WHITE PAPER

CIRCULAR ADVANCED RECYCLING OF PLASTICS THROUGH PYROLYSIS

Qenos

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Learn about how waste plastics are turned into circular plastics through pyrolysis-based advanced recycling
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March 2022

Pyrolysis of waste plastics is a promising pathway to recover plastics that are less suitable for mechanical recycling such as household soft plastics and mixed plastics. It is one of the most dominant techniques classified as advanced recycling, which is fully circular when the output is used as feedstock for new plastic production. This white paper provides an insight into pyrolysis techniques, the plastic types for which it is most suitable, the products it generates, and how it can be integrated with existing plastic production processes to produce circular plastics.

PYROLYSIS – ALSO KNOWN AS THERMAL ANAEROBIC CONVERSION – IS THE THERMAL DECOMPOSITION OF MATERIALS AT ELEVATED TEMPERATURES IN AN INERT ATMOSPHERE. PYROLYSIS IS INCREASINGLY BEING USED AS A METHOD FOR CONVERTING WASTE PLASTIC INTO PYROLYSIS OIL AND GAS THAT CAN EITHER BE USED AS FUELS (WASTE TO ENERGY) OR AS FEEDSTOCK IN THE PRODUCTION OF NEW PLASTIC (WASTE PLASTIC TO PLASTIC).

There are many different pyrolysis technologies, each producing a unique mix of gasses, liquids and solids. In a circular process where new virgin plastic is manufactured from waste plastic, the pyrolysis oil is further treated and upgraded and then converted in a steam cracker into the olefins used to make plastics such as polyethylene and polypropylene in the first place.

USING PYROLYSIS FOR CHEMICAL RECYCLING

Pyrolysis is an emerging technology for the chemical recycling of waste plastics that are difficult to recycle in conventional mechanical recycling processes. It is reaching maturity now with commercial plants in operation and a massive rollout of this technology expected across this decade. Mixed plastics derived from the residuals of the various mechanical recycling processes and plastics that are contained in municipal solid waste represent more than half of all plastic waste generated.

Figure 1 shows how mixed plastic waste can be converted back to virgin quality polymers in a fully circular process. Mixed plastic bales need to undergo sorting to remove incompatible plastics and other contaminants. Shredding will reduce the particle size to enable feeding of the mixed plastics into a pyrolysis process. Pyrolysis will convert the mixed plastics to a mixture of hydrocarbons by breaking the chemical bonds of the long chain polymers to produce smaller hydrocarbons. Fractionation and purification of the crude pyrolysis oil will isolate the fractions such as naphtha suitable for feeding into a steam cracker to produce monomers such as ethylene and propylene that are then polymerised using existing polymerisation plants.

Further detail on all the steps of this chemical recycling process is provided in the remainder of this document.

PYROLYSIS OIL

When waste plastics are processed through a chemical recycling pyrolysis process, a number of usable products are produced.

Starting with the lightest product which is a combination of C1-C5 compounds normally including the lighter gases such as methane, moving up to ethane, but also the building blocks of plastics ethylene, propylene, butenes, isobutylene, and others. A waste plastic pyrolysis plant collocated with an integrated steam cracker facility could use nearly the entire cracked gas stream for producing renewable recycled circular monomers.

The liquid fraction produced from the pyrolysis of waste plastic is defined by the "cut" from the distillation column. The cuts are defined by the temperature of the final boiling point of the liquid separated in the distillation column. Common cuts are 200°C, 400°C and 600°C.

The 200°C cut is normally referred to as the light cut or Naphtha cut and is the most desirable cut for injecting into a steam cracker to produce renewable recycled circular monomers such as ethylene and propylene to produce polyethylene and polypropylene, respectively.

The 400°C cut is the medium cut and can be injected into some steam crackers that can accept a heavier feed to produce renewable recycled circular monomers. Alternatively, this middle distillate fraction can be used as diesel or fuel oil.

The 600°C cut is the heavy cut and is just short of the asphalt range of feedstock and can be injected into some steam crackers when blended with the medium or light cut feedstock to produce renewable recycled circular monomers.

The final product produced by pyrolysing waste plastic is typically a char which is made of the inert materials and the left-over cracked carbon or coke residue from the process. This material can be used in road surfacing or in building material applications.

As demonstrated above, the vast majority of pyrolysis products can be used as petrochemical feedstock for new plastic production through steam cracking with minimal loss to energy recovery via fuels. The various liquid cuts can also be upgraded into a single fraction suitable as steam cracker feedstock via hydrocracking, as described in the text below.

USING PYROLYSIS OIL AS A FOSSIL FUEL REPLACEMENT

Pyrolysis oil can alternatively be refined into fuels such as gasoline, diesel, jet fuel and fuel oil. This is most efficiently done in a refinery where the crude pyrolysis oil is mixed with fossil crude oil and then processed using conventional refining techniques such as distillation, reforming, cracking, etc.

Refineries are optimised to maximise the production of liquid fuels, specifically gasoline, diesel and jet. The yield of petrochemical feedstock such as naphtha, LPG and refinery grade propylene is below 5%, therefore more than 95% of the pyrolysis oil is converted to fuels. The refinery route represents mostly a non-circular pathway and should be considered more as waste to energy than chemical recycling. The potential to recycle waste plastics is lost in this case as fuels are converted to CO_2.

CONVENTIONAL FEEDSTOCK FOR PLASTIC MANUFACTURING

Commodity plastics like polyethylene and polypropylene have been produced traditionally from oil or gas feedstock. Ethane gas, liquid petroleum gas (LPG) or naphtha are fed to a steam cracker, which transforms the feedstock into base chemicals such as ethylene, propylene, butadiene and benzene. Qenos' plants use ethane as the primary feedstock, with some supplementation from LPG, to produce ethylene monomer and a small proportion of byproducts. Ethylene monomer is polymerised to produce polyethylene, which is then converted by Qenos' customers into packaging and durable goods such as pipes.

WHICH WASTE PLASTIC FEEDSTOCK IS SUITABLE FOR PYROLYSIS AND PLASTICS MANUFACTURING

Waste plastic feedstocks in order of preference are LLDPE / LDPE, HDPE, PP and PS.

Feedstock containing oxygen (e.g. PET) and/or nitrogen (e.g. Nylon, ABS, urethane, aramid) are to be avoided. Together oxygen and nitrogen can form NOX which can create explosive compounds in the downstream section of a steam cracker. Nitrogen forms unwanted NH_3. Feedstock containing chlorine (e.g. PVC) must be minimised as it forms highly corrosive HCl in

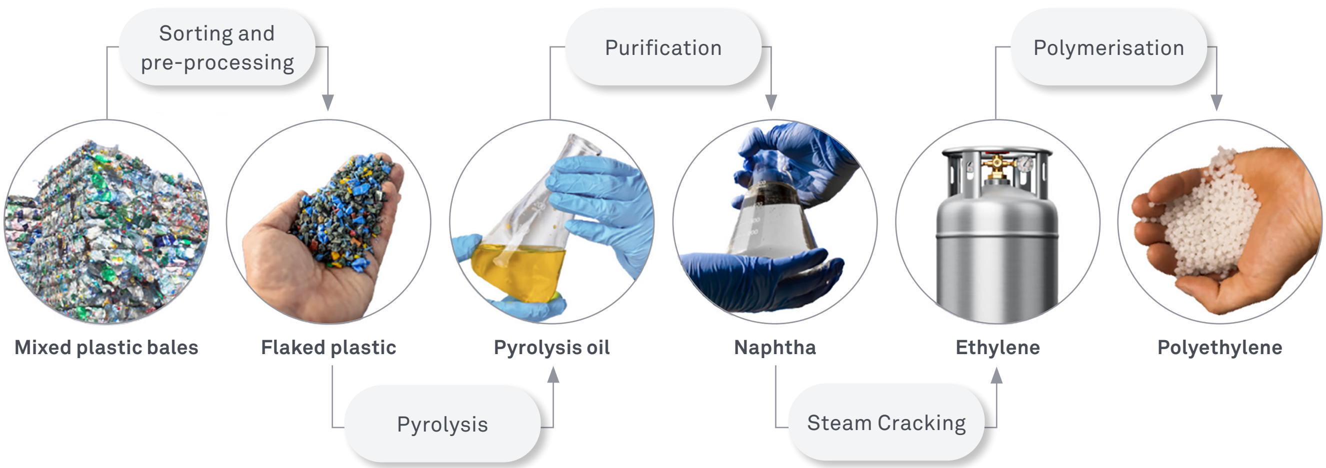

Figure 1. Process flow to chemically recycle mixed plastic waste to virgin quality polyethylene.

the process and chlorides that cannot be tolerated in the steam cracking process. Moisture and oxygen also need to be excluded from the pyrolysis reactor as they will increase the formation of carbon monoxide (CO) and carbon dioxide (CO_2), which are of low value.

To achieve the highest yield of ethylene and propylene, cracker feedstock has a high paraffinic content and contains very low aromatic and olefinic content. Paraffinic hydrocarbons increase the yield of ethylene and propylene whereas isomeric hydrocarbon yield high volumes of methane, which can only be used as a fuel gas. Aromatic and olefinic hydrocarbons in the feedstock will lead to faster coking of the cracker furnace tubes and thus shorter run lengths affecting overall cracker economics. The plastic feedstock as well as the pyrolysis process influence the product mix of paraffinic, isomeric, olefinic and aromatic hydrocarbons. Selection of the right feedstock and process is therefore critical to optimise the yield of the desired polyolefin monomers.

NON-REFINERY TREATMENT OPTIONS FOR UPGRADING PYROLYSIS OIL FOR PLASTICS MANUFACTURING

Filtration is a common process that removes the carbon particles, metals and other contaminants from the product. Micro filtration (<1 micron) can significantly reduce the presence of inert materials and insoluble elements in the product which could clog filters when the product is injected into a steam cracker or a refinery.

Chemical treatment can remove some of the contaminants by chemical reaction and precipitation during the process. These methods remove organic and inorganic compounds from the plastics during the reaction process and the byproducts become part of the pitch or char removed from the bottom of the reactor.

Antioxidant can be injected into the liquid stream immediately after condensation to stabilize the product and stop further oxidation of the product. This is particularly relevant when a waste plastic pyrolysis reactor is not integrated with a steam cracker and feedstock needs to be transported by road, rail or sea.

Hydrogenation is a process where hydrogen is introduced to a catalyst bed under temperature and pressure to stabilize the mono- and di-olefin content in the renewable chemical feedstock and to remove process impurities that are detrimental to the reliable operation of the downstream petrochemicals or refining units. Depending on the overall strategy for the use of the pyrolysis oil the hydrogentation step can include multiple processing steps, up-to 3 separate stages including di-olefin saturation, mono-olefin saturation and hydrotreating or other process to remove sulphur, nitrogen, oxygenates, metals and other components.

Dilution of pyrolysis oil with fossil feedstock is another strategy to reduce the concentration of contaminants and enable the use the oil as feedstock in a steam cracker. The effectiveness of this strategy will depend on the relative volumes of the fossil and pyrolysis feed, the quality of the pyrolysis oil and the quality of the fossil feedstock.

If the complete pyrolysis oil fraction is to be used as feedstock for a steam cracker a hydrocracking step would be advised. This would allow the conversion of distillate and heavy vacuum gasoil cuts into naphtha and LPG, which are excellent steam cracker feedstock for ethylene and propylene production.

> “ PYROLYSIS IS AN EMERGING TECHNOLOGY FOR THE CHEMICAL RECYCLING OF WASTE PLASTICS THAT ARE DIFFICULT TO RECYCLE IN CONVENTIONAL MECHANICAL RECYCLING PROCESSES.

MASS BALANCE CHAIN OF CUSTODY MANAGEMENT

The mass balance approach is emerging as the preferred chain of custody management tool for the tracing of recycled content from the source through to finished products. The mass balance approach makes it possible to track the amount and sustainability characteristics of circular content across the value chain and attribute it based on verifiable bookkeeping.

The mass balance principle upholds that when recycled feedstock is co-processed with fossil feedstock, the recycled product content can be allocated to selected products (Figure 2). This can apply to single factories but also to integrated complexes between petrochemical facilities and refineries as is often the case in chemical manufacturing. It allows up to 100% of recycled content to be allocated to a desired product.

The mass balance bookkeeping process is typically verified and certified by a third party scheme. This requires the whole value chain from waste plastic point of origin such as a municipal recovery facility to the brand owner who places the final plastic containing product on the market.

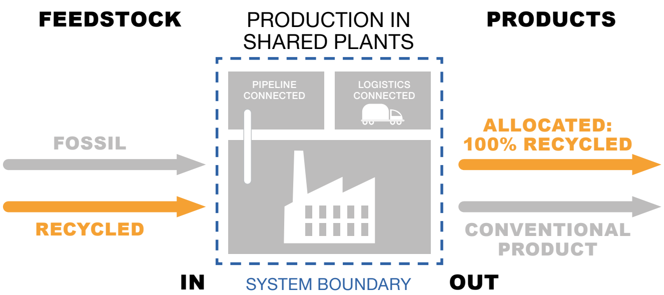

Figure 2. Mass Balance Principle (from Ellen MacArthur Foundation white paper).

CONCLUSIONS

Pyrolysis of waste plastics represents an important pathway to increase plastics' circularity and is highly complementary to mechanical recycling efforts. The technology for pyrolysis, purification, and using the output as a feedstock for plastics manufacturing is proven at commercial scale and expected to ramp up significantly this decade to assist with the meeting of global targets for plastic waste reduction, increasing recycled content, and lowering greenhouse gas emissions. Importantly, this will only be achieved when the yield of plastics from pyrolysis oil is maximised and the fraction of pyrolysis oil that is used as a fuel is minimised. Integration of waste plastic pyrolysis with steam cracking is the pathway to making advanced recycling circular.

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