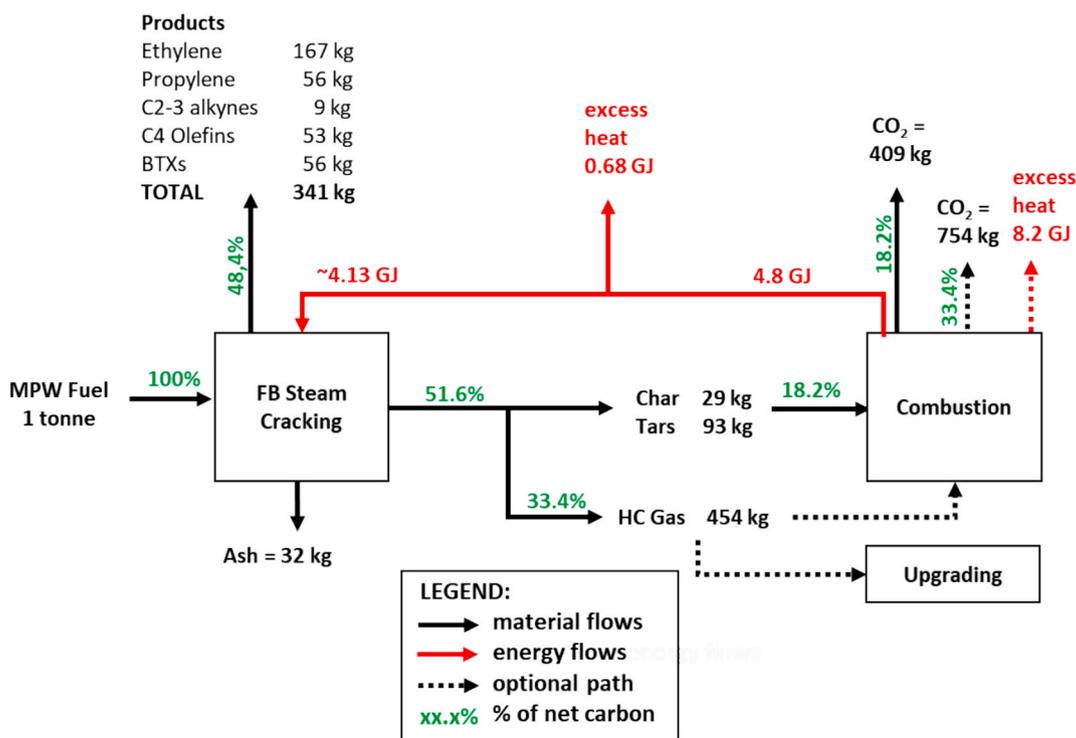


Fig. 15. Mass, energy, and carbon balance for Case 1 – direct steam cracking of MPW feedstock at 750 °C.

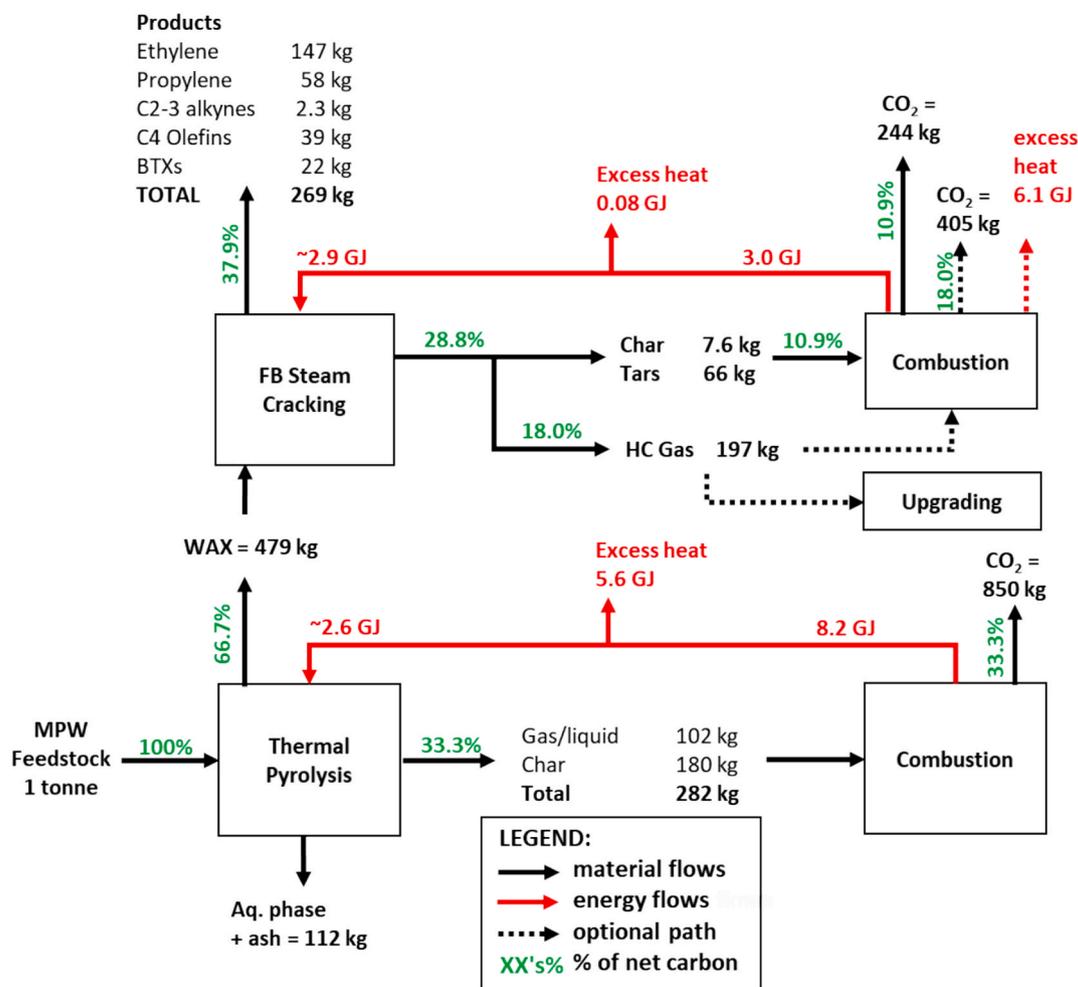


Fig. 16. Mass, energy, and carbon balance for Case 2 – thermal pyrolysis of MPW to WAX product, followed by FB steam cracking of WAX at 750 °C.

- It is assumed that the thermal pyrolysis process is decentralized, while the steam cracking process is centralized at a major petrochemical site.
- The WAX pyrolysis product is sent to steam cracking, while the remaining pyrolysis fractions are either disposed (aqueous fraction, ash) or combusted for energy recovery (char, pyrolysis gases). The generated energy is used to meet the energy demand of the pyrolysis process.
- In the steam cracking process, char and tar are combusted for energy recovery, using the generated energy to meet the energy demand of the steam cracking process. The other non-primary product fractions can either be combusted for energy recovery or sent for upgrading.
- Energy demand for steam cracking is estimated as 14 % of the LHV of the incoming feedstock.
- The energy demand for pyrolysis is estimated at 2.6 MJ/kg of feedstock (based on average of literature figures for pyrolysis of polyethylene [22,23]).
- Heating values for intermediate products are calculated with the modified Dulong's formula, based on the C, H, O wt% of the product species [24].
- The material and energy input requirements for upgrading and potential carbon capture are not included in the scope of the balance but are addressed further in the discussion.

Further to the assumptions listed above, the product yields determined from steam cracking experiments (Figs. 11 & 12) were normalized to give 100 % carbon balance closure. This normalization is

reasonable due to high pre-normalized carbon balance closure for the MPW and WAX experiments.

The balances presented in Figs. 15 and 16 indicate that in both cases the energy input required by FB steam cracking can be met via combustion of the char and tar that is generated in the steam cracking process. Similarly, for the thermal pyrolysis case, the pyrolysis energy demand can be met by combustion of pyrolysis char and pyrolysis gases. Furthermore, combustion of the char and tar produces excess heat, which can be utilized on-site or can be converted into electrical energy.

When comparing primary product yields, Case 1 results in the higher yields than Case 2. One differentiating aspect of the scenarios is the decision on utilizing the hydrocarbon gas byproducts of steam cracking. In Figs. 15-16, the option for combustion of these byproducts is shown with the associated CO₂ emissions and heat production. However, these byproducts can be upgraded to useful products instead of being combusted for energy recovery. The main components in the hydrocarbon gas byproduct consists of H₂, CH₄, CO, CO₂, C5-6 olefins, and paraffins. From these species, the minor amounts C5-6 olefins and C5 + paraffins can be separated and recycled back to the steam cracking unit to further improve primary product yields. The lower order paraffins (ethane, propane, butane) can be processed in an ethane cracker, if available, to further yield additional ethylene product. If no ethane cracker is available, these fractions can be combusted for energy recovery. The highest fraction of the byproducts is made up of CH₄, CO, CO₂, and H₂. Since CO is a poison for the catalysts used in catalytic hydrogenation (process used to convert C₂H₂ to C₂H₄), CO is typically converted to CO₂ through the water-gas shift reaction: CO + H₂O → CO₂ + H₂. The CO₂ is then

scrubbed and removed from the byproduct stream. The water–gas shift process yields additional hydrogen and production of excess heat. With conversion of CO to CO₂, the remaining useful products are CH₄ and H₂. Both are commercially valuable products that can be sold or utilized elsewhere at the plant site.

To consider conversion of the steam cracker byproduct gases to useful products, rather than simply combusting the byproduct gases, additional calculations were performed. Table 3 re-summarizes the main product yields of steam cracking for the cases presented above but adds the yields of CH₄ and H₂ products that can be realized with the water–gas shift. Table 3 also quantifies the “recyclable” fraction of the steam cracker byproducts stream (C5-6 olefins, paraffins). Furthermore, to compare the cases presented above with the incineration of MPW feedstock, which is how medical waste material is currently utilized, “Case 3 – Incineration” is added to Table 3. To facilitate comparison of the steam cracking cases with incineration of MPW feedstock, Table 3 presents an estimate of what would be required to mitigate the combustion-based CO₂ emissions at the steam cracking/incineration site through carbon capture and utilization (CCU). Several key assumptions are made for CCU estimates:

- MPW feedstock contains 23 wt% wood fiber and 9.1 wt% viscose (produced from wood fiber). Carbon contained in these fractions is biogenic and thus does not contribute to the overall process fossil CO₂ footprint.
- Since it is assumed that the pyrolysis site is decentralized, and likely to be of small scale, carbon capture at these sites would be cost prohibitive. As such, carbon capture and utilization (CCU) is only considered for the steam cracking/incineration site.
- CCU at the steam cracking/incineration site consists of capturing the CO₂ and carrying out methanol synthesis as per the following reaction $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$
- CO₂ is captured an amine-based scrubbing system, with an estimated heat requirement of 3.7 MJ/kg CO₂ for amine regeneration [25,26]. Electricity input and cooling requirements for the capture process are not considered.
- Heat generated during methanol synthesis is calculated as 50 KJ/mol CO₂

All material flow figures in Table 3 are expressed in kg/tonne of MPW feedstock, and in percent of net MPW carbon. Energy demand and output figures are in GJ/tonne of MPW feedstock. The results presented in Table 3 show that CH₄ and H₂ yields, as well as the amounts of the potentially recyclable byproducts, follow the same trend as the yields of the primary products. Yields are the highest for Case 1, followed by Case 2. Case 3, of course, yields no primary or secondary products. The excess energy production from combustion of pyrolysis byproducts and steam cracking byproducts shows the opposite trend to the product yields. Energy produced is highest for Case 3, followed by for Case 2, and Case 1, respectively.

In considering potential CO₂ emissions, it is important to note that about 13.9 % of the carbon contained in medical waste is biogenic. Thus, assuming that biogenic CO₂ emissions are carbon neutral, less than 100 % of the potential process CO₂ emission would have to be captured and utilized to consider the overall process carbon neutral. With respect to CCU, the results presented in Table 3 show that only Case 1 and Case 3 can achieve fossil CO₂ neutrality. This is because CCU is not considered for the pyrolysis sites due to the assumption that pyrolysis sites are decentralized and smaller scale, thus making CCU at these sites cost-prohibitive. The CCU process, that consists of amine-based CO₂ capture and subsequent methanol synthesis, requires energy and H₂ inputs. While Case 1 and Case 2 require import of heat to facilitate CCU, Case 3 can cover the energy demand for CCU from MPW feedstock combustion. In terms of H₂ input into the CCU process, all cases require an import of H₂. Case 3 has the highest demand, followed by a much lower H₂ demand for Case 1, and an even lower demand for Case 2.

Table 3

Steam cracking product yields, energy, and carbon balances, and energy and material requirements for CCU.

	Case 1 – Direct		Case 2 – Indirect		Case 3 – Incineration	
Primary Products	kg/t MPW	%C	kg/t MPW	%C	kg/t MPW	%C
Ethylene	167	23.2	147	20.5	–	–
Propylene	56	7.8	58	8.1	–	–
C2-3 Alkynes	9	1.4	2	0.3	–	–
C4 Olefins	53	7.6	39	5.6	–	–
BTX	56	8.4	22	3.4	–	–
TOTAL	341	48.4	269	37.9	–	–
Secondary Products	kg/t MPW	%C	kg/t MPW	%C	kg/t MPW	%C
CH ₄	89.2	10.9	74.6	9.1	–	–
H ₂	19.4	–	6.3	–	–	–
Potentially Recyclable Steam Cracking Byproducts	kg/t MPW	%C	kg/t MPW	%C	kg/t MPW	%C
C5-6 Olefins, Paraffins	34.8	4.8	29.0	3.9	–	–
CO₂ Emissions	kg/t MPW	%C	kg/t MPW	%C	kg/t MPW	%C
CO₂ Emissions – Combustion at Pyrolysis Site	0	0	850	37.7	0	0.0
CO₂ Emissions – Combustion at Steam Cracking Site	409	18.2	244	10.8	2254	100.0
CO₂ Emissions – Steam Cracking Product Steam	427	19.0	98	4.4	–	–
Biogenic CO₂	312	13.9	312	13.9	312	13.9
Net fossil CO₂ Emissions	524	23.3	880	39.1	1941	86.1
Energy Production – Combustion	GJ/t MPW		GJ/t MPW		GJ/t MPW	
Pyrolysis Site	–		5.6		–	
Steam Cracker Site	0.68		0.08		29.50	
Requirement for CCU of CO₂ Emissions	kg/t MPW	%C	kg/t MPW	%C	kg/t MPW	%C
CO₂ to be captured	524	23.3	343	15.2	1941	86.1
H₂ required for CCU to MeOH	72.0	–	47.1	–	266.8	–
Energy required for CCU to MeOH	GJ/t MPW		GJ/t MPW		GJ/t MPW	
Heat input required for amine regeneration	1.94		1.27		7.18	
Heat produced in methanol synthesis	0.60		0.39		2.21	
Net heat input required	1.34		0.88		4.98	
CCU Products	kg/t MPW	%C	kg/t MPW	%C	kg/t MPW	%C
MeOH Product	381.6	23.3	249.4	15.2	1413.4	86.1
Net Fossil CO₂ Footprint for Scenario	kg/t MPW	%C	kg/t MPW	%C	kg/t MPW	%C
Net fossil CO₂ footprint	0	0.0	538	23.9	0	0.0

Finally, the carbon recycling efficiencies for the direct steam cracking and pyrolysis cases are summarized in Table 4 in terms of % of fossil carbon that is incorporated into primary, secondary, and CCU products; i.e. the % carbon figures from Table 3 were normalized to the fossil carbon content of the medical waste (86.1 % of the carbon in the medical waste is fossil carbon, while 13.9 % is biogenic). The calculated values assume that C5-6 olefins and paraffins can be recycled, contributing equally to primary and secondary products.

The summary presented in Table 4 shows that only Case 1 can achieve full fossil carbon recycling. Case 2 cannot achieve 100 % efficiency since the CO₂ released from incineration of pyrolysis byproducts at the decentralized pyrolysis sites exceeds CO₂ emissions that can be considered biogenic due to the MPW's biogenic content.

4. Summary and further discussion

In comparing the presented cases on the basis of product yields, energy balance, carbon neutrality, and fossil carbon recycling efficiency, direct centralized steam cracking of MPW feedstock (Case 1) appears to have several advantages, these include:

- Higher primary and secondary product yields
- Carbon neutrality with CCU
- Higher incorporation of fossil carbon into primary and secondary products
- 100 % overall fossil carbon recycling efficiency

The indirect case (Case 2) assumes thermal pyrolysis pre-processing medical waste to WAX at a decentralized site, with subsequent transport of WAX to a centralized site for steam cracking. This path results in lower primary and secondary steam cracking product yields and lower fossil carbon recycling efficiency. However, the pyrolysis process reduces the feedstock weight to 47.9 wt%, while retaining 66.7 % of the carbon contained in the original MPW feedstock. This occurs due to the release of most of the oxygen, ash, and some of the carbon with the pyrolysis byproducts. The feedstock transformation that occurs in the pyrolysis process results in several key practical advantages.

Logistical advantages: Medical plastic waste in its original form has a very low bulk density. The supply points of medical plastic waste (hospitals, medical care facilities) are decentralized. The low feedstock density and decentralized supply locations are likely to make medical waste transport to a centralized steam cracking plant uneconomical vs. taking the feedstock to local pyrolysis plant. The transport of the pyrolysis WAX feedstock to a centralized steam cracking site holds several key advantages vs. transport of the original MPW feedstock:

- WAX feedstock has a higher density than the original plastic waste feedstock
- WAX feedstock reduces the transport weight to 47.9 wt% of the original plastic waste feedstock, which will reduce transport-associated CO₂ emissions by roughly half vs. transport of MPW feedstock
- WAX feedstock can be easily handled as it liquifies at 50–60 °C, so it can be pumped and transported by means of tanker truck or rail car

Reduced need for feedstock preparation: Experience with large-

Table 4
Fossil carbon recycling efficiency and distribution.

	Case 1 – Direct	Case 2 – Indirect
Primary Products	59 %	46 %
Secondary Products	15 %	13 %
CCU Products (methanol)	26 %	18 %
Fossil carbon recycling efficiency	100 %	77 %
<i>All figures in % fossil carbon</i>		

scale fluidized bed systems indicates that MPW feedstock would need to be milled and pelletized for efficient feeding into the FB steam cracker with an extrusion feeder. Feedstock milling and pelletizing is costly and would be avoided in pyrolysis case because large batch pyrolysis reactors can accept MPW feedstock either in its original form, or with minimal pre-processing, such as shredding. At the steam cracking site, WAX feedstock can be easily fed into the FB steam cracker in liquid form.

Cleaner input into the steam cracking process: Taking only intermediate WAX feedstock to the FB steam cracking plant means that most of the ash impurities, and heteroatoms such as oxygen and chlorine, are rejected in the pyrolysis process. Avoiding ash and heteroatoms in the FB cracker feedstock is an advantage because ash, and chlorine are known to result in corrosion and agglomeration issues in high-temperature fluidized bed conversion processes [27]. Rejecting most of the oxygen at the pyrolysis stage is advantageous as it limits CO and CO₂ release at the steam cracking site, where excessive CO and CO₂ formation can overwhelm the post-cracker gas treatment units. Further to removing impurities, pyrolyzing medical waste to a WAX feedstock greatly improves the homogeneity of the input material to the steam cracking process. With increased feed homogeneity, it should be possible to optimize steam cracker operation to a greater degree than if fed with highly heterogeneous medical plastic waste.

5. Key limitations and Future work

The broad scope of the study warrants acknowledgement of several key limitations of the presented methodology and results. These are outlined below:

Feedstock variability: The results of the pyrolysis and steam cracking experiments are limited to the MPW feedstock used in this study, which consisted of unused medical waste products. In a full-scale implementation of the steam cracking process, whether via the centralized or decentralized approach, medical product waste feedstock would have a higher moisture content due usage in medical procedures, higher share of inorganic contaminants due to co-disposal of non-carbon-based materials and have a varying composition of polymers and biogenic materials. Thus, the FB steam cracking product composition would vary. This variability was not evaluated in this study. Future investigations will evaluate a wide variety of other potential plastics-rich waste feedstocks.

Feedstock availability: Since the proposed FB steam cracking process is meant to replace conventional fossil fuel cracking, the availability of the plastic-rich waste feedstock would have to match the scale of the displaced fossil resources. For example, in Sweden, most of the light olefin production occurs at the Stenungsund steam cracking plant which uses approx. 300 kt/year of naphtha feedstock [1]. Replacing the olefin production capacity of such a plant with FB steam cracking of waste plastics would be challenge. Scaling the MPW resource considered in this study for the Västra Götaland region (1.3 kt/year MPW produced, 1.8 M population) to all of Sweden (10.6 M population), indicates that only approx. 7–8 kt/year of MPW resource is generated in all of Sweden. Thus, to replace naphtha cracking with FB steam cracking of waste plastics, multiple sources of plastic wastes, well beyond medical plastic waste, would need to be utilized (packaging waste, industrial waste plastics, etc.). While creating a collection system for a wide variety of waste plastic streams is challenging enough, the feedstock variability that would come with multiple waste streams would need to be considered in the overall FB steam cracking process scheme. Both the feedstock sourcing and variability problems were not addressed in this work. However, the experimental results presented here contribute to the ongoing buildup of the knowledge base of FB steam cracking of multiple waste plastics streams.

Liquid feedstock cracking: As mentioned in the discussion, experiments with POil showed poor carbon balance closure due to the inability to quantify the observed soot formation. As such, the results for the POil experiments represent an incomplete overview of catalytic

pyrolysis pre-treatment strategy. Future experimental work will focus on optimizing the liquid feedstock feed rate to optimize light olefin yields by maintaining a higher steam to hydrocarbon ratio. The product analysis methodology will also be developed to detect and quantify soot formation, such that the carbon balance can be closed.

Material, energy and carbon balances: The material, energy, and carbon balances presented in the study were developed using simplifying assumptions and covered the scope of the main chemical processes: pyrolysis, steam cracking, CO₂ capture, and methanol synthesis. This approach allowed for a first-look assessment of the direct and indirect FB steam cracking pathways, showing the relative product yield potentials. Future work should focus on a more in-depth investigation that considers unrecoverable heat and energy losses, as well as energy and material requirements for feedstock preparation, transport, pyrolysis product separation, FB steam cracking product gas filtration, product separation, and byproduct upgrading.

Feedstock transport CO₂ emissions: The cost and CO₂ emissions associated with the transport of the medical plastic waste or the intermediate pyrolysis products is a central consideration in the evaluating the centralized vs. decentralized approaches. However, the scope of the study did not include the investigation of a specific geographic scenario. Rather, the study demonstrated the practical advantages that can be realized from using thermal pyrolysis as a feedstock pre-treatment step. Of these, the reduced transport weight and ease of handling of a WAX product vs. raw MPW feedstock would be more beneficial in a low population density geography, where large transport distances would have a high cost and transport CO₂ emissions impact. Consideration of a specific geography for applying the waste plastics FB steam cracking process would require a detailed study of feedstock transport along with a full lifecycle analysis of the overall CO₂ emissions associated with all the steps involved in collection, pre-treatment, and processing of the feedstock.

6. Conclusions

Centralized FB steam cracking of medical plastic waste (MPW) was evaluated vs. decentralized pyrolysis pre-treatment of MPW to a hydrocarbon-rich and easily transportable fraction followed by transport and subsequent centralized FB steam cracking of this intermediate fraction. This evaluation was performed experimentally. MPW pyrolysis trials were carried out in a lab-scale pyrolysis reactor. Two pyrolysis cases, thermal and catalytic, were tested. Thermal pyrolysis yielded a transportable WAX fraction, and catalytic pyrolysis yielded a transportable pyrolysis oil (POil) fraction. The three feedstocks (MPW, WAX, POil) were subjected to FB steam cracking in a lab-scale FB steam cracking reactor. MPW and WAX steam cracking experiments showed good results, while the POil steam cracking experiments suffered from suboptimal conditions that resulted in poor carbon balanced closure. The MPW and WAX cases, representing the centralized and decentralized cases, respectively, were further evaluated through development of basic material, energy, and carbon balances. These balances included calculations to simulate carbon capture and utilization (CCU) of the central FB steam cracking site's CO₂ emissions to produce methanol through CO₂ capture with subsequent methanol synthesis.

The investigation showed that centralized direct FB steam cracking of MPW feedstock results in the highest product yields and that the process can theoretically be implemented to achieve 100 % recycling of the feedstock's fossil-sourced carbon into primary, secondary, and CCU products. Assessment of the decentralized approach showed that thermal pyrolysis pre-treatment of MPW can produce an intermediate WAX feedstock which contains 66.7 % of carbon content but constitutes 47 wt % of the original MPW feedstock. When steam cracked, the WAX feedstock can still achieve high product yields and up to 77 % recycling of MPW's fossil-sourced feedstock to primary, secondary, and CCU products. The study highlights that the reduced product yields associated with the pyrolysis pre-treatment step are balanced with several practical

advantages. These include reduced feedstock transport weight, increased ease of feedstock handling, homogenization of the input to the FB steam cracking process, as well as rejection of oxygen, heteroatoms, and inorganic contaminants in the pyrolysis pre-treatment process.

CRedit authorship contribution statement

Ivan Gogolev: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Nidia Diaz Perez:** Validation, Methodology, Investigation, Data curation. **Chahat Mandviwala:** Validation, Formal analysis, Data curation. **Renesteban Forero Franco:** Validation, Data curation. **Ann-Christine Johansson:** Writing – review & editing, Validation, Supervision, Project administration, Conceptualization. **André Selander:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis, Data curation. **Martin Seemann:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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