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Material Value Chains

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Luntama, Matti Nieminen & Jutta Laine-Ylijoki**

# **Thermal conversion of plastic- containing waste: A review**



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**Name of the report: Thermal conversion of plastic-containing waste: A review**

**Key words: plastic recycling, pre-treatment, thermal conversion, pyrolysis, PTL, gasification**

## Summary

We have a dual problem: resources are depleting and wastes are accumulating. A development of novel, efficient pre-treatment and conversion method for heterogenous waste streams would not only provide an answer to this dilemma but introduction of these systems could also reduce emissions of greenhouse gases, and importantly provide a boost to local economy.

The use of thermal conversion methods such as pyrolysis and gasification as a recycling method for plastic-containing waste is not yet a common practice although the commercialization of these methods has been pushed forward for a long. However, the recent developments of thermal conversion methods as well as the pressure to move towards circular economy create an interesting starting point for the final commercialization.

This review identifies suitable flows of plastic and rubber containing waste streams for thermal conversion and summarises the most potential pyrolysis and gasification concepts. In addition, the need for pre-treatment and characterization of the feedstock material is discussed.

Based on the review, there seems to be room for thermal conversion of plastic-containing wastes. In order to overcome the obstacle of present demonstration initiatives focus should be put on improving the efficiency and decreasing the costs of waste pre-treatment. Integration of technologies is here the key issue. The target should be to minimize the pre-treatment steps and handle heterogenous waste streams. The characteristics of the feedstocks as feed for thermal processes should be investigated. It is of great importance to form a consortium covering the whole chain from plastic waste producers to liquid end-users. A comprehensive risk management plan should also be carried out and the business and operation environment clarified. Also development of technologies should be included.

Helsinki, January 2017





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## List of acronyms

ABS	Acrylonitrile butadiene styrene
AIV	Silage for cattle
ASR	Automotive shredder residue, "car fluff"
BFB	Bubbling fluidised bed
Br	Bromide
BTL	Biomass-to-liquids
C&D	Construction and demolition
C1 ... Cn	Hydrocarbons
C <sub>2+</sub>	Carbon ion
Ca(OH) <sub>2</sub>	Calcium hydroxide
CEMS	Continuous emission measurement system
CFB	Circulating fluidised bed
CH <sub>3</sub> OH	Methanol
CH <sub>4</sub>	Methane
CHN analysis	Carbon hydrogen nitrogen analysis
CHP	Combined heat and power
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
CSBR	Conical spouted bed reactor
DFB	Dual fluidised bed
DME	Dimethyl ether
DTO	See: SDTO
EF	Entrained flow
ELB	End-of-life boat
ELV	End-of-life vehicle
EU25	Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden and United Kingdom
EU27+2	EU27 (=EU25 + Bulgaria and Romania) + Switzerland and Norway
EU28	EU25 + Bulgaria, Croatia and Romania
FPBO	Fast pyrolysis bio-oil
FT	Fischer-Tropsch synthesis
FTO	Fischer-Tropsch-to-olefins
GC-MS	Gas chromatography-mass spectrometry
H <sub>2</sub>	Hydrogen
H <sub>2</sub> O	Water
HC	Heat carrier
HCl	Hydrochloric acid
HCN	Hydrogen cyanide
HF	Hydrofluoric acid
HIPS	High impact polystyrene
ICP-MS	Inductively coupled plasma mass spectrometry
MMA	Methyl methacrylate
MRF	Material recovery facility
MRL	Manufacturing readiness level
MSW	Municipal solid waste
MTO	Methanol to olefins
NH <sub>3</sub>	Ammonia





NIR	Near infrared
NO <sub>x</sub>	Nitrogen oxides
O <sub>2</sub>	Oxygen
odt	Oven dried tonne
PA	Polyamide
PA-6	Nylon
PBDD/Fs	Polybrominated dibenzo dioxins/furans
PC	Pulverized coal
PCDD/F	Polychlorinated dibenzo dioxins and furans
PDU	Process development unit
PE	Polyethylene
PE-HD	High-density polyethylene
PE-LD	Low-density polyethylene
PE-LLD	Linear low-density polyethylene
PET	Polyethylene terephthalate
PF	Phenol resin
PMMA	Polymethyl methacrylate
POM	Polyoxymethylene
POP	Organic persistent pollutant
PP	Polypropylene
PS	Polystyrene
PSW	Plastic solid waste
PTL	Plastic to liquids
PUR	Polyurethane
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
PVDC	Polyvinylidene chloride
Py-GC/MS	Pyrolysis–gas chromatography–mass spectrometry
REACH	Registration, evaluation, authorisation and restriction of chemicals
Sb	Antimony
SBR	Styrene-butadiene rubber
SDTO	Syngas via dimethyl ether to olefins
SNG	Synthetic natural gas
SO <sub>2</sub>	Sulphur dioxide
SR	Shredder residue
SRF	Solid recovered fuel
TC	Total carbon
TOC	Total organic carbon
tpd	Tonnes per day
TRL	Technology readiness level
WEEE	Waste electrical and electronic equipment
WtE	Waste-to-energy
XRF	X-ray fluorescence



## 1 Introduction

Today, regulations and norms guide waste from landfilling to material utilisation and secondly to energy use. For example, in Finland a ban for landfilling organic waste came into force in January 2016, and also the European Commission has set higher recycling targets e.g. for municipal and packaging wastes. In addition, the long-term objective of societies is to replace fossil and first generation renewable fuels and solvents with liquids and gases produced from low-value organic by-products and wastes, such as municipal and industrial waste streams.

Organic and other plastic-containing waste forms complex and heterogeneous stream that is currently poorly exploited. In 2014, around 26 million tonnes of post-consumer plastic waste was generated in Europe, of which less than one third was collected for recycling. Thus, there is a clear need either to boost the current recycling solutions for plastic-containing complex waste streams or create new approaches beside them, to be able to fulfill the targets set. Thermal conversion could be one answer to this dilemma as it poses a necessary contribution to converting organic and plastic-rich complex waste feedstocks into secondary resources in those many cases where direct reuse or mechanical recycling are not viable.

Thermal conversion methods such as pyrolysis and gasification are recognized as feedstock recycling technologies when the products are used for the production of fuels or raw chemicals. However, their use as a recycling method for plastic-containing waste is not yet a common practice although the commercialization of these methods of has been pushed forward for long. For example, patent applications on “plastic pyrolysis” during the past 27 years are shown in Figure 1. It is seen that there has been considerable interest on this topic globally during a number of years, and the interest is continuous. However, there has been obstacles towards commercialization.

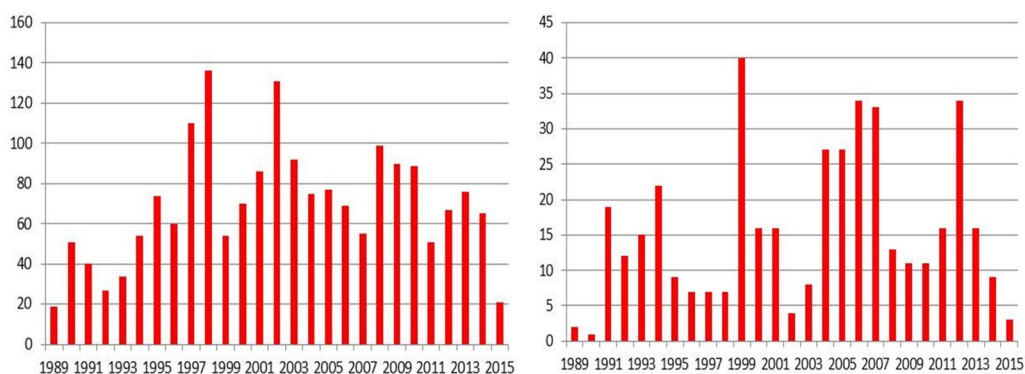


Figure 1. Number of patent applications/year, “plastic” and “pyrolysis” (left), and “tyre” and “pyrolysis” (right).

In the past, there has been numerous trials for thermal conversion of plastic-containing wastes that failed due to different reasons. In addition, the status of





feedstock recycling as a material recycling method has been unclear in many countries, which in its part has also diminished the interest towards industrial thermal conversion plants. However, the recent developments of thermal conversion as well as the increasing pressure to move towards circular economy create an interesting starting point for the final commercialization of these methods.

Together with industrial partners Kuusakoski Ltd. and Borealis Polymers Ltd., VTT Technical Research Centre of Finland Ltd. started a research focusing on thermal conversion of plastic-containing wastes within the ARVI (Material Value Chains) program in 2015. The aim of this review was to provide background information for the experimental work carried out in the project. The document identifies suitable flows of plastic and rubber containing waste streams for thermal conversion, and summarises the most potential pyrolysis and gasification concepts. In addition, the need for pre-treatment and characterization of the feedstock material is discussed.



## 2 Plastic wastes and feedstock recycling

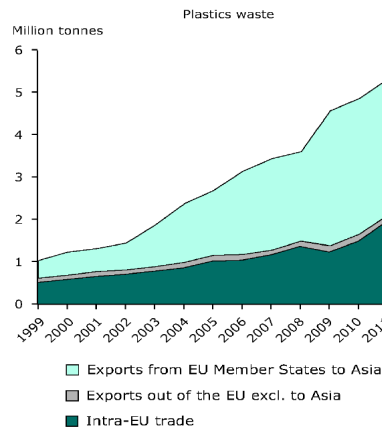
### 2.1 Current status of plastics recycling

The complex and heterogeneous nature of plastics hinder their recycling. In 2014, 25.8 million tonnes of post-consumer plastic waste was generated in Europe, of which only 29.7 % was collected for recycling, and the rest either recovered as energy (39.5 %) or landfilled (30.8 %) (Plastics Europe 2016) (Figure 2). The low recycling rate stems from the fact that plastics recycling is almost entirely focused on mechanical recycling (e.g. 99.7 % of the European plastic wastes led to recycling in 2012 were collected for mechanical recycling (Plastics Europe 2013)) that is suitable only for homogenous and contaminant-free plastic waste, which most of the plastic-containing wastes are not. For example, end-of-life vehicles (ELVs), wastes from construction and demolition (C&D), and waste electrical and electronic equipment (WEEE) all contain large share of plastics that cannot be recycled via mechanical routes. Also plastic packaging wastes often contain whose mechanical recycling is challenging.



Figure 2. Plastic waste management in Europe in 2014 (modified from Plastics Europe 2016).

The amount of plastic waste generated is generally low in Finland and in the other Nordic countries compared to many other regions. On the other hand, it is not yet a very common practice to collect e.g. source separated post-consumer plastic wastes for recycling. Recycling technologies need high volumes of waste to be economically profitable, thus, waste exports have been an attractive alternative. According to Figure 3 the amount of plastic wastes exported to Asia was over 3 Mt in 2011 (European Environment Agency 2012). This means that within the EU, nearly half of the plastic waste collected for recycling is exported to Asia, mostly to China (Fråne et al. 2015). Also the fluctuating supply of wastes may hamper recycling; the feedstock quantities should be rather constant as the processes are optimized for certain flow rates (RTI International 2012).



Source: EEA, 2012

Figure 3. Plastic waste exports from the EU to Asia in 2011 (European Environment Agency 2012).

A wider overview on the status of the plastics recycling is presented in the ARVI Deliverable D4.1-3 titled “*Muovien kierrätyksen tilanne ja haasteet*” by Eskelinen et al. 2016.

## 2.2 What is feedstock recycling?

Feedstock recycling (also known as tertiary recycling or chemical recycling) can be used to convert plastic wastes into monomers, other chemical raw materials, or fuels by means of chemical agents, catalysts and heat (e.g. Aguado & Serrano 1999, Aguado et al. 2008, Panda et al. 2010). The end products of feedstock recycling can be used as feedstocks for many downstream industrial processes or as fuels (Panda et al. 2010).

Depolymerisation, gasification, and cracking (thermal, catalytic and hydrocracking) are the most important conversion technologies (Panda et al. 2010) amongst many different approaches used for feedstock recycling. Under ISO 15270, these technologies are recognized as forms of feedstock recycling when the products are used (a) for the production of fuels or raw chemicals or (b) as a reduction agent in the smelting process (blast furnace), rather than for combustion and energy recovery which would be considered a waste-to-energy process.

According to Aguado & Serrano (1999) gasification requires least pre-treatment amongst these three methods, followed by pyrolysis methods (thermal and catalytic cracking). Most pre-treatment is required by depolymerisation. The value of the end product seems to follow almost the reverse order; monomers obtained from depolymerisation are commercially the most valuable, followed by catalytic oils, whereas the price of thermal oils and synthesis gases is in the lower level. (Aguado & Serrano 1999) Pyrolysis and gasification concepts are described in more detail in Sections 5.1 and 5.2.



### 3 Potential feedstocks for thermal conversion

Finland has followed the other EU Member States and put an end on landfilling of organic and biodegradable waste since the beginning of 2016. This limits the amount of biodegradable and other organic municipal waste, construction and demolition waste, and other waste in a landfill, as well as the use of such waste in a landfill. The landfilling ban of organic waste channels approximately 2 Mt of waste into waste treatment plants for further treatment annually and thereby increases the material and energy recovery, thus busting the circular economy.

The following general boundary conditions for waste-derived feedstock for thermal conversion can be set:

- Sufficient hydrocarbon content
- Volume and availability
- Price
- Location

Keeping these boundaries in mind, plastic-containing feedstocks of particular interest for thermal conversion were identified and are listed in Table 1. The table contains information on the composition and characteristics of the feedstocks, estimates on feedstock quantities both in Finland and in the European level, as well as other remarks such as the current use or estimated future quantities.

Challenges related to feedstock quality and volume are described in Sections 5.1.8.1 and 5.1.8.2, respectively.



Table 1. Potential feedstocks for thermal conversion.

FEEDSTOCK	COMPOSITION	QUANTITY ESTIMATE (kt/a)	CURRENT MANAGEMENT	REMARKS	REFERENCES
<b>Agricultural plastic waste</b>	Includes: foils, sacks, canisters, frost cloths, bale ties, hoses, tarpaulins, pipes etc.  Main polymer type is PE (e.g. PE-LD, PE-LLD, PE-HD). Also PVC, PP, PA etc.  Waste contains stabilisators and other additives. Multi-material and multilayer structures used. Contaminated with dirt, other packaging materials, package content etc.  Estimated ash content: 0.6-3.2 %, moisture: 0-10 %	Finland: 7-10  Europe: 700 – 1,316 (~2-5 % of all plastic waste generated within EU27+2)	No wide-ranging collection systems.  In Finland, Ekokem collects agricultural plastics. 4H, in cooperation with Yara Suomi Oy and Taminco Finland Oy, collects fertilizer and seed sacs, and AIV-canisters.  Europe: Collection systems exist in Sweden, France, Ireland, Iceland, Norway, Spain, the United Kingdom and Germany.	Primary production; fragmented market.  High logistics costs. Decreasing domestic production is cutting down the amounts of plastic waste from agriculture in Finland.  Despite the market fragmentation, the use of agricultural plastics is concentrated geographically in certain agricultural areas; Spain and Italy are the two major waste producers in Europe.  Feeding of plastics into thermal processing requires further development.	e.g. Merta et al. 2012, EPRO 2012, Briassoulis et al. 2013, EUPC 2016
<b>Plastic packaging waste from commercial &amp; industrial (C&amp;I) sources</b>	Industrial plastic packaging from the production of electronics and electric appliances, sawmill and wood products, pulp and paper, chemicals, chemical products and synthetic fibres, rubber and plastic products, food processing and beverages etc. Plastic packaging materials from commercial sources.  Mostly PE-LD foils, other common polymer types: PE-HD, PP, PS, PVC  Rather clean and homogenous stream  Estimated ash content: 0.6-3.2 %, moisture: 0-10 %	Finland: 36  Europe: ~4,700 (The total amount of plastic packaging wastes (incl. consumer packaging) in Europe in 2013 was 15.7 Mt. 4.7 Mt is based on estimate that 30 % of the total quantity is from C&I sources (similar to Finland)	Under producer responsibility in Finland. A collection system (30 collection points for industrial plastic packages in Finland) is mandatory. These plastics will be mechanically recycled by Ekokem.  Currently most plastic packaging from C&I are still collected as energy waste or mixed waste and incinerated.	Plastics packaging material has been and will be the packaging material with the highest growth rate.  Available in larger quantities and more centralized than many other streams.  Suitable also for mechanical recycling (that is at higher level in the waste hierarchy).  Feeding of plastics into thermal processing requires further development.	e.g. Plastics Europe 2013, Moliis et al. 2014, Salmenperä 2015
<b>Separately collected plastic packaging waste from consumers</b>	Main polymer types: PE, PP, PS, PET  Estimated ash content: 0.6-3.2 %, moisture: 0-10 %	Finland: 1.9 – 27 (Estimate for the collection system of 500 collection points)  12.7 PET bottles  Europe: ?	Under producer responsibility in Finland. A collection system (500 collection points for collection of consumer plastic packages in Finland) is mandatory. These plastics will be mechanically recycled by Ekokem that is currently the only company receiving plastics packages that are collected under the producer responsibility scheme in Finland. The estimated yearly amount of plastics to be processed in their plastics refinery is around 20 kt (including C&I plastics).  In addition 12.5 kt (i.e. 94% of the PET deposit bottles) are collected and recycled through PALPA's deposit scheme. Of the sorted PET fraction 10 kt/a (80 %) is treated in Finland and the remaining in Sweden and Latvia. (PALPA 2013).	Already mechanically recycled. In practise, most packages still end up in mixed household waste.	e.g. Moliis et al. 2014, PALPA 2014, Ekokem 2016

FEEDSTOCK	COMPOSITION	QUANTITY ESTIMATE (kt/a)	CURRENT MANAGEMENT	REMARKS	REFERENCES
<b>Plastics in mixed municipal solid waste (MSW)</b>	Household plastic waste + similar C&I wastes (excl. separately collected fractions)  Diverse waste stream containing e.g. consumer packagings, non-packaging small plastic items, plastic bulky waste: furniture, household plastics, toys, sports equipment etc. Majority of plastics in MSW are plastic packaging wastes (around 90 % in the metropolitan area in Finland)  In Finland, the estimated mass fraction of plastics in mixed household waste is 19 %  Many polymer types: PE-LD, PE-HD, PP, PS, PET etc. Waste contains additives and contaminants (food residues, other packaging materials etc.).  Estimated ash content: 0.6-3.2 %, moisture: < 10 %	Finland: 140 - 270  270 kt is theoretical estimate on the amount of plastic waste (both packaging and non-packaging small plastic items) in mixed MSW.  Others: 690 in the Nordic countries  In 2012 households in EU28 generated 137,680 kt of mixed ordinary wastes. If 20 % were plastics, their amount would be 27,536 kt.	Incineration. The majority of plastic waste from households is collected within the energy waste fraction or in mixed household waste, of which part is recovered as energy.  In Finland, the separate collection of plastic waste from MSW sources in 2014 was 51 kt, of which 4.5 kt (9 %) was sent to recycling and 46 kt to energy recovery.  Europe: Waste companies in municipalities, restaurants, shops. In 2012, ten largest municipal waste management companies in Europe were: Veolia (France), Suez Environment (France), Remondis (Germany), Alba (Germany), FCC (Spain), Indaver (Netherlands), Urbaser (Spain), van Gansewinkel (US/UK), Cespa (Spain) & Biffa Group (UK). A Finnish company Lassila & Tikanoja was listed as 13 <sup>th</sup> largest.	Municipal / Commercial; Locally and municipally managed and operated; strongly driven by political targets and situation.  In practise follows the mixed household waste. Separation from mixed waste is difficult. Many countries will find it extremely difficult to meet EU-mandated targets to recycle 50 % of household and similar waste by 2020.  Amount is estimated to rise.	e.g. Hall & Nguyen 2012, HSY 2013, Frâne et al. 2014, Tilastokeskus 2015, Eurostat 2016, JLY 2016
<b>Wastes from the manufacturing and use of plastics</b>	Plastic wastes from plastic manufacturing and plastic products manufacturing that are not reused or recycled onsite  Clean and homogenous stream	Finland: 5-15  Europe: ?	Landfilling, incineration, energy utilisation, material utilisation, etc.	Industrial waste. Many producers and locations, batch-type waste amounts. Some already utilised.  Suitable also for mechanical recycling (that is at a higher level in the waste hierarchy).	
<b>End-of-life vehicles (ELV), boats (ELB)</b>	Car and boat components containing plastics, e.g. bumpers, fuel tanks, electronics, battery housing, dashboard, paddings, seatbelts etc. Share of plastics in ELV is increasing (currently around 12-15 %).  Main polymer types:  ELV: PUR, PP, PET, PA, PE-HD, PVC, ABS. Waste contains additives & flame retardants  ELB: fibre-reinforced plastic and ABS (80 % of weight)	Finland: 12– 15 (Est. amount of plastics in ELV)  Europe: 775-969 (Est. amount of plastics in ELV)	Under producer responsibility. 95 % of a vehicle (by weight) has to be recovered and reused by 2015. For reuse and recycling the requirement was 85 % for 2015. Currently about 75 % of ELV total weight is recyclable.  Currently only around 60 % of ELV is scrapped via official recycling system in Finland.  Finland: collection: vehicles 100,000 pieces/a (119 kt) in 2012, boats 3,000 pieces/a.  ELV: Kuusakoski, Stena Recycling, Kajaanin Romu, Eurajoen Romu have seven plants in Finland (Suomen Autokierrätys Oy is the producer organisation). Kuusakoski recycles 250-300 ELB/a.  Europe: Germany, the United Kingdom, France, Spain and Italy are responsible for ~75 % of EU25 de-registrations. 352 shredder plants (+ illegal facilities).	Waste may contain metals whose separation may be challenging?  The number of ELVs for the EU25 is estimated to increase.  As a result of the stringent landfill legislation (landfill bans) and the objectives and legislation related to ELV treatment of various countries, the treatment and disposal of ELV has become very challenging.  ELB: In Europe no exact numbers available. In Sweden there are around 100,000 boats, however only < 100 boats scrapped /a. In Norway the number of ELB is around 5,500.	e.g. ENVI 2010, Eklund 2013, Heiskanen et al. 2013, Recycling Today 2014, Suomen Autokierrätys Oy 2016, Eurostat 2016



FEEDSTOCK	COMPOSITION	QUANTITY ESTIMATE (kt/a)	CURRENT MANAGEMENT	REMARKS	REFERENCES
<b>End-of-life tyres</b>	Used tyres. Tyres contain around 45-47 % of rubber/elastomers, 21.5-22 % of carbon black, 12-25 % of metals, 5.5-10 % of textile, 1-2 % of sulphur, 5-7.5 % of additives. Carbon based materials 67-76 % of the total.  Estimated ash content: < 15 %, moisture: < 5 %	Finland: 55 Europe: 2,700	Under producer responsibility in Finland. Kuusakoski (Suomen Rengaskierrätys Oy is the producer organisation).  Producer responsibility works well in tyre recycling. The collection and recovery rate of used tyres in Finland, Sweden and Norway is 100 %. In 2015 (Finland): coating 0.8 kt, material utilisation 35 kt, other utilisation 6 kt, energy 10 kt, export 0.3 t.  In 2010, 96 % of used tyres were recovered in EU25+2.  Genan is the largest tyre recycler, counting four large recycling plants in Europe (one in Denmark, three in Germany) with overall input capacities of 65-70 kt each.	Due to its aromatic nature, maybe not suitable for cracker feed in large amounts	e.g. WRAP 2006 , ETRMA 2011, Genan 2016, Suomen Rengaskierrätys Oy 2016
<b>Wastes from shredding/crushing of metal-containing wastes</b>	Wastes from shredding of metal-containing wastes; Shredder waste or residue (SR) is generated from businesses that recover metals from cars or end-of-life vehicles (ELV) and discarded metal (iron) containing products  Composition: Plastics 30 %, wood 1-7 %, glass 5-16 %, textiles 3%, rubber 10-20 %, metals 10 %, copper wires 3 %, minerals 35-45 %. Waste contains contaminants and other harmful substances (e.g. oil residues, flame retardants, PCBs)  Estimated ash content: 20-50 %, moisture: < 15 %	Finland: 70 Europe: 2,000-2,500	Industrial waste / under producer responsibility  Landfilling as non-hazardous or hazardous waste, also energy recovery exists. The organic content hinders landfilling.  Kuusakoski, Stena Recycling, Kajaanin Romu and Eurajoen Romu have seven plants in Finland (Suomen Autokierrätys Oy is the producer organisation).  Europe: Top 3 ELV countries (France, Italy, the UK) probably produce most of automotive shredder residue (ASR) also. The number of shredders is 352 + illegal facilities. There are around a dozen large shredders in the EU, incl. two mega shredders in the UK.		e.g. Ranta 1999, Heiskanen et al. 2013, Recycling Today 2014, Suomen Autokierrätys Oy 2016
<b>Rubber wastes from construction &amp; demolition (C&amp;D)</b>	Rubber containing materials, contaminants  Estimated ash content: < 15 %, moisture: < 5 %	Finland: 0? Europe: 40	Industrial waste.	The Waste Framework Directive (2008/98/EC) sets targets for the reuse and recycling of waste from households and for C&D waste by 2020.	e.g. Eurostat 2016
<b>Plastic wastes from construction &amp; demolition (C&amp;D)</b>	Pipes, insulation, packaging films, cables, ceiling/wall covers etc.  Main polymer types: PVC, PE-HD, PP, PS, PUR. Waste contains additives and contaminants.  Estimated ash content: 0.6-3.2 %, moisture: 0-10 %	Finland: 14 Europe: 970	Industrial waste.  Production of solid recovered fuel and utilisation as energy, incineration.  Sorting practices vary by company.	The Waste Framework Directive (2008/98/EC) sets targets for the reuse and recycling of waste from households and for C&D waste by 2020.	e.g. Eurostat 2016

FEEDSTOCK	COMPOSITION	QUANTITY ESTIMATE (kt/a)	CURRENT MANAGEMENT	REMARKS	REFERENCES
<b>Waste electrical &amp; electronic equipment (WEEE)</b>	<p>Equipment housing, cables, fans etc. Share of plastics vary by product group (16-35 wt-%)</p> <p>The WEEE plastics fraction is a heterogeneous mix of different type of polymers (e.g. ABS, HIPS, PC, PP, PS, PVC), from which around 30 % include flame retardants to ensure the safety of the equipment. However, only 40 % of this share contains halogenated flame retardants.</p> <p>Estimated ash content: 0.6-3.2 %, moisture: 0-10 %</p>	<p>Finland: 10 – 15 (amount of plastics in WEEE)</p> <p>Europe: 1,100 (amount of plastics in WEEE in 2008)</p>	<p>Under producer responsibility (Five producer organizations: SELT Association, FLIP Association, ICT Producer Co-operative, European Recycling Platform (ERP) Finland and SER-tuottajayhteisö ry SERTY). Actors e.g. Kuusakoski and Stena Recycling.</p> <p>Material recycling of plastics in WEEE is difficult, e.g. due to flame retardants and additives present. The assumed WEEE plastics recycling rate in Finland is 10 %.</p> <p>Around 1.1 Mt of WEEE plastic waste was generated in EU-27+2 in 2008, of which around 55 % (0.6 Mt) was landfilled, 36 % (0.4 Mt) recovered as energy, and the rest 8 % (0.09 Mt) recycled mechanically.</p>	<p>The generation of WEEE has increased significantly over the past years and it is amongst the fastest growing waste streams in the EU, with an annual growth rate of 3-5 %. Also the share of plastics in WEEE is increasing.</p> <p>Contains metals that cause challenges to pre-treatment.</p>	<p>e.g. European Commission 2011, Baxter et al. 2014, Salmenperä 2015, Pirkanmaan ELY Keskus 2016, Eurostat 2016</p>
<b>Artificial turfs</b>	<p>Polymer types: PE, PP, PUR, SBR. There are &gt; 500 artificial turfs in Finland, containing 1-2 kt of PE, and 0.3 kt of PP. Contains dust, sand, and fillers.</p> <p>Estimated moisture content: &lt; 10 %</p>	<p>Finland: 1-2</p> <p>Europe: ?</p>	<p>Incineration. May be reused.</p>	<p>The amount of turfs will increase in the future. The estimated life varies between 3 (stadium use) and 30 (landscaping) yrs.</p>	<p>e.g. Hiipakka 2012</p>





## 4 Pre-treatment and characterization

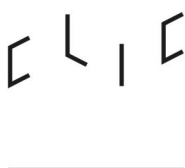
Mechanical pre-treatment targets to treat profitably and adaptably heterogeneous feedstocks to be suitable for thermal conversion. Applied mechanical unit operations comprise size reduction and control processes, such as crushing and sieving, together with washing, drying, homogenization, re-granulation and compounding technologies. On demand, dry mechanical separation (magnetic, eddy current, density separation) can supplement pre-treatment operations to separate certain valuable or harmful substances. In addition, sensor based smart pre-treatment techniques are efficient for processing complex organic waste streams, and e.g. near infrared (NIR) light sensor based autosorters, which use optical readers to identify materials passing on the conveyor belts and separate them using air currents, are nowadays commonly used in the plastic waste processing and recycling facilities.

Prior to the pre-treatment, feedstock material needs to be well characterized in order to find suitable treatment conditions, as the characteristics of the materials fed into thermal conversion have an influence on the quality and value of the end product. The pre-treatment should be optimized case-by-case over the whole process chain in order to avoid losses and to achieve recovery rate as high as possible without decreasing the quality of the end products. Each unit process has its own limitations and requirements which must be considered when a process chain is designed for the feed.

### 4.1 Pre-treatment needs and technologies

Pyrolysis and gasification usually require only limited use of pre-treatment before materials can be fed into the system (Delgado et al. 2007, Siddique et al. 2008, 4R Sustainability Inc. 2011) as thermal conversion processes are designed to accept heterogeneous feedstocks, can tolerate many forms of contamination (e.g. food rests or moisture) and are able to remove impurities. As the amount of different cleaning and separation phases can be diminished, cost savings can be created in the pre-treatment phase. However, it should be always reflected whether it is efficient to create savings in the pre-treatment (and possibly have a low valued end product) or invest in it if there is a chance to achieve a more valuable end product.

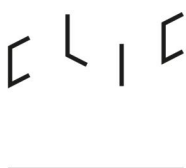
As the contamination in the feed may reduce the end product quality (Borsodi et al. 2011), at least a robust mechanical pre-treatment is to be carried out (Delgado et al. 2007, 4R Sustainability Inc. 2011) to increase the feedstock quality by removing impurities, and the overall process efficiency (RTI International 2012). The pre-treatment structure and equipment vary from case to case. As an example, one of the main European technology suppliers Cynar pyrolyses plastics packaging wastes that are first handpicked by the waste management company to separate contaminants and non-plastic materials, and then transported to Cynar that only shreds the plastics to a right particle size suitable for their process (Cynar Plc 2016).





Based on this study, it seems that pre-treatment processes for thermal conversion are not very precisely reported in the literature. To be able to obtain an overall picture of the pre-treatment methods used in general, different blast furnace, pyrolysis and gasification procedures were surveyed, including both research and pilot/industrial scale examples (Table 2). Common criteria to all the procedures listed was that regarding to them at least some information was given concerning their pre-treatment activities. However, it should be noticed that most of the processes described in the Table 2 are rather old and may not be valid anymore as such.

Mechanical pre-treatment processes in general are described in the ARVI Deliverable (D4.4-1, D4.4-2 & D2.5-1) titled *“Review on Elemental Recovery Potential of Ashes”* by Laine-Ylijoki et al. (2014), and pre-treatments used when aiming for mechanical recycling of plastics in the deliverable (D4.1-3) *“Muovien kierrätyksen tilanne ja haasteet”* by Eskelinen et al. (2016). In addition, a good description of pre-treatment processes and equipment is described by Hiipakka (2012). As the processes as such are similar in the pre-treatments for thermal conversion, the general description of the treatment processes are excluded from this report. In addition, also removal of chlorine may be required before thermal conversion.



*Table 2. Pre-treatments used for plastic-containing wastes prior to thermal conversion processes.*

TARGET	FEEDSTOCK	PRE-TREATMENT METHODS	REFERENCES
Blast furnace	Mixed municipal plastics Max. chlorine content: 1.5 % Particle size: < 18 mm	1. Separation of oversized materials (> 18 mm), fibres and metal particles	Tukker et al. 1999
Blast furnace	Plastic waste incl. bottles, scrap, magnetic tapes. PVC not allowed. Particle size: 6-10 mm	<p><u>Solid plastics:</u></p> <ol style="list-style-type: none"> <li>1. Shredding to a particle size of 7 cm</li> <li>2. Separation of magnetic material</li> <li>3. Crushing to a particle size of 6–10 mm in two stages, the remaining metals are magnetically separated after the first stage</li> <li>4. Granulation</li> </ol> <p><u>Plastic foils:</u></p> <ol style="list-style-type: none"> <li>1. Shredding</li> <li>2. Melting</li> <li>3. Pelletizing</li> </ol> <p>Mixing of pellets and granulated solid wastes</p> <p>Equipment used: Crushers, ballistic separator, magnetic and wind-powered waste sorters, PVC separation by gravity separator, PVC removal system, granulator</p>	NKK Corporation 1998, Ziębik & Stanek 2001
Blast furnace	MSW Chlorine content: 0.5-5 %	<ol style="list-style-type: none"> <li>1. Separation of plastics and paper from MSW</li> <li>2. Separation of plastics from paper</li> <li>3. Dehalogenation</li> </ol>	Vinyl 2010 2002
Blast furnace	Mixed plastic waste from households and industry	<ol style="list-style-type: none"> <li>1. Separation of non-combustibles and other impurities (e.g. metals)</li> <li>2. Pulverization and packing (to reduce volume)</li> <li>3. Granulation of non-PVC containing plastics</li> <li>4. Dehydrochlorination of PVC containing plastics</li> </ol>	Plastic Waste Management Institute 2009
Liquefaction & gasification	Municipal plastic waste Particle size: < 10 cm (< 1 % under 250 µm) Other criteria: Dry to the touch, not sticky, PSW > 90 wt-%, free metals < 1 wt-%, PVC < 10 wt-%, ash < 6 wt-%, residual moisture < 5 wt-%, paper < 10 wt-%	1. Shredding/chipping of baled/agglomerated waste	Tukker et al. 1999, Brems et al. 2013
High temperature gasification in a sand filled fluidised bed	PE, PS, PVC, mixed plastics Particle size: < 2.5 cm	1. Shredding	Tukker et al. 1999
Gasification in a molten salt bath	Streams containing up to 100 % PVC. All PVC types, both hard and softened	<ol style="list-style-type: none"> <li>1. Crushing</li> <li>2. Separation of steel and non-ferrous metals</li> </ol> <p>Washing and drying are not necessary. Separation of steel and non-ferrous metals is performed with magnet or gravity shifter</p>	Tukker et al. 1999
Gasification	E.g. contaminated wood, waste water purification sludge (incl. industrial sludges), solid recovered fuel (SRF), paper, mixed plastics, WEEE plastics, ASR, liquid organic waste Particle size: 20-80 mm Chlorine content: Max. 2 % recommended, up to 6 % tolerated Ash content: < 10 % or more	1. Pelletizing	Tukker et al. 1999



TARGET	FEEDSTOCK	PRE-TREATMENT METHODS	REFERENCES
Gasification	Mixed household plastic waste	1. Shredding	Plastic Waste Management Institute 2009
Gasification	Small amount of tires amongst biofuel Particle size: Should be the same as with other gasified materials or less	1. Shredding	Ranta 1999
Gasification	Plastic solid waste, MSW, sludges, tires	1. Drying 2. Sorting out incombustibles 3. Granulation to optimum particle size	Brems et al. 2013
Entrained-flow gasification	MSW plastics, ASR, other plastic waste Particle size: 8-25 mm	1. Separation of metals and combustibles 2. Shredding 3. Drying (if needed)  Separation of paper, woods, and ash is not required	Shoji et al. 2001
Gasification	MSW, SRF from sorted MSW, pelletized SRF, wood, C&D waste, commercial and industrial waste, agricultural and forest residues Other criteria: Moisture content < 15 %. Inorganic matter content 15 % for SRF and commercial and industrial wastes, < 5 % for C&D wood	1. Drying 2. Sorting (MSW, SRF, commercial and industrial waste) 3. Shredding (C&D wood, commercial and industrial waste)  Pre-treatment performed onsite	RTI International 2012
Gasification	Recycled MSW	1. Recovery of metals 2. Shredding	RTI International 2012
Liquid-metal gasification	Mostly wood based waste: creosote treated railroad ties (90 %) and clean wood (5 %). Also non-recycled source separated plastics (5 %) Other: Moisture content after pre-treatment < 20 %, inorganic matter content < 5 %	Plastics 1. Sorting 2. Shredding 3. Drying  Sorting and shredding performed offsite	RTI International 2012
2-stage gasification	PVC, other plastic waste, MSW, also 100 % plastic waste accepted, shredder dust, wood and soil waste	1. Shredding 2. Drying	Yamamoto et al. 2004
Liquefaction, pyrolysis and catalytic breakdown	Almost all miscellaneous plastic wastes, also heavily contaminated, e.g. packaging scrap from material recovery/sorting, oil/detergent bottles, nappy production wastes, agricultural plastics, post-consumer plastics, scrap from bottle recycling, packaging wastes from commercial activities Particle size: 12-15 mm Other criteria: Contamination (e.g. organic matter, paper) level should be < 10 wt-% (effects on the yield)	1. Shredding 2. Granulating 3. Washing/sorting if contaminant level is exceeds 10 % or the share of unsuitable plastics is too high  Identification of plastics by type not needed once PET and PVC are removed.	Ozmotech 2004, Thorat et al. 2013
Pyrolysis: Thermal anaerobic conversion (TAC)	End of life plastics from commercial and industrial (or other) sources, e.g. plastic packaging wastes (PE-HD, PE-LD, PP, PS). Particle size: 15 mm	1. Separation of contaminants or non-plastic materials (metal, nylon, paper etc.) 2. Shredding 3. Extruding  Separation performed offsite, apparently also handpicking is used. Size reduction onsite.	Cynar Plc 2016
Catalytic pyrolysis using a non-stirred semi-batch reactor	Plastic packaging waste Particle size: ≤ 8 mm	1. Separation into different material groups (e.g. steel cans, tetra-briks, aluminum cans, plastics) 2. Crushing/shredding  Separation performed offsite. Equipment used: rotating trommel screens, ballistic separators, magnetic and eddy current separation. Plastics separated with autosorters (based on optical readers). Crushing with a cutting mill.	Lopez et al. 2010, Adrados et al. 2012



TARGET	FEEDSTOCK	PRE-TREATMENT METHODS	REFERENCES
Thermal cracking in a sand filled fluidised bed	Clean plastic waste, mostly addition polymers Other: Pre-treated feed contains polyolefins (80 %), PS (15 %), PET (3 %) and PVC (2 %). Min. amount of plastics 90 wt-%.	1. Shredding 2. Separation of of most non-plastics (metals)	Tukker et al. 1999, Baquero & Pozo 2010
Pyrolysis with laboratory scale continuous tubular reactor	PE-HD waste motor oil flasks (contaminated with motor oil) and off-grade PE-LD Particle size: < 3 mm	1. Washing with light naphtha & drying in vacuum (some cases) 2. Crushing 3. Extruding	Borsodi et al. 2011
Low temperature pyrolysis	Plastic waste Other criteria: Max.: 4 % contaminants, 4.5 % ash, 2.5 % chlorine, and 1 % moisture tolerated	1. Separation of PET (goes to mechanical recycling) 2. Crushing/shredding 3. Separation of unsuitable materials	Perugini et al. 2005
Pyrolysis	Printed circuit boards Particle size: 3-5 mm	1. Mechanical separation of the batteries, capacitors and other electronic devices 2. Two crushing steps: Crushing with a jaw crusher to 3-5 cm, followed by size reduction to 3-5 mm using a manual cutter	Mankhand et al. 2012
Pyrolysis: Non-pressurised modular catalytic reactor	All plastics, PVC accepted	1. Shredding	Panda et al. 2010
Pyrolysis under nitrogen in a 3.5dm <sup>3</sup> autoclave	Four WEEE samples: PE wires, table phones, mobile phones and printed circuit boards Particle size: ~0.1 cm (PE wires) and ~2 cm (others)	1. Crushing  Crushing performed offsite	de Marco et al. 2008
Analytical pyrolysis (Py-GC/MS)	WEEE: three printed circuit board samples	1. Removal of components (e.g. capacitors, batteries, plastic sockets) 2. Shredding 3. Homogenization (by mixing of the pulverized material)	Evangelopoulos 2014
Liquid phase thermal cracking (pyrolysis/depolymerisation)	Packaging waste Other criteria: Max. 8 % PVC accepted. No separation of PVC	1. Shredding 2. Separation of other materials (e.g. metals) 3. Agglomeration	Tukker et al. 1999
Pyrolysis with subsequent metal extraction	PVC waste (e.g. cables, flooring, profiles) Other criteria: No restrictions on the chlorine content	1. Separation of light plastics, wood, sand, metals 2. Shredding  Equipment used: Shredders, magnetic separation, sink-float separation, wet shaking table	Tukker et al. 1999
Fast pyrolysis (or steam gasification) in a circulating fluidised bed system (two reactors) with subsequent combustion	Many waste types accepted: wood, biomass, mixed plastic waste, pure PVC waste Other: High PVC share accepted	1. Shredding	Tukker et al. 1999
Liquefaction (pyrolysis)	Household plastic waste	1. Shredding 2. Separation 3. Sorting 4. Dehydrochlorination	Plastic Waste Management Institute 2009
Pyrolysis in a 1 dm <sup>3</sup> autoclave	Recycled PE, PP and PS (most common plastic types in MSW) Particle size: < 3 mm	1. Washing 2. Grinding	Pinto et al. 1999
Pyrolysis	MSW Particle size < 30 cm	1. Shredding 2. Treatment with lime and sewage sludge to absorb acidic gases	Ranta 1999



TARGET	FEEDSTOCK	PRE-TREATMENT METHODS	REFERENCES
Pyrolysis	Thermoplastic waste and/or biomass, municipal waste plastics containing PVC, industrial plastic waste	1. Shredding 2. Drying 3. Separation (pneumatic, magnetic) 4. Pelletizing	UNEP 2009
Pyrolysis: rotary kiln designed with screen solid circulation	All plastics, plastics contaminated with biomass, metal, asbestos, bacteria etc., biomass	1. Shredding	UNEP 2009
Pyrolysis, tank reactor	Thermoplastics waste Other criteria: Chlorine-containing plastics not accepted	1. Crushing	UNEP 2009
Pyrolysis, tank reactor	Thermoplastics waste Other criteria: Chlorine-containing plastics not accepted	1. Shredding 2. Extruding	UNEP 2009
Pyrolysis	Any type of waste plastics Other criteria: Density target of grinding/shredding is 20-21 lbs/ft <sup>3</sup>	1. Grinding/shredding	RTI International 2012
Pyrolysis	100 % plastics. PS, PE-HD, PE-LD, and PP preferred. Only small amounts of PET and PVC accepted. Particle size: < 3.8 cm Other: Moisture content < 2 %. Organic contaminants (approx. 6 %) are not removed	1. Shredding 2. Separation of magnetic material 3. Melting (300 °C) 4. Screening to filter non-plastic contaminants (glass, non-magnetic metals)	RTI International 2012
Pyrolysis	Mixed post-consumer plastic wastes Other: Moisture content varies between 0-5 %	1. Shredding	RTI International 2012
Pyrolysis	Mixed, non-recycled plastic waste commercial and industrial sources, also MSW could be used Other: Moisture content < 10 %	1. Shredding/pre-melting	RTI International 2012
Hydrolysis & pyrolysis	Feedstock: PVC	1. Shredding 2. Sorting (metal, rubber and PE from PVC) 3. Granulation 4. Dechlorination by hydrolysis	Procida & Bloch 2004
Modular pyrolysis and gasification at high temperatures	e.g. MSW, ASR, end-of-life tyres, industrial and plastic waste, contaminated soil	1. Separation 2. Screening 3. Shredding	Malkow 2004

As it can be seen from the Table 2 separation of desired material or contaminant either prior to or followed by size reduction or controlling seem to be the minimum requirement for the pre-treatment. Size reduction (or control) can be performed using different equipment (e.g. crushers, shredders, granulators, extruders etc.) depending on the structures of the plastics (e.g. rigid, films, sheets, foams). The aim of size reduction is usually to homogenise and compact the feedstock in order to increase the feeding rate of material into thermal conversion and improve the processing efficiency. Also decline in transportation costs can be achieved by compaction and volume reduction. (UNEP 2009)

Separation of unsuitable materials is often linked to the separation of metals, which can be removed during the pre-treatment phase using magnetic separation or Eddy Current separation, although it is possible to recover metals also from the by-products formed in the thermal processing. Depending on a case also other materials can be separated prior to processing, e.g. removal of inorganic materials such as rocks, ceramics and glass may be advisable.

In addition, some other treatments such as drying if the feed is very moist (small moisture content is not usually problematic), or removal of e.g. chlorine are also used. Various commercially relevant dechlorination methods are available.

## 4.2 Feedstock characterization

According to Baquero & Pozo (2010), the particle size, density, and moisture content are especially important material characteristics for the thermal conversion process performance and the proportions of the end products achieved, and should therefore be noticed during the pre-treatment and optimization phases to increase the performance and to improve the end product characteristics:

- **Particle size** has effects on the transfer of mass and heat in the pyrolysis reactor, as heating of larger particles takes more time than heating of the smaller ones. Particle size may affect the shares of liquid, gaseous and solid end product fractions.
- Higher plastic waste **densities** fed in the pyrolysis lead to the generation of higher tar degradations and reduce the solid fraction and heavy hydrocarbons production
- **Moisture or water content** of the feedstock affects to the composition of the end product as well as consumes more energy. (Baquero & Pozo 2010)

In addition, chemical composition of the feedstock as well as liberation of different components are important characteristics and should be investigated. For characterization purposes, e.g. the performance of the following analyses may be advisable:

- Elemental composition, especially total organic carbon (TOC), sulphur, chlorine, CHN (carbon, hydrogen, nitrogen)
- Dry matter content
- Ash content





- Material content (e.g. visual identification of different materials)

In order to adjust pyrolysis conditions the types of plastics in the mixture should be known. The identification of plastics can be performed e.g. using equipment based on NIR identification. Also the presence of harmful components, such as flame retardants, in the feedstock and in the end products should be studied.





## 5 Thermal conversion concepts

### 5.1 Pyrolysis

The production of fast pyrolysis bio-oil (FPBO) from woody biomass is entering the market with first full-scale demonstration plants using fluid-bed technology in Finland and the Netherlands with TRL (Technology Readiness Level) and MRL (Manufacturing Readiness Level) of 8. This technology has also potential for plastic waste applications. In Finland, industry, Tekes and VTT have invested together to bio-oil development during the past years. As a result of the consistent work (Solantausta et al. 2012, Lehto et al. 2013) an integrated fluid-bed demonstration plant producing bio fuel oil is currently operational in Joensuu, Finland. (Figure 4)



Figure 4. Scale up of biomass fast pyrolysis.

#### 5.1.1 Thermal plastic to liquid (PTL) process

Pyrolysis of plastics or plastic to liquids (PTL) is a thermal decomposition of a material in an oxygen-free environment into liquid product. Plastic-containing waste streams contain various resins, which degrade to wide range of products from monomers to a mix of waxes, paraffins, and olefins. Depending on the resin mixtures and the operating conditions yields vary widely. As a rule both gaseous and liquid products are mixtures of numerous different compounds. (Buekens 2006)

Plastics pyrolysis proceeds from low (< 400 °C) to high temperatures (> 600 °C). The pressure is generally atmospheric. Subatmospheric operation, whether using vacuum or diluents, e.g. steam, may be selected if the most desirable products are thermally unstable, e.g. easily repolymerizing, as in the pyrolysis of rubber. The process yields carbonised char and volatiles that may be separated into hydrocarbon oil/wax and noncondensable gas. Figure 5 shows a



schematic presentation of the PTL process. Different pre-treatment steps may exist depending on the quality and properties of plastic feedstocks (See Section 4). (Buekens 2006) Various reactor technologies are described in Section 5.1.7.1.

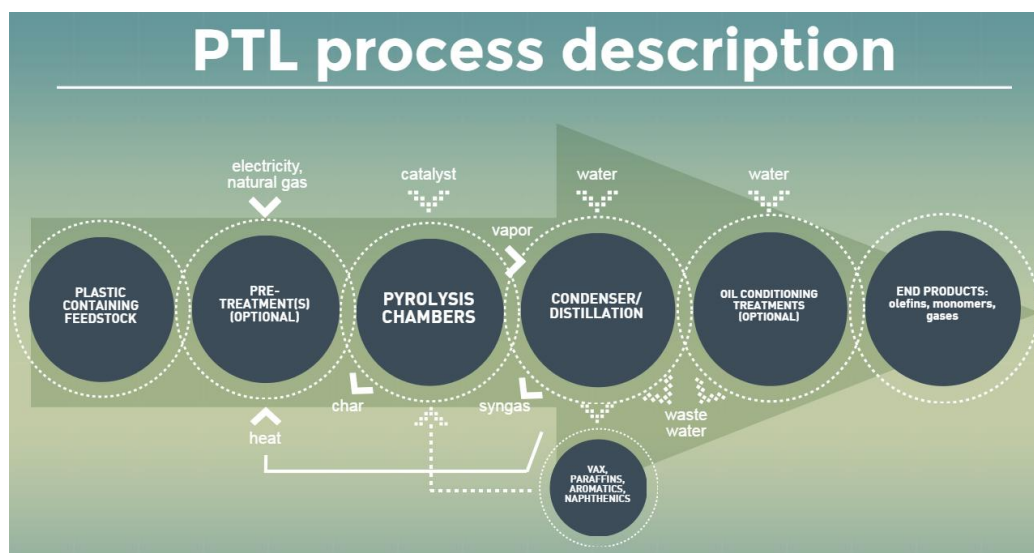


Figure 5. Schematic presentation of PTL (plastic to liquids) process (Modified from Ocean Recovery Alliance 2015).

### 5.1.2 Catalytic PTL process

Catalysts can significantly improve the quality of the product by increasing selectivity for desired components. Heterogeneous catalysts are the most commonly applied catalyst for plastic pyrolysis. Zeolites and mesoporous materials are the most important heterogeneous catalysts due to their porous structure and acid properties. Depending on the acid strength of the catalyst, cracking proceeds either by random or end-chain scission giving rise to waxes and middle distillates (gasoil, gasoline) or light hydrocarbons (C3–C5 olefins) respectively. (Almeida & de Fátima Marques 2016)

Since polyolefin plastics and their thermal degradation products are inherently olefinic (and unstable) and target components for diesel and gasoline are paraffinic, hydrogenation of the double bonds is beneficial either in a hydrocracking or fuel finishing (hydrotreatment). While the process requires high pressure process equipment, consumes significant amounts of hydrogen and the catalysts are prone to fouling, the infrastructure may already be available in a refinery and a simple thermal pyrolysis step prior to hydroprocessing can remove contaminants. (Butler et al. 2011)

The advantages of catalytic cracking are (1) lower cracking temperature, (2) increased reaction rate, (3) increased production of isoalkanes, branched and cyclic molecules and aromatics, (4) increased efficiency, and (5) improved selectivity and quality of the product (Table 3). Commercial examples of catalytic processes include the Smuda/Nanofuel, Thermofuel (vapour phase catalysis), and Reentech (catalyst continuous regeneration). (Butler et al. 2011)





Table 3. Effect of catalyst in PTL processes (modified from Miandad et al. 2016).

CATALYST USED	CATALYST QUANTITY (%)	FEEDSTOCK	EFFECT ON YIELD			CATALYST EFFECT
			Liquid	Gases	Char	
HZSM-5	20	HDPE	NR	NR	NR	<ul style="list-style-type: none"> <li>Increased the yield of volatile compounds</li> <li>Increased the cracking process and the overall yield of pyrolysis</li> </ul>
FCC	50	LDPE, HDPE, PP	72.1 44.2 64.7	19.4 52.5 20.0	8.5 3.3 15.3	<ul style="list-style-type: none"> <li>Thermal cracking of HDPE was most difficult, followed by LDPE and PP</li> <li>Thermal cracking of PE produced wax</li> </ul> <p>Thermal cracking increased the demand of energy, however, the use of catalyst increased the cracking process. Hence reduced the demand of energy.</p>
Na <sub>2</sub> CO <sub>3</sub>	2, 5, 10	Tires	NR	NR	NR	<ul style="list-style-type: none"> <li>Decreased the reaction temperature</li> <li>Increased the conversion with increase in liquid yield</li> </ul>
ZSM-5	5	HDPE, PP	NR	NR	NR	<ul style="list-style-type: none"> <li>Increased the process of cracking</li> <li>Increased the overall yield of each fraction i.e. gases, gasoline and light oil</li> <li>Yield of lighter fraction (gasoline) increased</li> </ul> <p>Promoted the production of i-butane in gases</p>
HZSM-5, Zeolite Y and Mordenite	30	PE wax	47.18 66.98 82.59	51.04 28.95 15.11	1.78 4.08 2.3	<ul style="list-style-type: none"> <li>Overall increase the aromatic compounds in the oil</li> <li>Catalyst dimension played a vital role in the conversion of wax into light hydrocarbon</li> </ul> <p>Catalyst with more than one dimension (HZSM-5 and zeolite Y) showed higher conversion of wax into light hydrocarbon than one dimension (mordenite) catalyst</p>
ZSM-5	10	Industrial packaging waste	41.5	8.6	49.9	<ul style="list-style-type: none"> <li>Decreased the temperature of pyrolysis process from 500 °C to 440 °C</li> <li>Liquid oil produced from catalytic pyrolysis contained high fraction of aromatic, while gases contained high amount of C3-C4</li> </ul>
ZSM-5	10	PE, PP, PS, PET, PVC	56.9	40.4	3.2	<ul style="list-style-type: none"> <li>Dechlorination step was carried out at low temperature. It reduced the chlorination but also had a negative affect on the catalyst performance.</li> <li>Increased the yield of gases that decrease in liquid yield. Moreover, a very slight increase in solid fraction</li> <li>80 % of the liquid yield contained C5-C9 compounds due to presence of catalyst</li> </ul> <p>However, dechlorination step with catalyst decreased the C5-C9 fraction, meaning that it affected on the catalytic activity of ZSM-5</p> <ul style="list-style-type: none"> <li>Dechlorination step increased the yield of C13 compounds in liquid yield</li> </ul> <p>Catalytic pyrolysis produced liquid with 95 % aromatic compounds</p>
Natural Zeolite (Ni/Z, NiMo/Z, Co/Z, CoMo/Z)	5	LDPE	23.88 12.20 23.92 14.91	75.18 86.30 76.00 83.71	0.94 1.51 0.92 1.39	<ul style="list-style-type: none"> <li>Natural zeolite modification was carried out by metal (Ni, Ni-Mo, Co and Co-Mo) impregnation on natural zeolite to increase the catalyst activity and its selectivity for hydrocracking process</li> <li>Impregnation of catalyst did not affect the crystallinity of the natural zeolite</li> <li>Ni/Z composite produced high liquid yield. However, maximum gasoline (71.49 %) was produced from Co-Mo/Z at 350 °C due to its high acidic nature.</li> <li>Liquid oil produced contained compounds between C6 and C19, showing that it contained paraffins, naphthenes and olefins.</li> </ul>
H-Y Zeolite	50	PE, PP, PS	42 44 71	46 52 24	8 10 5	<ul style="list-style-type: none"> <li>Polyolefin (PE and PP) showed high yield of gaseous hydrocarbons while PS showed high yield of liquid hydrocarbons due to its stable benzene ring structure</li> <li>Polyolefin produced wax while PS did not</li> <li>Liquid oil produced from PS mainly consisted of styrene (81 %)</li> </ul>

Despite the potential advantages of the catalytic pyrolysis, some limitations such as high parasitic energy demand, catalyst costs and less reuse of catalyst are remaining. The recommended solutions for these challenges include exploration of cheaper catalysts, catalyst regeneration and overall process optimization. (Miandad et al. 2016) The effects of metal-impregnated catalysts on the process performance should be studied more (Wong et al. 2015).

### 5.1.3 Effect of resin type on product composition

Plastic-containing waste streams contain various resins, which degrade to a wide range of products. Some polymers, like polystyrene (PS), Nylon (PA-6), and polymethyl methacrylate (PMMA) can be pyrolyzed back to their monomers (Section 5.1.3.1), whereas some resins, like polyolefins (PE, PP) degrade into a mix of waxes, paraffins, and olefins (Section 5.1.3.2). Table 4 shows main resin types in plastic waste streams and their pyrolysis products.

*Table 4. Main resin types in recycled plastic waste streams and their pyrolysis products.*

RESIN	MAJOR ORIGIN OF WASTE	PYROLYSIS PRODUCT
PE	Households, industrial plastic packagings, agricultural plastics	Waxes, paraffins, olefins → Gases, light hydrocarbons
PP	Household and industrial plastic packagings, automotive	Waxes, paraffins, olefins → Gases, light hydrocarbons
PS	Households, industrial plastic packagings, construction, demolition, WEEE	Styrene, its oligomers
PA-6	Automotive	Caprolactam
PVC	Construction plastics	Hydrochloric acid (< 300 °C), benzene → Toluene
PET	Household plastic packagings	Benzoic acid, vinyl terephthalate
PMMA	Automotive, construction	Methyl methacrylate
PUR	Construction, demolition, automotive	Benzene, methane, ethylene, NH <sub>3</sub> , HCN

#### 5.1.3.1 Monomers from polymers

Polystyrene can be depolymerized to styrene up to 80 % yields (Table 5). After vacuum distillation styrene monomer with 99.6 wt-% purity can be obtained. Residual dimer might be recycled to the next run to produce more monomer. (Liu et al. 2000)

*Table 5. Mass balance of PS pyrolysis at 450 – 700 °C (Liu et al. 2000).*

Pyrolysis temperature	450 °C	500 °C	550 °C	600 °C	650 °C	700 °C
Liquid products	97.6	96.4	95.3*	98.7	90.7	90.2
Cracking gas	–	0.04	0.26	0.65	1.51	3.54
Coke	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Total products	97.8	96.6	95.8	99.5	92.5	93.9

\*Somewhat low due to the relatively high loss during the experiment.

Polymers formed by ring-opening can be converted back to their monomers for purification and repolymerization, for example, Nylon 6 to caprolactam. Ethyl cyanoacrylate, a binder for metal and ceramic powders, can be recovered for reuse by pyrolysis at 180 °C. Monomers can be obtained also by pyrolysis of polymethyl methacrylate in 92-100 % yield, poly(alfa-methylstyrene) in 95-100 % yield, and polytetrafluoroethylene in 97-100 % yield.



### 5.1.3.2 Pyrolysis of polyolefins

Polyolefins including PE-HD, PE-LD, PE-LLD and PP are the most used resins, which account for around 50 % of all plastic market demands (Plastic Europe 2013). This group of thermoplastic polymers is characterized by having similar physical and chemical properties, which makes separation processes between each component very complicated and cost intensive. This fraction is highly recommended to be used as a single fraction. It can be easily isolated from other MSW/plastic waste fractions such as PVC, PET and PS, using commercially available density-based separation methods, e.g. a sink-float technique. (Dodbiba et al. 2002)

Degradation of polyolefinic polymers proceeds via a radicalic mechanism, leading to the formation of free radicals. These radicals are responsible for the formation of low molecular weight gases. Thermal cracking of polyolefines is usually carried out either at high temperatures (700 °C), to produce an olefin mixture of C1–C4 gases and aromatic compounds (benzene, toluene and xylene) or at low temperatures (400–500 °C) where the yield structure comprises a high calorific value gas, condensable hydrocarbon oils and waxes. Two of the main problems associated with thermal cracking of polyolefines are (1) limited conversion of the feedstock at low pyrolysis temperatures and (2) large carbon and molecular weight distribution in the pyrolysis product, resulting in limited market value. These effects can be reduced through the use of catalysts in the cracking process. (Donaj et al. 2012)

Cracking of PE can favor propene and isoalkanes. Butenes and pentenes are also formed. Figure 6 presents the effect of temperature on reaction time and product distribution of virgin PE-LD. (Kumar & Singh 2013)

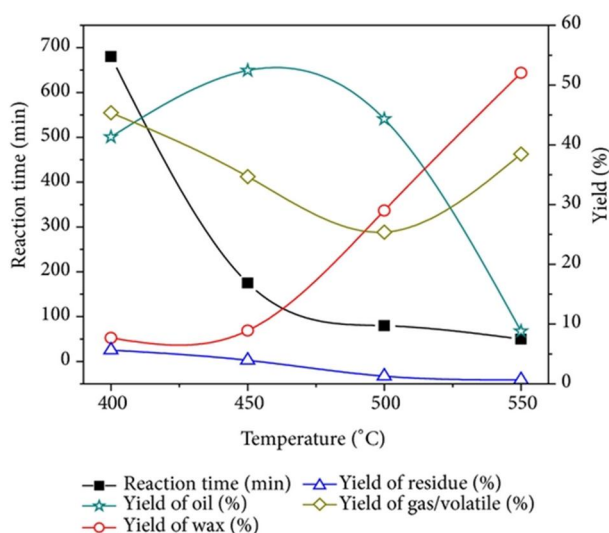


Figure 6. The effect of temperature on reaction time and product distribution of virgin PE-LD (Kumar & Singh 2013).

PE-HD has been cracked to light olefins (Figure 7) by a two-step thermal process in a conical spouted bed reactor (CSBR). At 500 °C, 67 % waxes (C21+) and 26 % C12-C21 hydrocarbons were obtained. In the second step, volatiles



were cracked at 900 °C and ethylene, propylene, and butenes were obtained at yields of 40.4, 19.5, and 17.5 wt-%, respectively. (Artetxe et al. 2012)

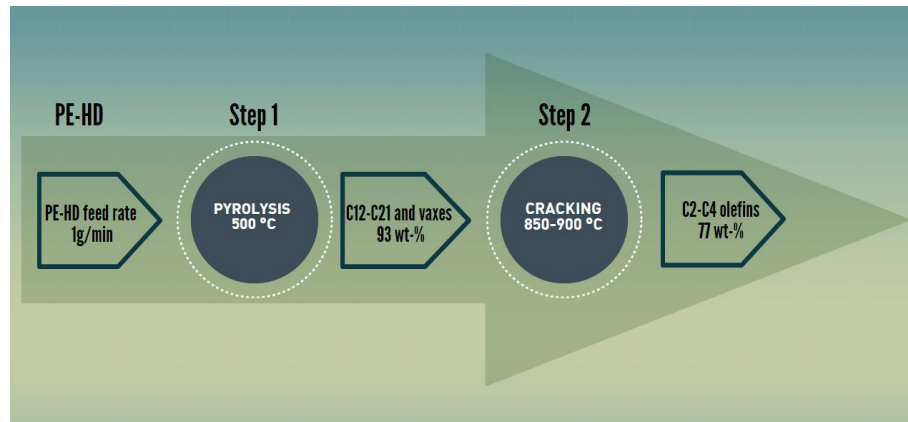


Figure 7. Diagram of two-step process producing olefins from PE-HD (Modified from Artetxe et al. 2012).

Pyrolysis of PP gives a mixture of C4-C9 hydrocarbons, mostly mono-olefins. PP has more tertiary carbon atoms and therefore is more reactive than PE-LD. As a result of this, more gas is generated at low temperatures in the presence of PP. Pyrolysis of PP and PE-LD produces tar containing paraffinic and olefinic structures. (Donaj et al. 2012)

PE and PP decompose into a range of paraffin and olefins. Paraffin to olefin ratio increases with decreased temperature and time (Figure 8). Further cracking of long-chain waxes can be carried out using catalysts. Hydrogen as a reactive carrier gas increases the condensed and paraffinic product yield.

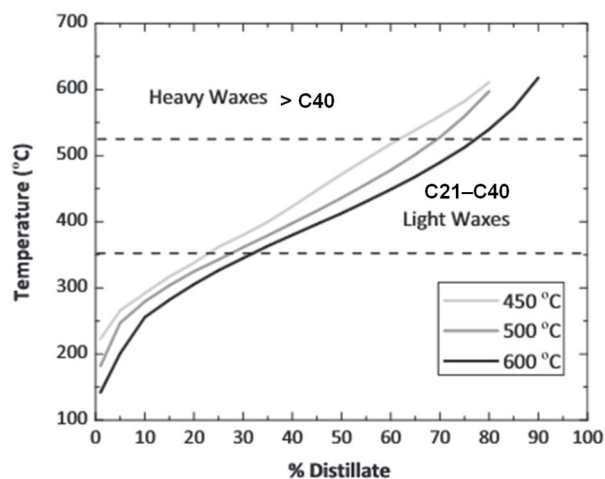


Figure 8. Simulated distillation curves for PP waxes obtained at three temperatures (Modified from Arabiourrutia et al. 2012).

Figure 9 presents catalytic pyrolysis of a polyolefins mixture at different temperature. The yield of ethylene+propylene was below 30 %. (Donaj et al. 2012)

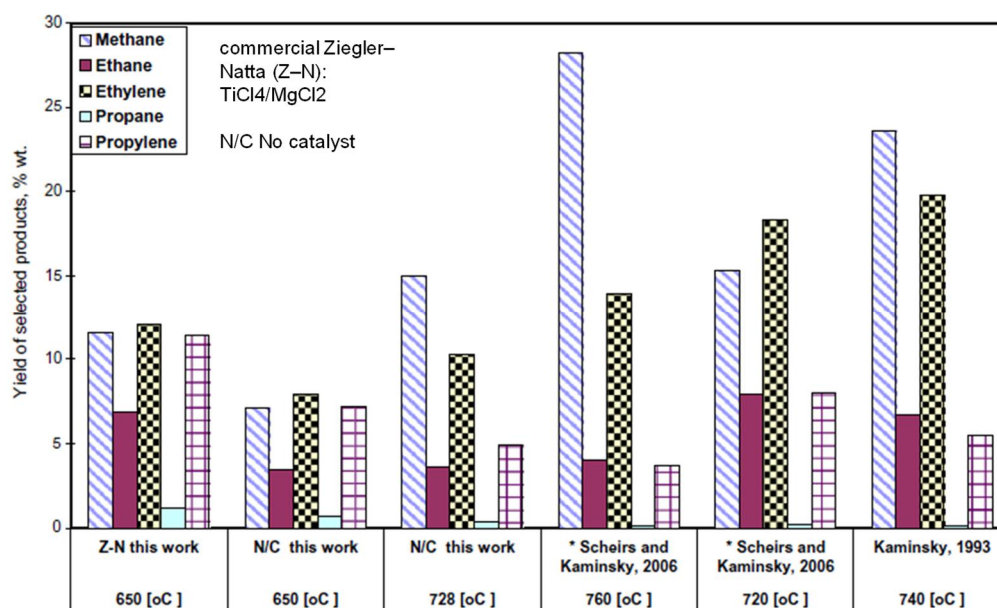


Figure 9. Product distribution from pyrolysis of a polyolefin mixture having 46 wt-% of low density polyethylene (PE-LD), 30 wt-% of high density polyethylene (PE-HD), and 24 wt-% of isotactic polypropylene (PP) (Modified from Donaj et al. 2012).

Table 6 shows the share of waxes and volatiles obtained from pyrolysis of polyolefines at different temperatures.

Table 6. Yield of waxes and volatiles (% in weight) obtained from different polyolefins at three temperatures (Modified from Arabiourrutia et al. 2012).

MATERIAL	T ( °C )	WAXES (wt-%), ABOVE C20	VOLATILES (wt-%), BELOW C20
PE-LD	450	80	20
	500	69	31
	600	51	49
PE-HD	450	80	20
	500	68	32
	600	49	51
PP	450	92	8
	500	75	25
	600	50	50

Waxes are defined as the hydrocarbons above C20 and volatiles those below C20.

#### 5.1.4 Pyrolysis of heteroatoms containing polymers

Tables 7 and 8 summarize heteroatoms containing polymers and their challenges in fuel oil production.



*Table 7. Polymer as feedstock for fuel production (Modified from UNEP 2009).*

POLYMER TYPES	DESCRIPTION	EXAMPLES
Polymers consisting of carbon and hydrogen	Typical feedstock for fuel production (high heat value and clean exhaust gas)	PE, PP, PS Thermoplastics melt to form solid fuel mixed with other combustible wastes and decompose to produce liquid fuel
Polymers containing oxygen	Lower heat value than above plastics	PET, phenolic resin, polyvinyl alcohol, polyoxymethylene
Polymers containing nitrogen or sulfur	Fuel from this type of plastic is a source of hazardous components such as NO <sub>x</sub> or SO <sub>x</sub> in flue gas. Flue gas cleaning required to avoid hazardous components emission in exhaust gas.	Nitrogen: PA, PUR Sulfur: polyphenylene sulfide
Polymers containing halogens of chlorine, bromine and fluorine	Source of hazardous and corrosive flue gas upon thermal treatment and combustion	PVC, PVDC, bromine-containing flame retardants and fluorocarbon polymers.

*Table 8. Product types of some plastic pyrolysis (Modified from UNEP 2009).*

Main products	Type of plastics	As a feedstock of liquid fuel
Liquid hydrocarbons	PE, PP, PS, PMMA	Allowed
Liquid hydrocarbons	ABS	Allowed, but not suitable. Nitrogen-containing fuel is obtained. Special attention required to cyanide in oil.
No hydrocarbons suitable for fuel	PVA POM	Not suitable. Formation of water and alcohol. Not suitable. Formation of formaldehyde.
Solid products	PET	Not suitable. Formation of terephthalic acid and benzoic acid.
Carbonous products	PUR, PF	Not suitable
HCl and carbonous products	PVC, PVDC	Not allowed

#### 5.1.4.1 Pyrolysis of PET

PET residues represent on average 7.6 wt-% of the different polymer wastes in Europe. The polymer structure and the thermal cleavage mechanism of PET is shown in Figure 10. Among the thermally weak linkages, that is, the C–O bonds along the polymer chains, those located at the adjacent position of C=O bonds are most likely subject to thermal cleavage with further degradation to phthalic and benzoic acid and possibly to benzene with CO<sub>2</sub> release. BFB or CFB might be the most appropriate pyrolysis reactors for PET pyrolysis. (Brems et al. 2011)





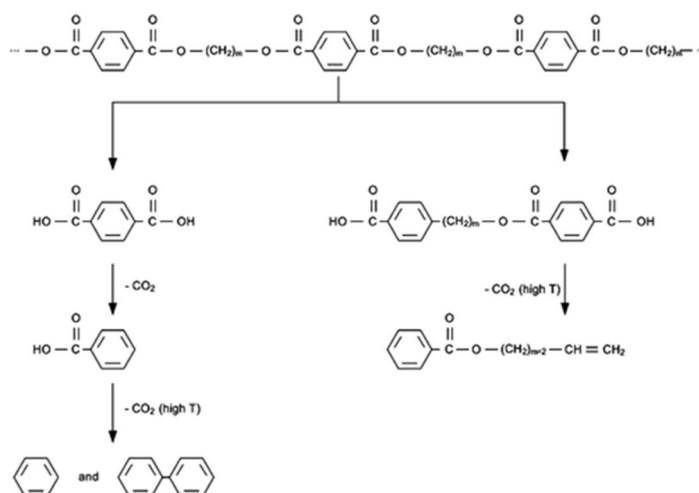


Figure 10. PET and its most likely thermal cleavage mechanisms to various products ( $m=2$ ) (Brems et al. 2011).

PET pyrolysis leads to the formation of tar, which has mostly aromatic structure. C1 + C2 are the main hydrocarbon types generated in PET pyrolysis. Oil yield from PET are similar than from polyolefines (Figure 11). Oil is aromatic (benzoic acid, monovinyl terephthalate, divinyl terephthalate, vinyl benzoate, benzeneare). (Cit et al. 2010)

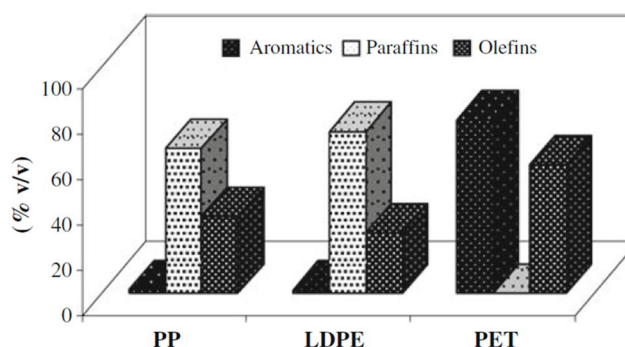


Figure 11. The amounts of hydrocarbon types in the tars obtained from the pyrolysis of PP, PE-LD, and PET at 700 °C (Cit et al. 2010).

Depending on the polymers or polymer mixtures and the operating conditions used, yields vary widely. As a rule both gaseous and liquid products are mixtures of numerous different compounds. Product yields from resins depend on the composition of feed, pyrolysis conditions, reactor technology, and post-treatments. (Scheirs & Kaminsky 2006)

#### 5.1.4.2 Pyrolysis of WEEE

WEEE plastics are an important environmental problem because these plastics commonly contain toxic halogenated flame retardants that may cause serious environmental pollution, especially the formation of carcinogenic polybrominated dibenzo dioxins/furans (PBDD/Fs) (Yang et al. 2013).



Figure 12 presents the pyrolysis of metal fraction containing plastic insulation material from WEEE. After pyrolysis, almost 85 % of the material is metal, mainly copper and aluminium. Metallic yields of copper, aluminium, and zinc were 98.3 %, 93.1 %, and 96 %, respectively. About 60 % of bromine and over 95 % of chlorine were removed to gases. (Diaz et al. 2015)

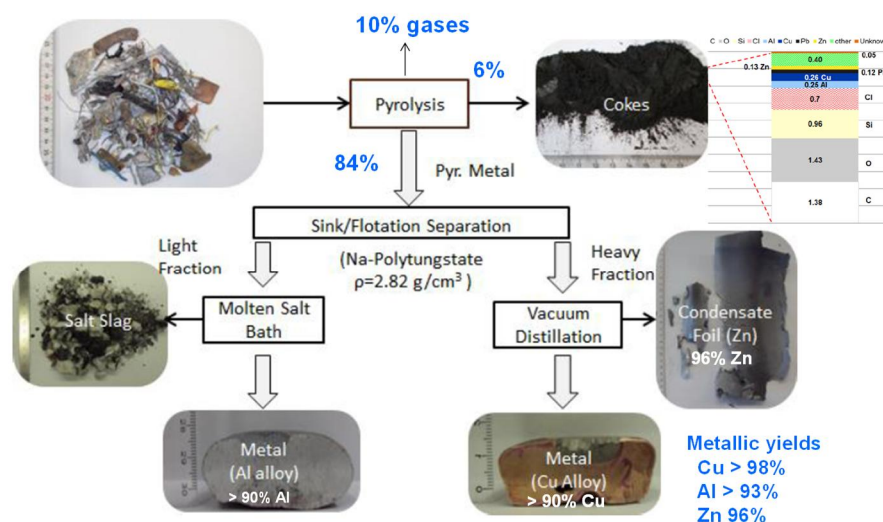


Figure 12. Flowchart of the recycling path applied to the metallic fraction containing plastic insulation material from WEEE (Modified from Diaz et al. 2015).

#### 5.1.4.3 Pyrolysis of automotive shredded residue (ASR)

Directive 2000/53/EC sets a goal of 85 % material recycling from end-of-life vehicles (ELVs) by the end of 2015. Flotation followed by pyrolysis of the light, organic fraction may be a suitable automotive shredded residue (ASR) recycling technique if the oil can be further refined and used as a chemical. Metals are liberated during thermal cracking and can be easily separated from the pyrolysis char, amounting to roughly 5 % in mass. (Santini et al. 2012)

#### 5.1.4.4 Pyrolysis of tires

There is growing interest in pyrolysis as a technology to treat tyres to produce valuable oil, char and gas products. Table 9 shows the composition of passenger and truck tyres. The most common reactors used are fixed-bed (batch), screw kiln, rotary kiln, vacuum and fluidised-bed. The key influence on the product yield, and gas and oil composition, is the type of reactor used which in turn determines the temperature and heating rate (Table 10). Tyre pyrolysis oil is chemically very complex containing aliphatic, aromatic, hetero-atom and polar fractions. Figure 13 shows rubber pyrolysis oils and its fractions. It is similar to a gas oil or light fuel oil and has been successfully combusted in test furnaces and engines. Variation in feed quality, high heavy metal, and sulphur contents, and low flash point are the most critical properties considering the fuel application. Examples of commercial and semi-commercial scale tyre pyrolysis systems show that small scale batch reactors and continuous rotary kiln reactors have been developed to commercial scale. (Williams 2013)





*Table 9. Composition of passenger and truck tyres (Evans & Evans 2006, cited by Williams 2013).*

COMPONENT	PASSENGER TYRE (wt-%)	TRUCK TYRE (wt-%)	COMMENTS
Rubber	47	45	Many different synthetic and natural rubbers used: e.g. styrene-butadiene, natural, nitrile, chloroprene, and polybutadiene rubbers
Carbon black	21.5	22	Strengthens the rubber and aids abrasion resistance
Metal	16.5	21.5	Steel belts and cord for strength
Textile	5.5	-	Used for reinforcement
Zinc oxide	1	2	Used (with stearic acid) to control the vulcanisation process and to enhance the physical properties of the rubber
Sulphur	1	1	Used to cross link the polymer chains within the rubber and also to harden and prevent excessive deformation at elevated temperatures
Additives	7.5	5	E.g. clay or silica used to partial replacement of carbon black

*Table 10. Range of pyrolysis reactors and product yields from the pyrolysis of waste tyres (Williams 2013).*

REACTOR TYPE	EXPERIMENTAL CONDITIONS	MAXIMUM OIL YIELD			
		T (°C)	Oil (wt-%)	Char (wt-%)	Gas (wt-%)
Fixed bed, batch	400–700 °C	500	40.26	47.88	11.86
Fixed bed, batch	500–1000 °C; 1200/min heating rate	500	58.0	37.0	5.0
Closed batch	350–450 °C; 30/min heating rate; 20 g tyre	450	~63	~30	~7
Fixed bed, batch	300–720 °C; 5–80 °C/min heating rate; 50 g tyre	720	58.8	26.4	14.8
Fixed bed, batch	450–600 °C; 5 °C/min heating rate; 3 kg, tyre	475	58.2	37.3	4.5
Fixed bed, batch	950 °C (max.); ~2 °C/min heating rate; 1 t tyre	950 <sup>a</sup>	20.9	40.7	23.9
Fixed bed, batch	350–600 °C; 5 °C/min and 35/min heating rate	400	38.8	34.0	27.2
Fixed bed, batch	300–700 °C; 15 °C/min heating rate; 175 g tyre	700	38.5	43.7	17.8
Fixed bed, batch	375–500 °C; 10 °C/min heating rate; 10 g tyre	425	60.0	~30	~10
Fixed bed, batch, internal fire tubes	375–575 °C; 750 g tyre	475	55	36	9
Moving screw bed	600–800 °C; 3.5–8.0 kg/h mass flow rate	600 <sup>b</sup>	48.4	39.9	11.7
Rotary kiln	550–680 °C; 4.8 kg/h throughput	550	38.12	49.09	2.39
Vacuum, conical spouted bed	425 °C and 500 °C; 25 and 50 kPa vacuum	500	~60	~34	~4
Rotary kiln	450–650 °C; 12–15 kg/h throughput	500	45.1	41.3	13.6
Fluidised bed	740 °C; 1 kg/h throughput; tyre powder	740	30.2	48.5	20.9
Fluidised bed	750–780 °C; 30 kg/h throughput; tyre pieces	750	31.9	38.0	28.5
Fluidised bed	700 °C; 200 kg/h throughput; whole tyres	700 <sup>c</sup>	26.8	35.8	19
Fluidised bed	450–600 °C; ~220 g/h throughput; tyre granules	450	55.0	42.5	2.5
Circulating fluidised bed	360–810 °C; 5 kg/h throughput	450	~52	~28	~15
Conical spouted bed	425 and 500 °C	500	~62	~35	~3
Vacuum	485–550 °C; batch (80–180 kg) and continuous	520 <sup>d</sup>	45	36	6
Vacuum	500 °C; pilot scale semi continuous	500	56.5	33.4	10.1
Vacuum	450–600 °C; batch (100 g)	550	47.1	36.9	16
Drop tube	450–1000 °C; 30 g/h throughput	450 <sup>e</sup>	37.8	35.3	26.9
Fixed, wire mesh, fast reactor	390–890 °C; 70–90 °C/s heating rate; 0.2 g	860	~5	~22	~73

<sup>a</sup>12.9 wt-% Steel also produced; 950 °C was the maximum pyrolysis temperature

<sup>b</sup>Tyre mass flow rate of 8.0 kg/h

<sup>c</sup>13.3 wt-% steel and 5.1 wt-% water also produced

<sup>d</sup>Operated in batch mode; 10 wt-% steel and 3 wt-% water also produced

<sup>e</sup>Product yields average of two experiments





Crude, and distilled (< 150, 200, 250°C) rubber oils

*Figure 13. Crude and distilled rubber oils (Modified from Piluza & Muzenda 2013).*

### 5.1.5 Commercial and pilot approaches to dechlorination

Japanese Sapporo Plastic Recycling Co. uses a single screw extruder for dechlorination of waste plastics in pilot scale (5 tpd). Some technical challenges remain such as corrosion and generation of metallic oxides which clog pipes, strainers and heat exchangers.  $\text{Ca}(\text{OH})_2$  addition can reduce corrosion problems. (Butler et al. 2011)

In the process by BASF plastic feedstocks are dechlorinated in a stirred tank pre-treatment unit and the HCl recovered and subsequently used for manufacturing of chemicals. In the Zadgaonkar process coal (used as a hydrogen-donating material) as well as other patented additives are used in a pre-pyrolysis dechlorination operation. The Reentech process uses a catalyst-coated paddle for feedstock dehalogenation. (Butler et al. 2011)

Pyrolysis reactor can be also used to carry out dechlorination. For example, in the Agilyx approach both thermal and vacuum pre-treatment steps are employed in the batch reactor before the temperature and pressure are ramped up for pyrolysis. This approach enables fractionating of moisture and HCl from the feedstock. In addition, in the Hamburg/BP process sorbents like limestone were used in the fluid bed to absorb chlorine. (Butler et al. 2011)

Dow/BSL is a fully commercial plant in Schkopau, Germany, which uses mixed waste, and has been in operation since 1999. The process can handle mixed PVC waste, contaminated oil, bio-sludge and hazardous solids containing chlorinated substances. HCl and energy are recovered. The annual capacity is 45 000 tonnes of waste intake. An average of 90 % of the chlorine from the PVC input is recovered as 20 % HCl (aqueous). The HCl quality is within the specification for use in the on-site chlor-alkali plant via membrane electrolysis. PVC waste has a lower calorific value than other plastic waste due to the high chlorine content. To treat PVC waste in the rotary kiln, other waste with high calorific value is added to support the combustion. A total energy recovery of 50 % is achieved for PVC. (Tukker et al. 1999)

The Nanofuel process uses a dechlorination/cracking catalyst. In this approach, the cation-donating catalyst absorbs chlorine and sinks to the bottom of the pyrolysis reactor where it can be removed. The Altis process removes HCl from hydrocarbon vapour in a dechlorination unit after pyrolysis. (Butler et al. 2011)



### 5.1.6 Co-pyrolysis

Co-pyrolysis is a promising technique that can produce a high grade pyrolysis oil from biomass waste (Figure 14). This technique also offers several advantages on its application (Abnisa et al. 2014):

- Co-pyrolysis can be easily applied to existing biomass pyrolysis plants
- Low costs are associated with upgrading processes from pyrolysis to co-pyrolysis: if a wood-based biomass is pyrolysed in the plant, no money needs to be invested in a special plant for waste plastics and tires
- No special equipment needs to be designed and constructed for co-pyrolysis. Some minor modifications maybe needed, but only for the feed preparation system.
- As a byproduct, solid fuel is sometimes poor in organic matter; the addition of waste plastics and tires to wood-based biomass may improve its quality
- The quantity and quality of desired products (oil, solid, or gas) can be easily controlled by adjusting the process parameters

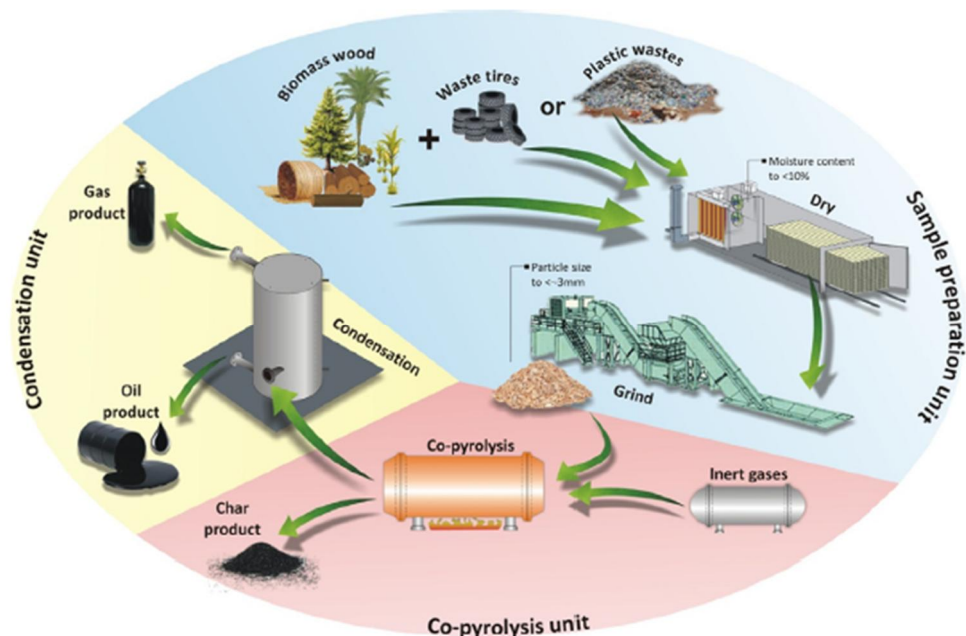


Figure 14. Co-pyrolysis of biomass and wastes (Abnisa et al. 2014).

The co-pyrolysis technique can improve the quantity and quality of pyrolysis oil significantly without the presence of any catalysts or solvents and free hydrogen pressure. This technique can be considered as simple, cheap, and effective method to obtain high-grade pyrolysis oil. The availability of plastic and tire waste plays an important role in the sustainability of this technique. From an economic point of view, co-pyrolysis is found to be a promising option in biomass conversion to produce pyrolysis oil. Due to the fact that biomass wastes are easy to find and available in abundant amounts around the world, co-pyrolysis has a huge development potential in many countries. Using biomass wastes to produce pyrolysis oil could reduce the need for landfills, decrease the cost of waste treatment, and solve some environmental problems. The primary disadvantage of co-pyrolysis lies in the biomass preparation unit. Given that this







technique deals with many types of biomass, an additional pre-treatment system is required that can substantially increase the cost for the installation and operation of such units. (Abnisa et al. 2014)

## 5.1.7 PTL technology

### 5.1.7.1 Reactor technology

Table 11 presents various reactor technologies for PTL. Presently stirred tank and drum type reactors dominate because they are the easiest technologies for heterogenous wastes. However, a fluid bed technology is also very potential for plastic pyrolysis. (Butler et al. 2011, Amutio et al. 2015)

*Table 11. Comparison of the pyrolysis technologies for plastics (Data from Butler et al. 2011, Amutio et al. 2015).*

Reactor type	Special features	Pilot/Demonstration for PTL
Bubbling fluidised bed (BFB)	+ Excellent heat and material transfer rates	Hamburg fluidised bed
Conical spouted bed	+ A smaller reactor volume for the same production rate compared to FB, simpler design, operation with much higher particle diameters, avoided bed defluidisation	No
Circulating fluidised bed (CFB)	+ Most widely used scalable process	Reentech process (Korea)
Rotating cone	+ No fluidization gas or cyclones are necessary, good solid polymer mixing achieved	No
Stirred tank	+ One of the most frequently applied reactors for plastics, good conversion, better heat transfer to the melt, can contain a heat transfer medium like hot oil (Nanofuel process) or upgrading can take place in a separate vapour upgrading tower (Thermofuel), char/spent catalysts/ contaminants are removed from the bottom of the reactor (Nanofuel, Thermofuel, Royco), with the exception of the Hitachi process, which vacuums the char from the bottom via a vertical vacuum line, uniform heat distribution, and scrapes char deposits from the reactor walls. - Requires frequent maintenance and oversized infrastructure, secondary reactions dominate, heat gradients may exist, end product upgrading is necessary	Thermofuel (Cynar Plc), Smuda (Poland), Polymer-Engineering (Nanofuel), Royco (Beijing, China), Reentech (Korea), Hitachi Zosen, Chiyoda (China)
Tube reactors	+ Potential for smaller scale applications + The reactor used is rather flexible and various conditions have been applied ranging between mild thermal pyrolysis of polyolefins for oil and wax production to catalytic cracking for the production of liquid fuels, to fuel additive production	BASF 9 kg/h demonstration plant in Hungary Dispons
Agilyx	+The temperature and pressure of the batch reactor can be controlled. This allows feedstock pre-treatment in the pyrolysis chamber for the removal of contaminants like water and hydrochloric acid. The pressure and thermal conditions are subsequently applied for the collection of a liquid fuel product.	Agilyx
Rotary kilns, Drum type	+ Robust technology - Low product quality	The Faulkner process, the Conrad recycling process (plastic and/or tyres) The Toshiba/Sapporo process employs a rotary kiln with ceramic balls to avoid coke build-up inside the reactor
Auger kiln	+ The kiln is fixed and a centred co-axial auger conveys the material through the reactor	Haloclean process
Reactive extruder	+ Variant from Auger, can be exploited on small scales (< 10,000 tpd)	No
Microwave	- Poor thermal conductivity of plastics is a problem	No
Freefall reactor	- Heat transfer to the plastics problematic	Blowdec process



Figure 15 shows the schematic presentation of some reactors typically used in PTL processes. Technologies used in PTL demonstration plants are presented in more detail in Section 5.1.7.3.

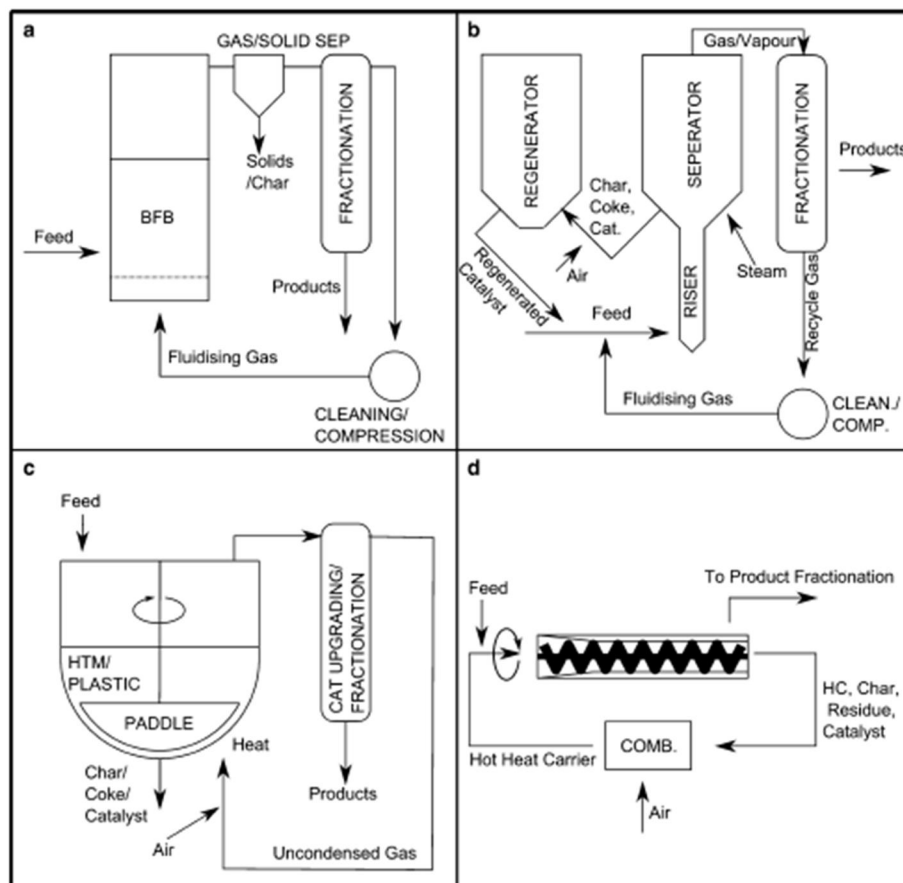


Figure 15. Reactors used in PTL processes: a) Bubbling fluidised bed, b) Fluid catalytic cracking, c) Stirred tank reactor, d) Screw/Auger reactor, HC = Heat carrier (Butler et al. 2011).

### 5.1.7.2 Integration with oil refining

Figure 14 illustrates the possibilities for integrating pyrolysis processes with existing oil refining infrastructure. These include (1) direct processing of plastic wastes in FCC units, (2) co-processing of plastic wastes in FCC units, (3) co-processing of polyolefin-derived pyrolysis waxes/oils in FCC units, (4) hydrocracking of plastic wastews, and (5) hydrocracking of pyrolysis products. Challenges for integration include transforming plastic oil into pumpable liquid, decomposition products of contaminants (e.g. PVC and PET are very corrosive to refinery infrastructure), and other contaminants that can cause operational problems such as catalyst deactivation. (Butler et al. 2011)



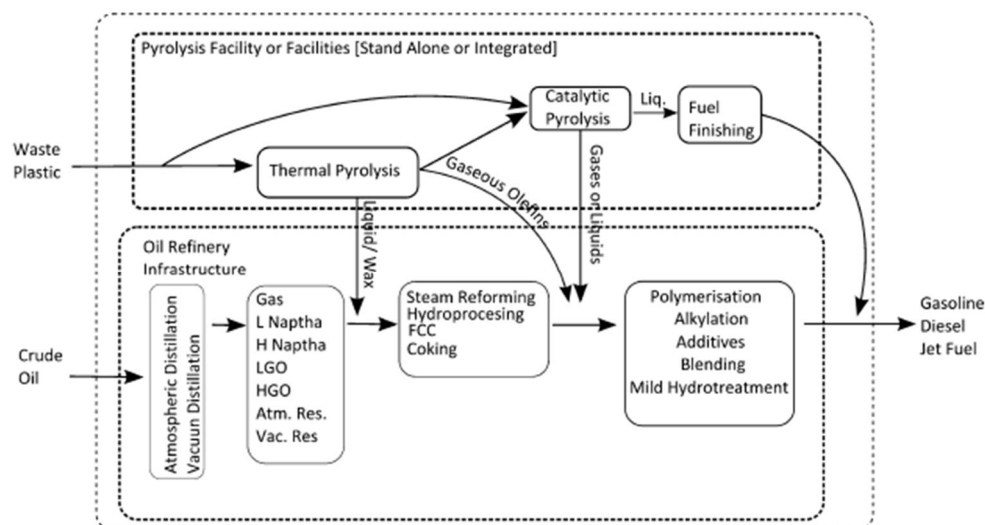


Figure 16. Integration of plastic waste processing with oil refining operations (Butler et al. 2011).

### 5.1.7.3 Pilot and demonstration plants

Several PTL pyrolysis demonstration plants exist and are planned in Europe and elsewhere (Table 12 - Table 15). In 2015, 16 commercial size PTL systems were in operation in India, 3 in USA, 3 in Europe, and 1 in Japan. Typical PTL system capacity varies between 10 and 60 tpd. Main technology suppliers are Cynar in Europe, Agilyx in USA, Toshiba Corporation in Japan, and Pyrocrat Systems LLP in India.

Table 12. Commercial scale PTL systems in 2015 (Ocean Recovery Alliance 2015).

TECHNOLOGY SUPPLIER	OWNER/OPERATOR	LOCATION	STATUS IN 2015
Not disclosed	SITA	Bristol, UK	In commissioning
Cynar	Plastic Energy SL *	Almeria, Spain *	In commissioning*
Agilyx	GenAgain Technologies LLC	Lithia Springs, Georgia, USA	Not disclosed
Agilyx	Rational Energies*	Plymouth, Minnesota USA *	Unknown*
Agilyx	Waste Management *	North Portland, Oregon, USA *	Unknown*
Toshiba Corp.	Sapporo Plastics Recycling, Co.	Sapporo, Japan	Not operational
Polymer Energy	MK Aromatics Ltd.	Tamil Nadu, India	Operational
Pyrocrat Systems LLP	Not disclosed	Maharashtra Province, India *	Operational*
Pyrocrat Systems LLP	Not disclosed	Rajasthan Province, India *	Operational*
Pyrocrat Systems LLP	Not disclosed	Rajasthan Province, India *	Operational*
Pyrocrat Systems LLP	Not disclosed	Maharashtra Province, India *	Operational*
Pyrocrat Systems LLP	Not disclosed	Maharashtra Province, India *	Operational*
Pyrocrat Systems LLP	Not disclosed	Karnataka Province, India *	Operational*
Pyrocrat Systems LLP	Not disclosed	Tamil Nadu Province, India *	Operational*
Pyrocrat Systems LLP	Not disclosed	Maharashtra Province, India *	Operational*
Pyrocrat Systems LLP	Not disclosed	Maharashtra Province, India *	Operational*
Pyrocrat Systems LLP	Not disclosed	Maharashtra Province, India *	Operational*
Pyrocrat Systems LLP	Not disclosed	Maharashtra Province, India *	Operational*
Pyrocrat Systems LLP	Not disclosed	Gujarat Province, India *	Operational*
Pyrocrat Systems LLP	Not disclosed	Maharashtra Province, India *	Operational*
Pyrocrat Systems LLP	Not disclosed	Andhra Pradesh Province, India *	Operational*
Pyrocrat Systems LLP	Not disclosed	Gujarat Province, India *	Operational*
Pyrocrat Systems LLP	Not disclosed	Not disclosed, Europe	Operational*

Hydrot Systems Ltd.	Not disclosed	Not disclosed, Europe
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\*Supplier reported data and/or information not verified by system owner/operator







*Table 13. Commercial Scale PTL systems planned for 2016 (Ocean Recovery Alliance 2015).*

TECHNOLOGY SUPPLIER	OWNER/ OPERATOR	LOCATION	STATUS IN 2015
Cynar	Plastic Energy SL*	Seville, Spain*	Under construction*
Cynar	Plastic Energy SL*	Undisclosed location, South America*	In planning*
Agilyx	Not disclosed	Not disclosed	In planning
Vadxx	Vadxx/Liberation Capital	Akron, Ohio, USA	Under construction
RES Polyflow	RES Polyflow	To be determined, Ohio or Indiana, USA	Site selection underway
Nexus Fuels	Nexus Fuels	To be determined, South Eastern USA	Site selection underway
PARC	PARC	Huaian, China	Equipment transfer underway
Pyrocrat Systems LLP	Not disclosed	Madhya Pradesh Province, India*	Equipment on order*
Pyrocrat Systems LLP	Not disclosed	Maharashtra Province, India*	Equipment on order*
Pyrocrat Systems LLP	Not disclosed	Gujarat Province, India*	Equipment on order*
Pyrocrat Systems LLP	Not disclosed	Maharashtra Province, India*	Equipment on order*
Pyrocrat Systems LLP	Not disclosed	Maharashtra Province, India*	Equipment on order*
Pyrocrat Systems LLP	Not disclosed	Maharashtra Province, India*	Equipment on order*
Pyrocrat Systems LLP	Not disclosed	Madhya Pradesh Province, India*	Equipment on order*
Pyrocrat Systems LLP	Not disclosed	Tamil Nadu Province, India*	Equipment on order*
Pyrocrat Systems LLP	Not disclosed	Maharashtra Province, India*	Equipment on order*
PK Clean	PK Clean	Salt Lake City, Utah	Capacity upgrade underway

\*Supplier reported data and/or information not verified by system owner/operator

*Table 14. Detail on select known PTL systems with potential to fully commercialize operations in 2015/early 2016 (Design capacity  $\geq 1$  tpd) (Ocean Recovery Alliance 2015).*

Location	Akron, OH, USA	Almeria, Spain	Seville, Spain	Bristol, England, UK	Ohio or Indiana	South Eastern USA
Owner/ Operator	Liberation Capital, Vadxx	Plastic Energy	Plastic Energy	SITA	RES Polyflow	Nexus Fuels and undisclosed strategic investor
Technology supplier	Vadxx	Cynar Plc	Cynar Plc	Not disclosed	RES PolyFlow	Nexus Fuels
Design capacity	60 tpd	20 mtpd*	20 mtpd*	20 mtpd	60 tpd	50 tpd
Planned feedstocks	Blend of post-consumer and post-industrial rigid and film plastics	Blend of post-consumer and post-industrial rigid and film plastics*	Blend of post-consumer and post-industrial rigid and film plastics*	Blend of post-consumer and post-industrial rigid and film plastics	Post industrial scrap, post-consumer #3-7 bales, agricultural film, marina and vehicle shrink wrap, contaminated /off spec compounds	Blend of post-industrial and post-consumer plastics
Feedstock source	Single stream material recovery facility (MRF)	Supply from co-located single stream MRF and other regional MRFs*	Single stream MRF*	Supply from co-located MRF owned/ operated by SITA	To be determined	To be determined
Oil product	On Spec Middle Distillate #2 Diesel	CynDiesel TM, CynLite TM and CynKero TM*	CynDiesel TM, CynLite TM and CynKero TM*	Not disclosed	Naphtha blendstock, distillate blendstock, heavy oil	Blend of light sweet crude, Fuel Oil #2 fractionated diesel blendstock, gasoline blendstock, kerosene blendstock, wax





<b>End use</b>	Direct terminal blending	Bulk sales to oil distributor, end use unknown*	Bulk sales to oil distributor, end use unknown*	Not disclosed	Blendstock sales to fuel blenders, heavy oil sales to consolidator or direct to end user	Light sweet crude sales to broker, fuel Oil #2 sales to strategic investor, fractionated fuel sales into local markets for blending into transportation fuels
<b>Status</b>	In construction	In commissioning*	In construction	In commissioning	Site selection underway, (existing demo scale system will be re-located)	Site selection underway
<b>Feedstock agreements in place? (% of feed covered)</b>	100 % secured	100 % secured*	100 % secured*	100 % provided by own internal supply	Letter of intents in place (100 %)	No
<b>Offtake agreements in place? (% of end product covered)</b>	Negotiations underway	100 % under contract*	100 % under contract*	100 % under contract	Letter of intents in place (< 100 %)	For #2 heating oil only

\*Supplier reported data and/or information not verified by system owner/operator

Table 15. Pre-qualified supplier technology offering (Ocean Recovery Alliance 2015).

TECHNOLOGY SUPPLIER	PTF SYSTEMS DEVELOPED (Location/ Scale/Status) <sup>17</sup>	REGIONS SERVED	DEPOLYMERIZATION/ FEED PROCESS METHOD	AVAILABLE DESIGN CAPACITIES (Plant availability)	PRE-SORTING /PRE-TREATMENT
<b>Agilyx</b> Participating supplier	<b>1. Tigard, OR, USA</b> Pilot (10 tpd) - Gen6; continuous operations, at capacity <b>2. Plymouth, MN, USA*</b> Commercial -Gen5; operating status unknown <b>3. Lithia Springs, GA, USA</b> Commercial - Gen5; did not disclose <b>4. North Portland, OR, USA*</b> Commercial - Gen5; operating status unknown	North America	Thermal depolymerization Generation 5 technology, batch feed  Generation 6 technology, continuous feed	50 tpd (92 %)	No/No
<b>Cynar</b> Participating supplier	<b>1. Portlaoise, Ireland</b> Pilot (10 mtpd); discontinuous operations <b>2. Almeria, Spain*</b> Commercial (20 mtpd); in commissioning <b>3. Bristol, UK</b> Commercial (20 mtpd); in commissioning <b>4. Seville, Spain*</b> Commercial (20 mtpd); in construction	Europe, Latin America	Thermal depolymerization, continuous feed	20 mtpd (82 %)	No/No
<b>Blest</b> Contributing supplier	<b>1. Whitehorse, Yukon Canada</b> Pilot (528 lbs/day); discontinuous operations <sup>18</sup>	Blest-International	Thermal depolymerization, continuous feed	528, 1320, 2640, 5280 lbs/day; 5, 16, 21 tpd (100 %) <sup>19</sup>	





<b>Golden Renewables</b> Participating supplier	<b>1. Yonkers, NY, USA</b> Demonstration (24 tpd); discontinuous operations	US	Thermal depolymerization, continuous feed	24 tpd (90 %)	No/Yes
<b>JB</b> Participating supplier	<b>1. Niagara Falls, NY, USA</b> Demonstration (25 tpd); not operational	US	Catalytic depolymerization, continuous feed	20-30 tpd (75 %)	No/No
<b>Klean Industries<sup>20</sup></b> Contributing supplier	<b>1. Sapporo, Japan</b> Commercial (40 mtpd); not operational	International	Thermal depolymerization, continuous feed	3, 5, 10, 15, 20, 25, 30, 50, 100, 150 mtpd (Unknown)	Unknown
<b>MK Aromatics Limited / Polymer Energy (Technology supplier)</b>	<b>1. Alathur, Tamil Nadu, India</b> Commercial (10 mtpd); continuous operations, at capacity, economic status unknown	India	Catalytic depolymerization, continuous feed <sup>21</sup>	10 mtpd (82 %)	Yes/Yes
<b>Nexus Fuels</b> Participating supplier	<b>1. Atlanta, GA, USA</b> Pilot (1.5-2 tpd) discontinuous operations	US	Thermal depolymerization, continuous feed	50 tpd (96 %)	No/Yes
<b>PARC<sup>21</sup></b> Participating supplier	<b>1. Xinghua, Jiangsu Province, China<sup>*22</sup></b> Demonstration (~15 mtpd); continuous operations; operating capacity unknown <b>2. Nantong, Jiangsu Province, China<sup>*22</sup></b> Demonstration (20 mtpd); discontinuous operations <b>3. Huaian, China</b> Commercial (60 mtpd); not operational (currently relocating equipment)	China	Catalytic depolymerization, continuous feed	15, 25, 60 mtpd (Unknown)	No/No
<b>PK Clean</b> Participating supplier	<b>1. Salt Lake City, UT, USA</b> Pilot (5 tpd); continuous operations, at capacity	US	Catalytic depolymerization, continuous feed	10, 20 tpd (90 %)	No/Option to include
<b>Pyrocrat Systems LLP</b> Participating supplier	<b>15 systems located across India and 1 in an undisclosed location in Europe*</b> Commercial (2-10 mtpd); continuous operations, at capacity, economic status unknown	India	Catalytic depolymerization, continuous feed	3,6,12 mtpd (82 %)	No/ Option to include
<b>RES Polyflow</b> Participating supplier	<b>1. Perry, OH, USA</b> Demonstration (60 tpd); not operational	US	Thermal depolymerization, continuous feed	60 tpd (100 %)	No/Yes
<b>Vadxx</b> Participating supplier	<b>1. Danville, PA, USA</b> Pilot (1 tpd); discontinuous operations <sup>23</sup> <b>2. Akron, OH</b> Commercial (60 tpd); in construction	US	Thermal depolymerization, continuous feed	60 tpd <sup>24</sup> (90 %)	No/No

\*Supplier reported data and/or information not verified by system owner/operator

<sup>17</sup> Processes a min. of 75 % plastic feedstock. Systems processing exclusively tire or other wastes are excluded.

<sup>18</sup> Best reports over 60 installations in Japan, Africa and Nepal. Ocean Recovery Alliance was not able to independently verify the location or operating status of systems aside from that in Whitehorse, Yukon

<sup>19</sup> Plant availability data based on marketing materials. Data not verified by supplier or facility operator.

<sup>20</sup> Ocean Recovery Alliance was not able to verify the nature of Klean Industries business relationship with Toshiba Corp.

<sup>21</sup> MK Aromatics utilized technology from Polymer Energy LLC. Polymer Energy was not reachable for comment as their website is no longer functioning.

<sup>22</sup> System does not represent company's current offering

<sup>23</sup> Not operational during study period

<sup>24</sup> Assumes 8 % moisture level with 55 tpd entering the extruder



### Cynar

Cynar Plc is the main PTL technology supplier in Europe. The technology (Figure 17) has also been sold to South America, Florida and the Caribbean. The first commercial scale plant in Almeria, Spain, is in commissioning. The plant will process a blend of post-consumer and post-industrial rigid and film plastic to produce a middle distillate diesel fuel blendstock meeting ASTM D975 and EN590 (CynDiesel™), light oil (CynLite™) and kerosene (CynKero™). All feedstock is secured for the facility. Another commercial plant is in Seville, Spain and a third one is being planned in South America. (Ocean Recovery Alliance 2015)

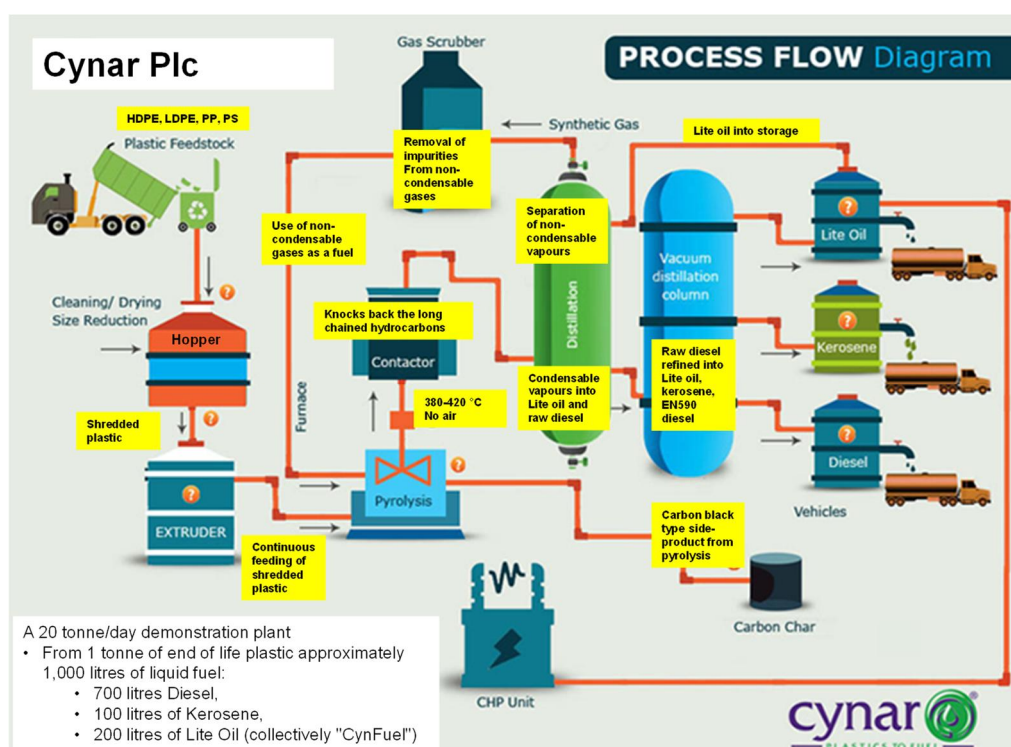


Figure 17. Cynar process (Ocean Recovery Alliance 2015).

### PK Clean

PK Clean began operating their pilot scale, 5 tpd PTL system in Utah in 2013 and it was relocated to a private site and achieved continuous, 4 day/week operations in 2014. A mixture of baled and pre-shredded plastics undergo hand or mechanical removal of visible and metal contaminants followed by shredding. The feedstock passes through a pre-melting process before entering the reactor where it is vaporized. The vapor enters a three-stage condensing system where it condenses into a diesel oil product, light oil and a wax. The diesel oil product and light oil are blended together and sold to a local refinery while the wax is re-circulated into the reactor for additional processing. (Ocean Recovery Alliance 2015)

PK Clean has developed a proprietary process (the key is the catalysts, which allow the reaction to happen at a lower temperature, vapors to vapour column and condenser) that allows their system to accept more heterogeneous

feedstocks from a variety of sources, including streams with combined quantities of PVC and PET as high as 40 %. (Ocean Recovery Alliance 2015)

### Agilyx

In 2013, Agilyx began operations at a pilot scale PTL facility in Tigard, Oregon, USA. Agilyx's Gen 6 is a continuously fed non-catalytic pyrolysis system that includes a heated, self-cleaning dual-screw reactor. The facility is currently processing an average of 10 tpd of waste plastics on a continuous basis. The light sweet synthetic crude oil is sold to a local refinery. (Ocean Recovery Alliance 2015)

Feedstock arrives at the system pre-treated by feedstock suppliers. Film plastics will be blended with pre-shred mixed rigid plastics and processed on site. Feedstock is shredded to a dimension of ½". In future commercial applications, Agilyx will seek to co-locate near a materials recovery facility, where pre-treatment systems are already in place to minimize front-end costs. Prepared plastics feedstock is placed on a hopper and loaded onto conveyer belts. On the conveyer a magnet pulls most remaining ferrous metals out of the input stream. Material is continuously fed into the system at automated 30-40 second intervals. Input material enters the reactor where heated dual screws rotating forwards and backwards at slightly different speeds feed it through several different heating zones. The relative movement of the screws creates a self-cleaning action. Any residues scraped off of the cartridge flights in this stage are collected as char. Plastics are converted into hydrocarbon gases which pass to a condensing tower chamber. The condensed oil and water emulsion is separated in a coalescing tank. The light hydrocarbons exit from the top of the condenser as gases and are subsequently condensed in a chiller as light oil which is sent directly to storage. The heavy oil is conditioned to adjust pH, remove particulates and lower organic salts before it is sent to storage as well. Agilyx is in the process of commissioning a system in North America in early 2016. (Ocean Recovery Alliance 2015)

## **5.1.8 Key challenges, opportunities**

### **5.1.8.1 Feedstock quality**

One significant challenge for companies is securing access to consistently more uniform and higher quality feedstock. Feedstock variability can have economic implications due to (Ocean Recovery Alliance 2015):

- Variation in product yields due to variation in type and amount of resins in the feed
- Increasing char management costs caused by increasing contamination
- Increasing feedstock pre-treatment costs due to variation in the composition of plastic bales (pre-sorting) or requirements of the process (shredding, drying, chipping). Additional costs incurred by the feedstock supplier are passed on to the PTL system operator, leading to an increase in material acquisition costs.



- Chlorine contamination is another challenge. Although PVC makes up a small percentage of the plastic waste stream and companies are intent on its removal, there are other sources of chlorine contamination in plastics, such as applied flame-retardants, in less easily detected sources. Suppliers reported conducting visual inspections, periodic burn tests and using instrumentation to assess incoming feedstock quality as well as testing chloride levels at the back end.

#### 5.1.8.2 Feedstock volume

PTL market is challenged by the need for a relatively desirable feedstock whose market price fluctuates with the value of crude oil. Feedstock suppliers are reluctant to commit to long-term binding agreements, as they often hedge on market fluctuations and future price expectations to yield higher profit margins. Furthermore, as recycling rates for PS, PP, PE-HD and other resins continue to rise, PTL operators may see reduced access to feedstock and have to pay higher acquisition costs. While PTL targets some resins that are not readily recycled, PTL may end up competing with traditional recycling markets for plastic feedstock raising environmental, economic and technical questions about whether the systems are sustainable. In locations where recycling markets and collection and sorting infrastructure are not well developed, opportunities exist to establish dedicated drop off centers for target feedstocks whereby citizens would deliver plastics to a centralized location in exchange for a small fee. This model is said to be successfully supplying feedstock for the MK Aromatics Limited system in India. (Ocean Recovery Alliance 2015)

#### 5.1.8.3 Waste water generation and energy requirements

Some companies generate waste water as a by-product of the process, especially for technologies that are desalting and conditioning oils. This is an additional back-end processing requirement for projects and may also require additional permitting. Electricity requirements vary across suppliers. In regions where electricity is produced with diesel generators and costs are high, supplemental renewable energy sources may need to be developed in parallel or a portion of the liquid petroleum product may need to be used to meet onsite electricity demand. (Ocean Recovery Alliance 2015)

#### 5.1.8.4 Offtake agreements and access to end users

Given that PTL is still an emerging industry, it has yet to establish a robust market for synthetic crude oil and distillate fuel oils. With variations in feedstock quality come variations in liquid petroleum product quality, which can lead to unpredictability and unnecessary risk for buyers. Furthermore, small quantities of liquid petroleum product produced compared with larger scale refineries may make it difficult to place into the market. In order for offtake agreements to be secured, it is necessary to identify end users that assign value to local waste-derived fuel supply. Additionally, developers in remote locations may be limited by their access to distribution networks and refineries, which may confine them to certain suppliers. Access to financing – Currently, there are a limited number





of financing players due to high levels of perceived investment risk, a limited understanding of the technology's capabilities and performance and a lack of long-term offtake and feedstock supply agreements. As a result, traditional debt structures are immediate scale up and commercialization, operators and suppliers are rising to the challenge with innovative engineering to overcome process bottlenecks and improve performance. (Ocean Recovery Alliance 2015)

#### 5.1.8.5 System sizing

Given the availability of suitable plastic feedstock in a defined area and the associated costs with sourcing plastic feedstock for a PTL system, many suppliers are aiming at smaller, more compact modular system designs (10-60 tpd). Suppliers are tending towards these design capacities to meet current demand, optimize economic performance and facilitate siting. RES Polyflow is also proposing a spoke and wheel system where they would operate decentralized pre-treatment facilities and a centralized PTL system. (Ocean Recovery Alliance 2015)

### 5.1.9 Operation and business environment

#### 5.1.9.1 Risk mitigation strategies

The development of a PTL system is a complex undertaking that can be costly and require the involvement of multiple stakeholders. In order to best safeguard the development of a PTL system, it is recommended that project stakeholders create a risk mitigation strategy at all stages 1) planning, 2) construction and development, and 3) operations. In many cases, project developers choose to work in a consortium of strategic project partners to mitigate project risks. One key advantage to strategic partnership agreements is the efficient distribution of project risks across multiple parties. (Ocean Recovery Alliance 2015)

## 5.2 Gasification

### 5.2.1 Principle of gasification

Gasification is a thermochemical process where carbon containing matter is converted into a gaseous form and also a variety of low-value feedstocks can be processed into high-value products. Different gasification technologies have been developed and demonstrated and/or commercialised for different types of feedstocks. The basic principle of the gasification process is shown in Figure 18.



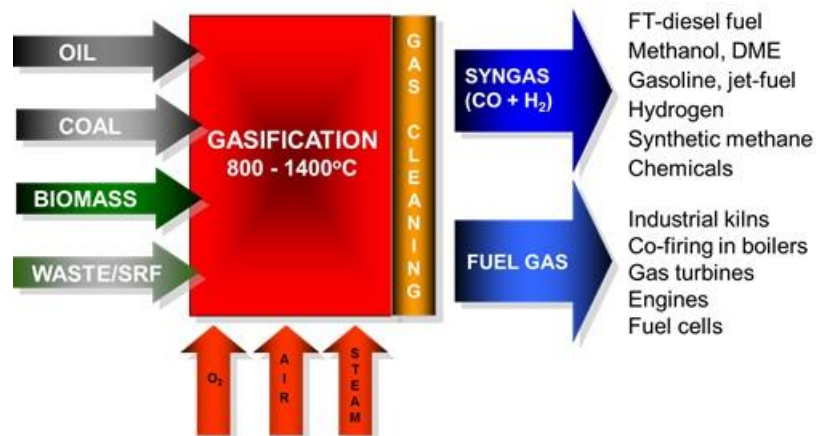


Figure 18. Principle of gasification to different high-value final products.

Feedstock is fed either into the top of the gasifier or into the side/bottom of it depending on the gasifier type. Oxygen, air, oxygen enriched air and/or steam are used as a gasification agent. Air blown gasification is typically used as a gasification agent when reactive fuels are gasified and the produced gas is used as a fuel in kilns or boilers. The disadvantage of the use of air as a gasification agent is nitrogen, which dilutes the resulting product gas - and therefore causes the reduction in the calorific value of the product gas. Nitrogen is also unwanted gas component in most of the chemical synthesis processes. The product gas is also called as synthesis gas or syngas.

Gasification technology offers feedstock flexibility and customization for generating a wide range of desirable products. The main product is valuable synthesis gas (syngas) which can be further processed into a variety of final products.

## 5.2.2 Types of gasifiers

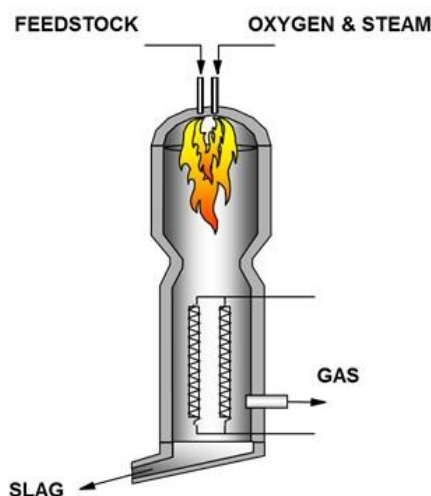
Many different generic types of gasifiers can be used also for waste/plastic gasification. The basic design of each type is built around the gasification reactor with feedstock feeding, and the main differences are related to the heating mechanism, the entry of gasification agents and the location of syngas output. The most usual types of the gasification technologies and their developers and/or suppliers are presented below.

### 5.2.2.1 Entrained flow gasifiers (EF)

Small droplets or fine particles of the feedstock are “entrained” in a flow of gasifying agent – in general oxygen and steam (Figure 19). A turbulent flame at the top of the gasifier burns some of the feedstock providing large amounts of heat at high temperature (1200-1500 m°C) for fast conversion into very high quality product gas. Due to the temperature the ash in the fuel can melt (sometimes additives are used) and the liquid slag flows down the gasifier wall. The ash is hence discharged as molten slag. (E4tech 2009)







*Figure 19. Principle of the entrained flow gasifier.*

Due to a short residence time EF gasifiers require very small feedstock particle size (below 0.1 mm). The composition of the feedstock should be consistent over time and therefore some pre-treatment steps for the feedstock could be needed. EF gasifiers have the most stringent feedstock requirements of the gasifier types discussed. (E4tech 2009)

Entrained flow gasifiers are mainly applied at larger scale for coal and petroleum-based feedstocks, and supplied by large companies such as Shell, Siemens, Prenflo and GE (E4tech 2009). EF gasification technology is not usually applied for biomass or waste because of several reasons: need to pulverize the fuel, low energy density of biomass and most of waste fractions and the scale of the EF gasifiers.

However, there are also some exceptions. An entrained flow gasifier has been in use for the gasification of hazardous wastes at SVZ Schwarze Pumpe GmbH (Germany). The SVZ gasifier was originally constructed for coal gasification but it was later modified to be able to allow also waste and plastic as a feedstock. The waste materials include e.g. demolition wood, used plastics, sewage sludge, automotive shredder residue and municipal solid waste. The waste materials are blended with coal. (E4tech 2009)

#### 5.2.2.2 Bubbling fluidised bed gasifiers (BFB)

In fluid-bed technology the feedstock is fed to the bed, which is fluidised by a gasification media (air, oxygen, steam or combination of these) that flows through the bed at a high enough velocity. The bed material may be inert (e.g. quartz sand) or it can have some catalytic behaviour. Main subtypes are the bubbling and circulating fluidised bed.

In BFB gasifier the fluidising velocity is typically 1-3 m/s, and the product gas leaves the gasifier upwards (Figure 20). Operating temperature is typically below 900 °C in order to avoid ash melting and agglomeration problems. BFB gasifier can also be pressurised. (E4Tech 2009)



A significant risk of bed agglomeration exists when gasifying feedstocks with low ash melting temperatures. However, in some cases ash melting related problems can be avoided by e.g. using some specific bed additives (such as dolomite) or by co-gasification with a feedstock with a higher ash melting temperature. BFB gasifier is fuel flexible and allows relatively large particle size of the feedstock with a maximum size of 50-150 mm. Moisture content of the feedstock may vary 10-55 %, although 10-15 % is optimal from a pre-treatment energy point of view. (E4Tech 2009)

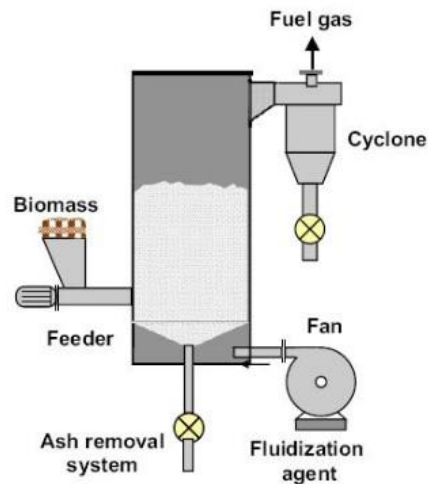


Figure 20. Principle of the BFB gasifier.

BFB gasifier technologies designed for biomass are commercially available mainly in power and heat applications.

### ANDRITZ Carbona

ANDRITZ Carbona has developed a biomass gasifier and gas cleanup system for use in gas engine-based combined heat and power (CHP) plants. The first plant (Figure 21) in Skive, Denmark, has been operating since 2008. The plant capacity is 100-150 odt biomass/day. (e.g. Horvath et al. 2011, Salo 2012, Patel 2014, ANDRITZ AG 2016a)

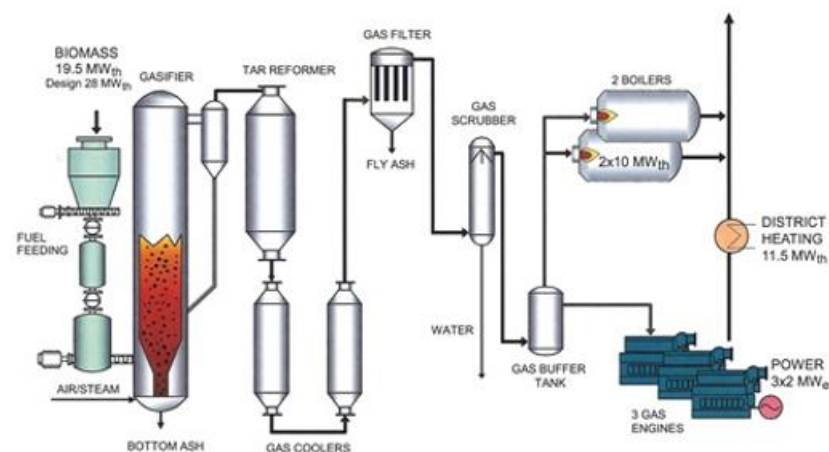


Figure 21. Biomass gasification – gas engine CHP plant in Skive (Horvath et al. 2011, Patel 2014).

In addition, ANDRITZ Carbona has developed in collaboration with GTI (Gas Technology Institute in Chicago) the oxygen blown gasification for biomass-to-synthesis gas production and biomass-to-liquids (BTL) in pilot scale (Figure 22). (Horvath et al. 2011)

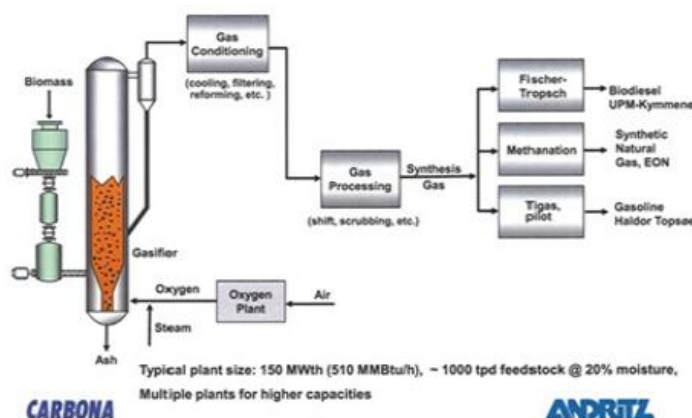


Figure 22. Scheme of biomass-to-synthesis gas production and biomass-to-liquids (BTL) (Horvath et al. 2011, Salo 2012, ANDRITZ AG 2016a).

### Amec Foster Wheeler (formerly Foster Wheeler Energy)

The first commercial application of the atmospheric BFB gasification in Finland was realised in Varkaus. Technology was directly heated, air and steam-blown process with produced gas used in a boiler. This process was developed at VTT in 1997. The technology was then demonstrated (25 odt/day scale) at Corenso's Varkaus plant before a full commercial 82 odt/day plant (Figure 23) was built on the same site in autumn 2001. Feedstock was aluminium foil containing plastic reject material originating from the recycling process for used liquid packages. (Power Online (undated))

This plant has been modified since 2013 to CFB and industrial tests have been carried out with other waste fuels.

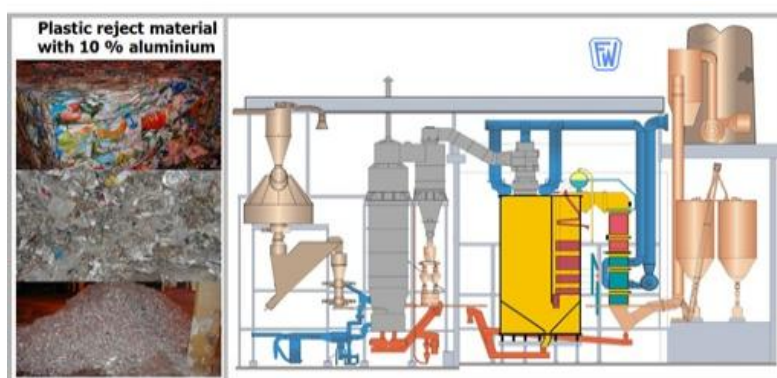


Figure 23. BFB gasification plant (40 MW<sub>th</sub>) for plastic residue of Corenso Oy (Foster Wheeler).

### Enerkem

Enerkem has tested and validated a number of different feedstocks since the year 2000 – from municipal solid wastes to dozens of other types of residues

(including various forms of plastics). Enerkem's system (Figure 24) converts these feedstocks into methanol, ethanol or other renewable chemicals. In turn, methanol is used as a chemical building block for the production of secondary chemicals, such as olefins, acrylic acid, n-Propanol, and n-Butanol. (Enerkem 2015)

The first full-scale MSW-to-chemicals and biofuels facility Enerkem Alberta Biofuels was officially inaugurated in June 2014 in Canada (Enerkem 2015).

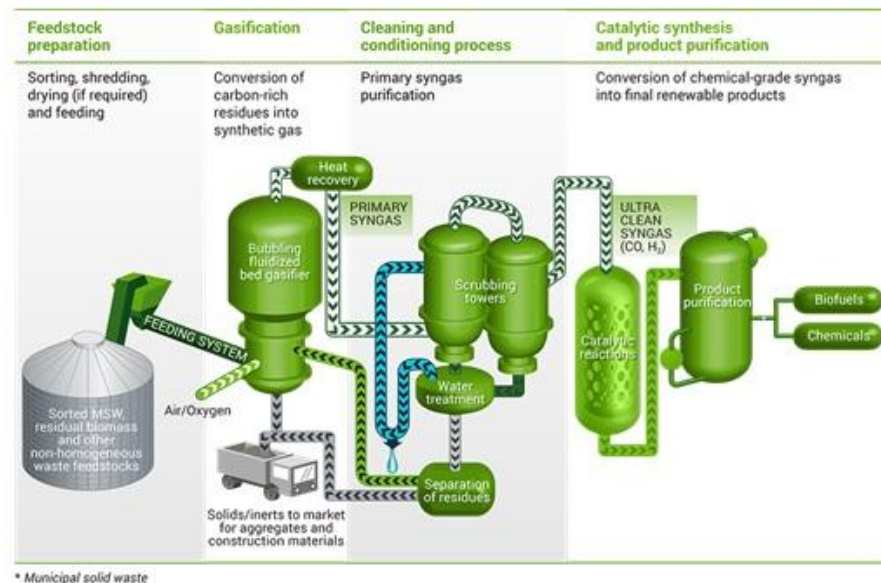


Figure 24. Enerkem's 4-step thermochemical process (Enerkem 2015).

### 5.2.2.3 Circulating fluidised bed gasifiers (CFB)

The atmospheric CFB gasifier (Figure 25) is very simple. Fine inert bed material is fluidised by air, oxygen or steam with the fluidising velocity of 5-10 m/s in order to recycle the bed material and feedstock particles throughout the gasifier. Feedstock is fed into the lower part of the gasifier. The gasification product gas leaves the gasifier upwards through the recycling cyclone. Most of the solid particles are separated from the gas in the cyclone and returned to the bottom of the bed. Operating temperature is typically below 900 °C in order to avoid ash melting and sticking problem. The CFB gasifier can also be pressurised. (E4tech 2009)

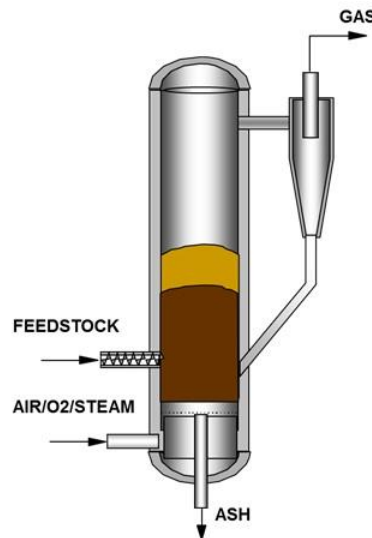


Figure 25. Principle of the CFB gasifier.

In general CFB gasifiers are very fuel flexible. When using waste as a feedstock foreign objects (e.g. glass, metals) need to be removed. Typically feedstock particle size must be below 20 mm. Like BFB gasifiers CFB gasifiers are also tolerant to fluctuations in feedstock moisture, which can be in the range of 5-60 %, although 10-15 % is optimal from a pre-treatment energy point of view. (E4tech 2009)

CFB technology is commercially available in the heat and power applications. Leading global technology suppliers are Finland-based companies ANDRITZ Carbona, Amec Foster Wheeler and Valmet.

#### Amec Foster Wheeler (formerly Foster Wheeler Energy)

The Kymijärvi biomass CFB gasifier (Figure 26) supplied by former FWE was commissioned in 1998 at the Kymijärvi power plant in Lahti. The gasifier had up to 336 odt/day biomass input (E4tech 2009). This technology is based on an air-blown, atmospheric directly heated CFB and the gasifier is connected to an existing coal-fired boiler to produce heat and power. There is not any product gas cleaning, it means that the raw gas is led directly to the PC boiler. This concept has been utilised for woody biomass fuels and clean waste-derived feedstocks (a.o. shredded tyres and plastics). The fuels have to be relatively clean because possible impurities (e.g. high amounts of chlorine, alkali metals or aluminium) in feedstock have tendency to cause severe corrosion and fouling problems in boilers. (power-technology.com (undated))



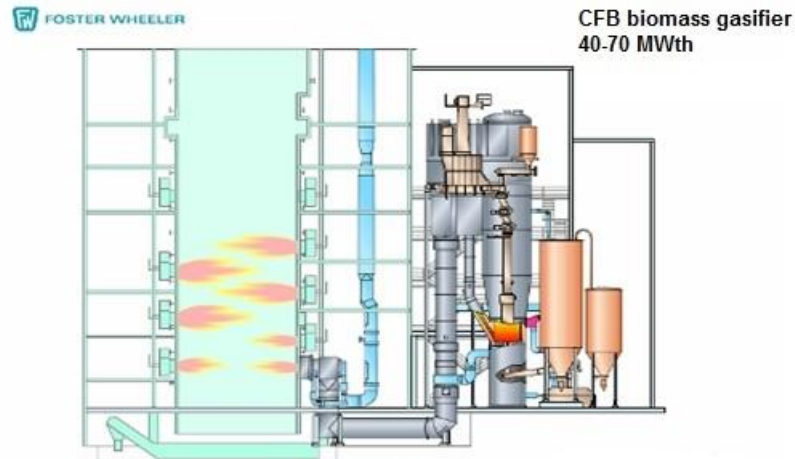


Figure 26. The CFB biomass gasifier (40-70 MW<sub>th</sub> depending on the feedstock) in Kymijärvi power plant (Foster Wheeler).

Foster Wheeler supplied a pressurised CFB biomass gasification plant at 1990's in Värnamo, Sweden. The Värnamo IGCC demonstration plant was the first of its kind in the world. It was operated 1993-1999 and was an important step forward in development highly efficient and environmentally acceptable technologies based on biomass. (Ståhl et al. 2004, VVBGC (undated))

#### Valmet (formerly Metso)

Lahti Energy's Kymijärvi II waste-to-energy (WtE) gasification plant (Figure 27) is the first of its kind in the world and it was commissioned in 2012. Waste gasification is based on CFB gasifier followed by gas cooling and cleaning – and combustion of the cleaned gas in the gas fired boiler. Gas cleaning prior combustion in the gas fired boiler protects the boiler and steam tubes against corrosion and thus the boiler can be operated with high steam parameters (121 bar and 540 °C) enabling high electricity generation efficiency. (Partanen 2013)

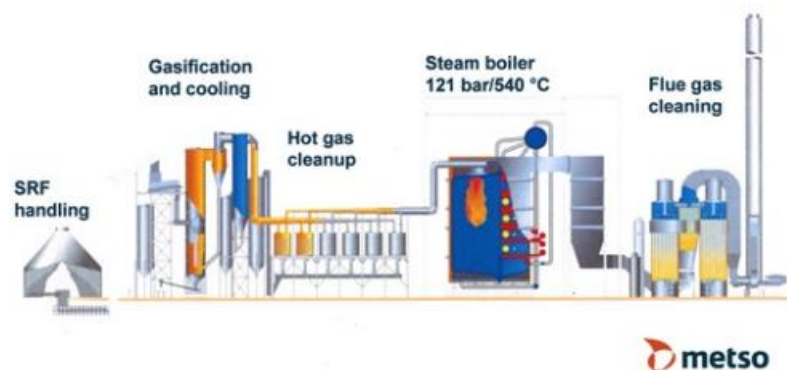


Figure 27. Kymijärvi II WtE gasification plant (160 MW<sub>fuel</sub>) (Partanen 2013).

Another commercial installation constructed by Valmet is Vaskiluodon Voima Biomass Gasification Plant (Figure 28) which was commissioned in December 2012. The produced gas replaces coal in PC boiler. This plant is the first in the world on such a large scale. (Partanen 2013)

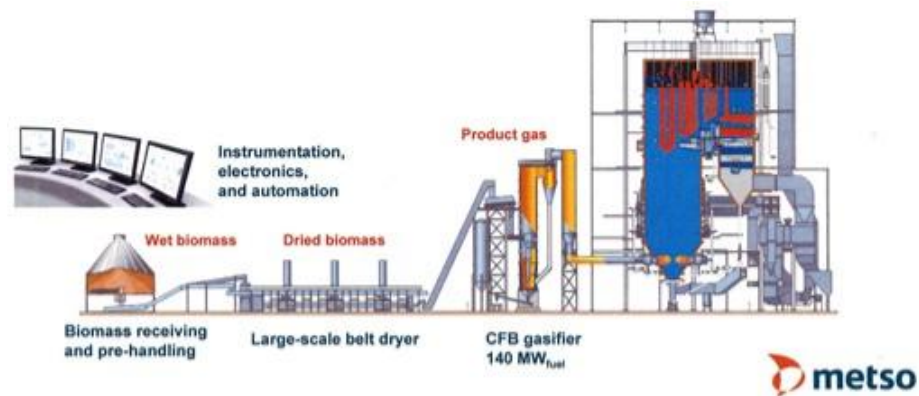


Figure 28. Vaskiluodon Voima Biomass Gasification Plant (140 MW<sub>fuel</sub>) (Partanen 2013).

### ANDRITZ Carbona

ANDRITZ Carbona supplied a CFB gasification plant (Figure 29) to Metsä-Botnia's Joutseno mill, Finland, in 2013. The 48 MW lime kiln gasifier generates green fuel gas from local biomass, making the mill independent of fossil fuels. (ANDRITZ AG 2016b)

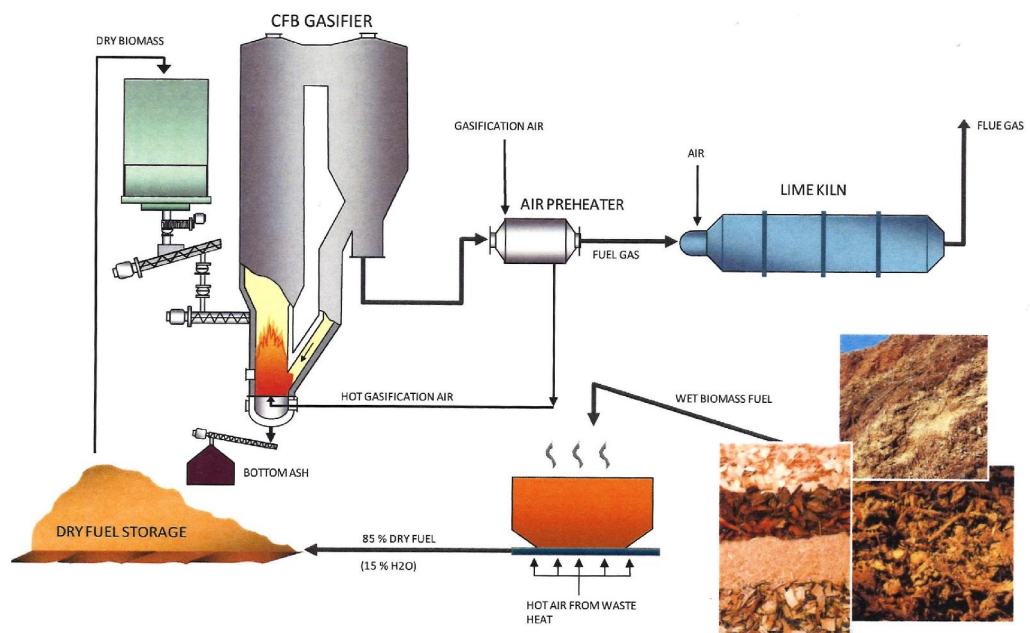


Figure 29. Lime kiln gasification plant (48 MW<sub>th</sub>) in Joutseno (ANDRITZ AG).

### VTT Technical Research Centre of Finland Ltd

Since the 1980s VTT has been involved in biomass and waste gasification research and development with many pilots and research programs. VTT's strong gasification and gas cleaning expertise has been utilised in co-operation with many power plant suppliers as well as with pulp and paper industry. VTT has developed fixed bed gasification, bubbling fluidised bed gasification and circulating fluidised bed gasification for wide variety of feedstocks and feedstock mixtures. Feedstocks have included different qualities of woody and agrobiomass, different high volatile coal qualities and several qualities of waste and waste-derived fuels from plastic waste to sewage sludge.



#### 5.2.2.4 Dual fluidised bed gasifiers (DFB)

This indirect gasification process has two reactors: a gasifier and a combustor (Figure 30). Feedstock is fed into the CFB/BFB gasification reactor and converted to nitrogen-free syngas and char using steam as a gasification and fluidising agent. The residual char is combusted by air in the CFB/BFB combustion reactor and hot bed material is recycled back into the gasifier. Indirect heating is provided by material exchange with a parallel combustor. (E4tech 2009)

The advantage of DFB gasification is avoidance of nitrogen in produced synthesis gas without investment on expensive air separation unit. This has a significant positive impact for the specific investment improving feasibility of the technology. In addition, DFB gasification technology can be down scaled (to 50...100 MW<sub>fuel</sub>) having positive impact on fuel logistics and also on investment.

Typically DFB gasifiers are operated below 900 °C in order to avoid ash melting and sticking problems, and these gasifiers can also be pressurised (E4tech 2009).

This DFB technology has been piloted/demonstrated in Güssing, Austria, and the first larger scale demonstration plant has been constructed in Gothenburg (GoBiGas project, [www.gobigas.se](http://www.gobigas.se)) by Valmet under the license of Repotec. The GoBiGas project aims to produce synthetic natural gas (SNG).

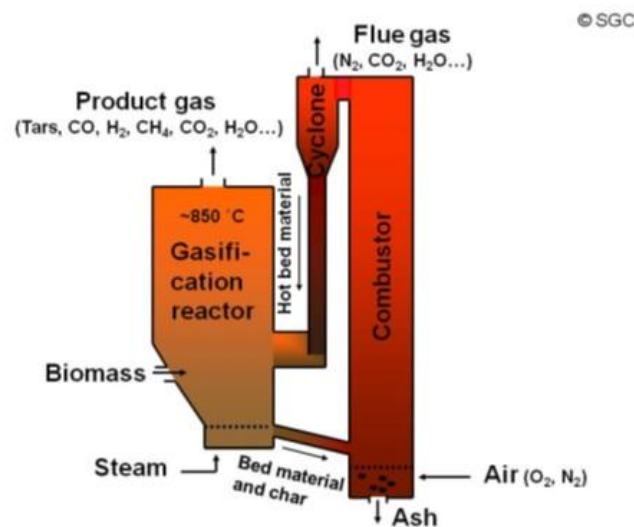


Figure 30. Principle of the DFB gasifier (SGC).

Some design examples of the DFB technology for biomass are the following:

##### Repotec/VUT (Vienna University of Technology)

The DFB gasification process (Figure 31) demonstrated at the Güssing power plant, is based on the steam gasification of biomass in the internally circulating fluidised bed developed by VUT (Vienna University of Technology). The heart of the plant - the fluidised bed steam gasifier - consists of two interconnected fluidised bed systems. In the gasification unit biomass is gasified under injection



of steam (instead of air), which creates a nitrogen-free, low-tar product gas with high calorific value. Technology was commercialized by Repotec GmbH. (Repotec GmbH (undated), Vienna University of Technology 2016)

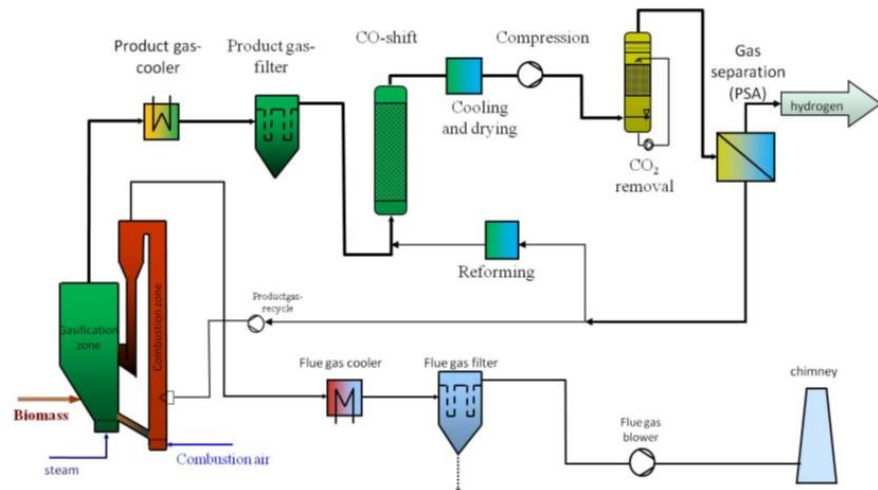


Figure 31. Diagram of indirect gasification principle (CFB combustor + BFB gasifier) (Repotec GmbH).

#### ECN (Energy research Centre of the Netherlands)

ECN has developed MILENA technology (Figure 32), which is similar to the Güssing technology but somewhat simpler. The main difference is the gasification in a riser reactor of CFB-type instead of bubbling fluidised bed (BFB). MILENA gasification process is an indirect fluid bed process and it was developed specially for bio-SNG production. (ECN 2011, 2016)

The MILENA gasification process has been verified at lab scale (25 kWth), and the 800 kW MILENA pilot plant was taken into operation in 2008 (ECN 2011). Presently Royal Dahlman ([www.dahlman.nl](http://www.dahlman.nl)) is the supplier of the MILENA gasifier.

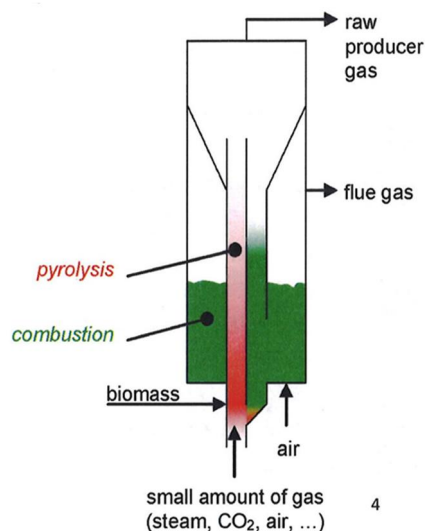


Figure 32. Simplified Scheme of MILENA gasification process (van der Drift 2014).

## RENTECH

Rentech has bought the SilvaGas technology (Figure 33), originally developed already in the 1980s at Battelle Columbus Laboratories, consisting of two CFB-reactors. The gasification technology has been operated successfully in a 40 MW biomass plant in Burlington, Vermont, USA. (Rentech 2016)

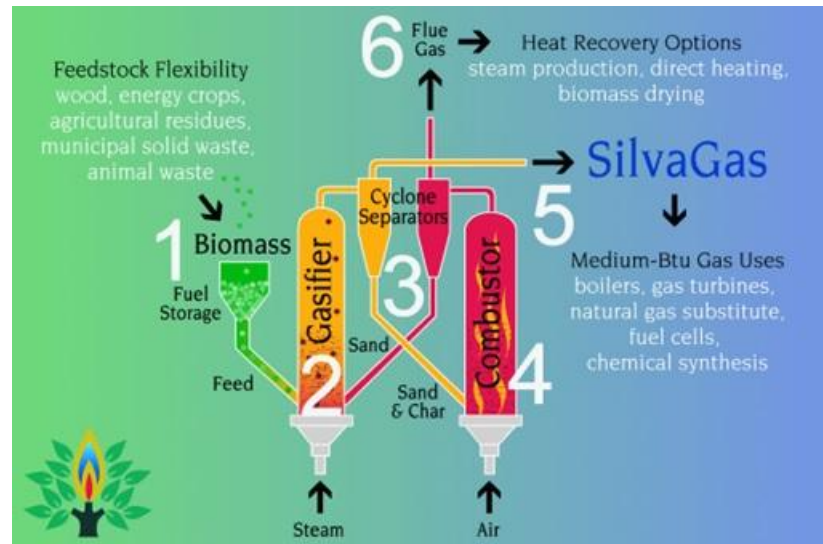


Figure 33. The SilvaGas Process (Green Car Congress 2009).

## VTT Technical Research Centre of Finland Ltd

A new gasification process at DFB pilot plant (Figure 34) is developed in Bioruukki. The primary target is a medium-scale BTL concept. The process can be energy-integrated to different kind of energy intensive industries or district heating power plants in order to improve the overall energy efficiency. The atmospheric-pressure DFB steam gasifier has a fuel feeding capacity up to 80 kg/h. The pilot is equipped with hot gas filtration followed by catalytic reformer.

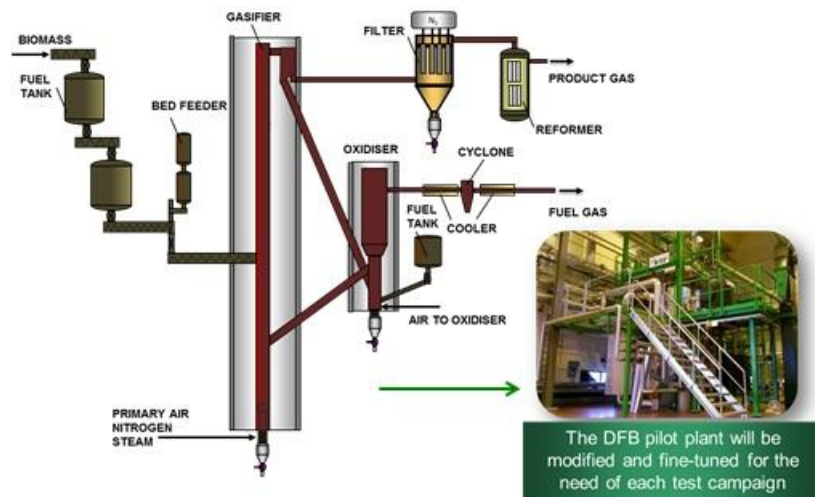


Figure 34. VTT's DFB steam gasification pilot plant (VTT).

### 5.2.2.5 Plasma gasifiers

In plasma gasification untreated feedstock is dropped into the gasifier and having a contact with an electrically generated plasma its organic matter is converted into syngas, and inorganic matter is vitrified into inert slag (Figure 35). Plasma gasification was developed primarily for waste-to-energy systems using e.g. municipal solid waste, tires, hazardous waste and sewage sludge as feedstock. Plasma gasifiers are usually operated at atmospheric pressure. The technology is characterised by the potential of very high level of destruction of the incoming waste, but low or negative net energy production and high operational costs. (E4tech 2009)

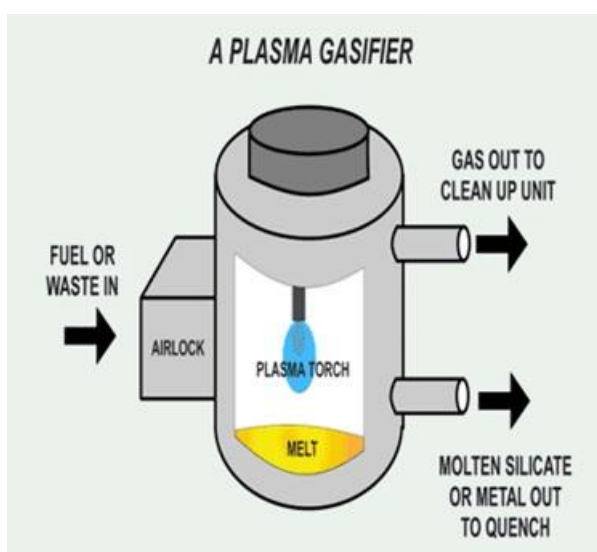


Figure 35. Principle of the plasma gasifier (Zafar 2015).

The most advanced company is currently Kaidi that has taken over the plasma technology developed by Westinghouse Plasma Corporation (WPC), InEnTec ([www.inentec.com](http://www.inentec.com)) and Plasco Energy Group ([www.plascoenergygroup.com](http://www.plascoenergygroup.com)). A few other companies such as Solena ([www.solenagc.com](http://www.solenagc.com)) and Europlasma ([www.europlasma.com](http://www.europlasma.com)) are also developing plasma-assisted processes for processing solid wastes and municipal solid waste.

#### Kaidi (formerly Westinghouse)

Chinese renewable energy investment company, Wuhan Kaidi, commissioned an Alter NRG Westinghouse plasma gasification waste to biofuel system (Figure 36) at its demonstration facility in Wuhan, China in 2013. Its advantages are e.g. fuel flexibility, multiple high-value product options from the syngas, beneficial use of by-products and a wide scaling range from 30 to 1000 t/day. (Westinghouse Plasma Corporation 2014, Alter NRG 2016)

Kaidi Finland plans to build the second generation biomass plant in Kemi, Finland by 2019. Kaidi is aiming to make the final investment decision by the end of 2016. The plant has been planned to produce 200 000 metric tons of biofuel per year. (Kaidi Finland 2016)



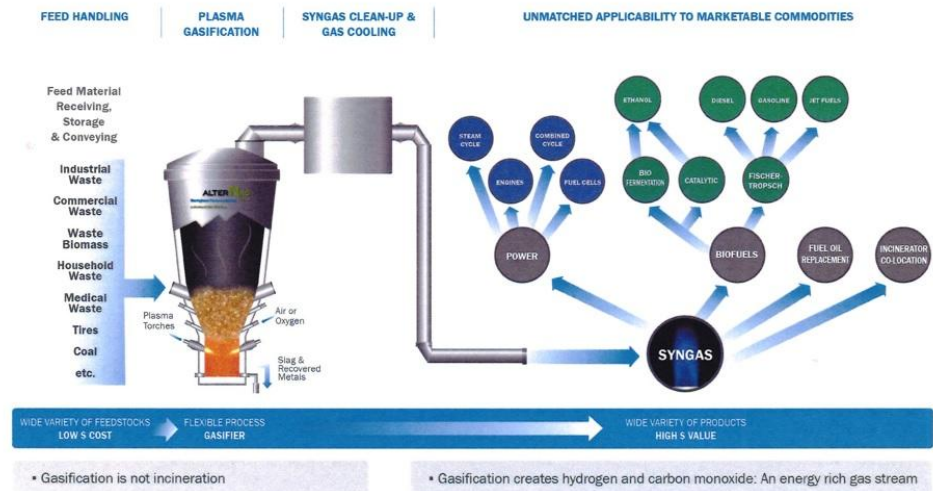


Figure 36. Principle of plasma gasification of Kaidi (Westinghouse Plasma Corporation 2014, Alter NRG 2016).

### 5.2.3 Comparison of different gasification technologies

Comparison of the presented gasification technologies have been summarised in Table 16. The selection of an optimal gasifier type for a particular application depends on several variables, for example feedstock requirements, required syngas characteristics, possible heat integration and desired final product type and quality.

*Feedstock requirements* mean pre-treatment of the feedstock if needed: e.g. shredding, drying and sizing before feeding it into the gasifier.

The characteristics of the feedstock determine the required pre-treatment, gasifier efficiency, amount and the quality of the final products that ultimately affect the economics of the facility. Pre-treatment of the feedstock adds both capital and operational costs to any gasification system. Some technologies require also input energy in order to reach the required operation temperature in the gasifier effecting directly on the economics of the system.

The required gas quality has direct impact on the selection of gasification technology. In practice, chemical synthesis requires inert gas free syngas when fuel gas applications can usually accept nitrogen in product gas. Absence of nitrogen results also in reduced volume of syngas and thus also reduced required size of downstream equipments and investments respectively. On the other hand, investment on oxygen blown gasification is significantly higher than investment of air blown gasification. Above described dual fluidbed gasification technology has been developed just in order to reduce investment and operation cost but still produce nitrogen free syngas.



Table 16. Comparison of the gasification technologies: ranking from ● (poor) to ●●●● (very good) (modified from E4tech 2009).

GASIFIER TYPE	FEEDSTOCK REQUIREMENTS	SYNGAS/ PRODUCT GAS QUALITY	OPERATING ENERGY REQUIREMENT	DEVELOPMENT STATUS	SCALE-UP POTENTIAL
Entrained flow (EF)	● Preparation to below 1 mm, 15 % moisture, low ash content, stable composition	●●● Very low CH <sub>4</sub> , C <sub>2+</sub> and tars High H <sub>2</sub> and CO	●●● Low	●●● Constructing BTL demos, integration and large scale experience, large industrial players	●●●● Very large gasifiers and plants possible
Bubbling fluidised bed (BFB)	●●● < 50-150 mm, 10-55 % moisture, care with ash	●● C <sub>2+</sub> and tars present High H <sub>2</sub> and CO only of O <sub>2</sub> -blown Particles	●● Moderate	●● Heat & power applications, modest scale up, some BTL interest	●●● Many large projects planned
Circulating fluidised bed (CFB)	●●● < 20 mm, 5-60 % moisture, care with ash	●● C <sub>2+</sub> and tars present High H <sub>2</sub> and CO only of O <sub>2</sub> -blown Particles	●● Moderate	●● Extensive heat & power expertise, research and scale up, but few developers, particularly for BTL	●●● Many large projects planned
Dual fluidised bed (DFB)	●●● < 75 mm, 10-50 % moisture, care with ash	●● C <sub>2+</sub> and tars present High H <sub>2</sub> and CH <sub>4</sub> Particles		● Few and small developers, early stages, only recent interest in BTL	●● Some projects planned, but only modest scale-up
Plasma	●●●● No specific requirements	●●●● No CH <sub>4</sub> , C <sub>2+</sub> and tars High H <sub>2</sub> and CO	● High	● Several developers, many power applications, early stage of scale-up	● Only small scale, modular systems



#### 5.2.4 Gasification of plastic solid waste (PSW)

Fluidised bed gasification of plastic wastes has been studied in some extent (e.g. Pinto et al. 2003, Aznar et al. 2006, Xiao et al. 2007, Brems et al. 2013) and it has recently been attracting increased attention as thermochemical recycling technique as a method of producing various hydrocarbon fractions from plastic wastes. As already earlier discussed, the main advantage of the gasification is the possibility to treat heterogeneous and contaminated feedstocks (now speaking of polymers) using limited amount of pre-treatments, whilst syngas production creates different applications in synthesis reactions or utilisation of energy. Additionally gasification is an attractive option to direct incineration of plastic wastes, as it diminishes the formation of dioxins and aromatic compounds. (Brems et al. 2013)

An ideal gasification process for waste plastics should produce a high calorific value gas, completely combusted char and an easily recoverable ash. It should not require any additional installations for air or water pollution prevention. (Brems et al. 2013) For the syngas quality can be effected by selecting suitable gasification conditions: e.g. gasification temperature, air ratio and fluidising agents. This means that undesirable products in the syngas and their concentration can be minimised. (e.g. Pinto et al. 2003, Aznar et al. 2006)

Plastic waste can also be added to coal or biomass gasification without a change in the process. Besides, the problem of seasonal availability of biomass can be solved simultaneously. The presence of plastic wastes in the feedstock leads higher tar and hydrocarbon contents, but they can be reduced by choosing suitable gasification conditions. (e.g. Pinto et al. 2003, Aznar et al. 2006, Xiao et al. 2007)

In the description of BFB gasification, Corenso's Varkaus plant (commercial application) for processing plastic reject material with metallic aluminium recovery was presented. This technology was directly heated, air and steam-blown process, which was developed at VTT in 1997.

Moreover, VTT has had several projects related to SRF (solid recovered fuel) gasification both in bench- and PDU-scale. SRF contains significant amounts of plastic. A special attention has been on product gas cleaning, energy recovery, metal recovery from ashes and processing/upgrading of the filter dusts.

#### 5.2.5 Gasification of automotive shredder residue (ASR)

ASR is a fraction, which is obtained from the process of shredding end-of-life-vehicles (ELVs), after recovery of metals. ASR is an extremely heterogeneous waste, and it contains significant amounts (20-50 %) of plastics with high energy content. ASR contains also a remarkable portion of inorganic material, valuable recyclables (e.g. metals and glass), which can be recovered.

VTT has developed the gasification of shredder residue (Nieminen et al. 2006). CFB gasification test trials showed that shredder residue can be gasified but some critical issues were also identified. High chlorine content together with







calcium and alkali metals might result in deposit formation. Many problems could be avoided if chlorine could be removed or reduced from shredder residue before feeding it to the gasifier.

Gas cleaning was efficient enough to remove bulk of chlorine and almost all heavy metals. The dry gas cleaning technique was based on the previous research and development at VTT and experiences from the gasification of different waste fractions (solid recovered fuel/refuse derived fuel, sewage sludge, etc.).

Air-blown gasification of complex waste streams with hot product gas cleaning is a promising and economically attractive method of utilising the energy content of shredder residue. The cleaned gas can be used in coal-fired boilers or industrial kilns. In gasification of shredder residue, additional metal recovery can take place from the solid residues - especially from the bottom ash it seems technically feasible.

In the report of GHK & Bio Intelligence Service (2006) there is an overview of post-shredder technologies used or potentially used for the treatment of ASR. There are two gasification based technology: the TwinRec and the SVZ Schwarze Pumpe Processes. TwinRec is developed by the Japanese company Ebara. It is designed to combine material recycling (metals, mineral components, ash) with energy recovery. The TwinRec gasifier, besides detoxification of the organic material, separates the remaining metals and large inert particles from the combustibles and fine ash, maximising total metal recovery from ELVs. On the other hand, Ebara's technology is more a staged combustion than real gasification because the product gas is oxidized in the secondary reactor immediately after gasification stage and produced gas cannot be used for other applications. (GHK & Bio Intelligence Service 2006)

The SVZ (Sekundaerrohstoff-Verwertungszentrum Schwarze Pumpe GmbH) plant has used the BGL-G (British gas Lurgi slagging-bed-gasifier) process to carry out "feedstock recycling". This process uses high-temperature gasification of waste materials, including shredder residue, to produce a synthetic gas and a vitrified slag. (GHK & Bio Intelligence Service 2006)

### 5.2.6 Olefin production

Figure 37 shows the pathways for the relevant potential products which can be produced from the synthesis gas. Methanol is one of the main product processed/upgraded from the syngas and it is utilised to be converted to various chemical e.g. olefins. Light olefins (ethylene and propylene) form the main petrochemical platform. They are used for main plastics (PE and PP), elastomers and rubbers as well as for different monomers.



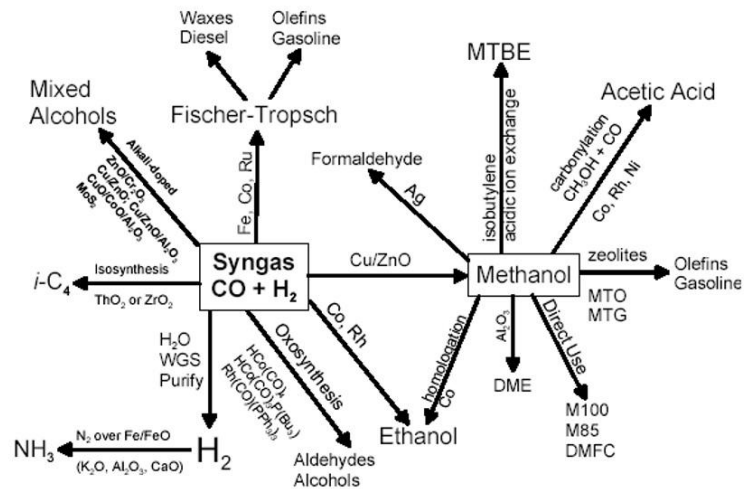
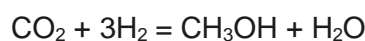
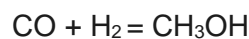


Figure 37. Pathways for potential products from the syngas.

Hannula (2015) has studied in his dissertation a.o. the performance of synthetic fuels and light olefins from biomass residues. Technically the production of light olefins from alternative feedstocks is very similar to gasoline, as both are produced by upgrading methanol.

First, methanol is synthesised by hydrogenation of carbon oxide over catalysts based on copper oxide, zinc oxide or chromium oxide. Synthesis of methanol can be described with the following reactions: (Hannula 2015)



Two generally accepted product quality standards exist for methanol: fuel-grade and chemical-grade; designated according to the use for which they are destined. The requirements for fuel-grade methanol are less stringent than those for chemical-grade methanol. (Hannula 2015)

Once technology for the production of renewable synfuels in large quantities becomes fully commercialised, it opens up a possibility to produce, not only fuels, but also light olefins that are main components of the petrochemical industry. Technology for the production of olefins from methanol is already commercial with several plants currently being built and operated in China for the production of olefins from coal. (Hannula 2015)

In addition to MTO (methanol to olefins) technology there has been developed also another indirect process to produce lower olefins from the syngas. The transformation of the syngas is carried out via dimethyl ether (DME). The process is known also as SDTO process (syngas via dimethyl ether to olefins) or simply DTO. There exists a direct conversion route of syngas into lower olefins via the Fischer-Tropsch synthesis. The idea of the Fischer-Tropsch-to-olefins (FTO) process has been considered decades, but there is no commercial application for this process yet. Background and potential of these other olefin



production routes are reviewed by Torres Galvis & de Jong (2013). Figure 38 presents the processes discussed in their review.

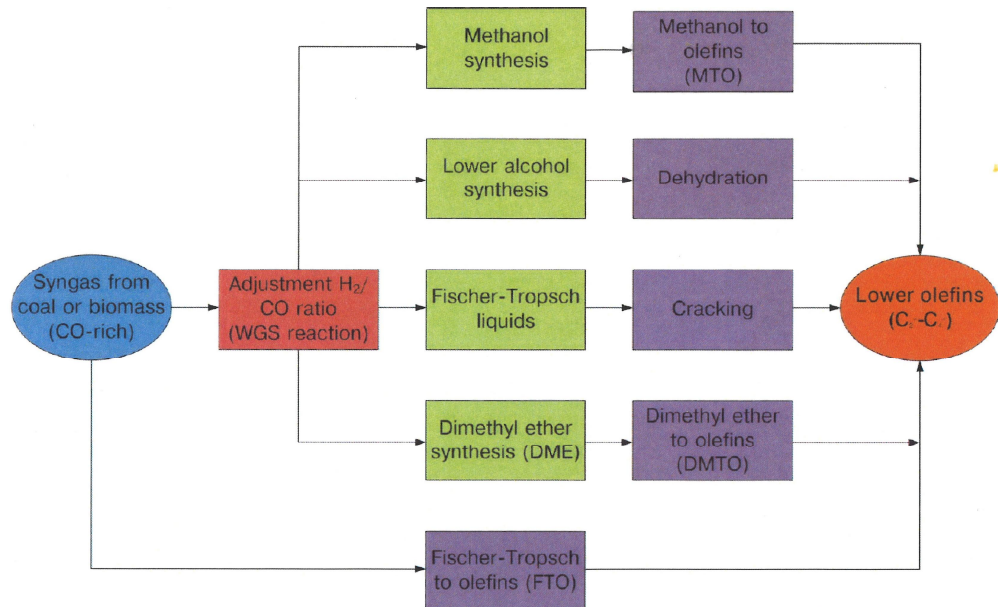


Figure 38. Processes for the transformation of CO-rich synthesis gas into lower olefins (Torres Galvis & de Jong 2013).

## 5.2.7 Conclusions

Gasification is a mature technology to convert solid feedstock to gaseous products. Gasification technology is used to produce fuel gas or synthetic gas for raw material of chemical synthesis. Fuel gas is usually produced by air blown gasification while synthetic gas is produced based on oxygen blown gasification and also in more recent applications applying dual fluidised bed gasification technology.

In gasification based processes produced gas can be cleaned from all impurities and thus impurities of the feedstock are not technically limiting feedstock quality. However, all additional cleaning steps increase investment and operation cost and thus requirements for the feedstock are based on economic reasons.

Plastic waste or plastic rich waste is already gasified in commercially operating gasifiers. Mature technology for plastic waste gasification is therefore available. Until now the chemical recycling of plastic waste based on gasification has not yet been economically attractive. However, the pressure to move towards circular economy may change the situation in the near future.



## 6 Conclusions

Plastic wastes form a complex and heterogeneous stream that is currently poorly exploited. In 2014, around 26 million tonnes of post-consumer plastic waste was generated in Europe, of which less than one third was collected for recycling (Plastics Europe 2015). This is due to the fact that plastics recycling is almost entirely focused on mechanical recycling that is suitable only for homogenous and contaminant-free plastic waste, which most of the plastic wastes are not. For example, ELVs, C&D wastes, and WEEE all contain large share of plastics that cannot be recycled via mechanical routes. Also plastic packaging wastes often contain composite materials and laminate structures whose mechanical recycling is challenging.

Applying thermal conversion to boost material recycling of plastic-containing wastes could be an answer to the dilemma of under-utilised plastic wastes. In addition, a development of novel, efficient pre-treatment and conversion method(s) for heterogeneous waste streams could reduce emission of greenhouse gases, and importantly provide a boost to local economy by generating jobs on regional level and in different branches of society.

Apart from the production of end products directly from waste plastics with thermal conversion, one can use these processes to convert waste fractions in a manner which enables their co-utilisation for example as a cracker feed in oil refining or petrochemical industry. This is considered both technically and economically an optimal route. These products have been and also can be employed for the production of energy.

However, we don't know yet how well these products from waste-derived feedstock fit current market needs and feeds to petrochemical industry and refineries. This needs to be analysed and set up productisation systems to match current and future standards and regulations. At least the following general boundary conditions for waste-derived feedstock for thermal conversion production can be set 1) sufficient hydrocarbon content 2) volume and availability 3) price and 4) location, but we also need to understand the needs of the potential markets and customers and identify the possible barriers related to the new products/services.

The principal reason for proposing co-refining of waste-derived liquids in existing petrochemical processes is economic. In pyrolysis, the aim is to remove much of the impurities on waste plastic fractions (chlorine, bromides, water, nitrogen, etc.). Once solid wastes are converted to liquid products, their storage and transportation becomes easier. It is believed that this makes it possible to increase international trade of these liquids. Co-feeding waste-derived liquids to an existing process requires much less specific capital investment than refining wastes to final products as such. It is also believed that pyrolysis is fairly well suited to a reasonable small plant size thus enabling transportation of product liquids to a centralized refinery.





Commercialization of thermal conversion processes has been pushed forward for long. In order to proceed with the commercialization it is of great importance to form a consortium covering the whole value chain from plastic waste producers to liquid end-users. A comprehensive risk management plan should be carried out and the business and operation environment should be clarified. The research topics which should still be covered include:

- Development of cheap and efficient pre-treatment equipment for heterogenous waste streams
- Further research for exploration and utilisation of cheap catalysts, such as natural zeolites, to further reduce the process cost, improve product quality and overall process optimization
- Regeneration and reuse of catalyst
- Detailed chemical characterization of end products
- Exploration of further applications of produced liquid oil, gases and char to make this technology more economically sustainable
- Comprehensive life cycle assessment (LCA).

In order to commercialize plastic conversion systems it is clear that the availability and quality of feedstock and legislation are the most important challenges to be solved. There are numerous EU and national regulations for the waste management, disposal and utilisation starting from waste classification (hazardous/non-hazardous waste) with legal procedures and traceability requirements throughout the whole waste handling chain from storage and shipment to ban on the mixing of hazardous waste. The use of waste feedstocks requires that the operations and practices are in line with this waste related legislative framework and the legal obligations concerning waste handling and utilisation are taken care of. In the utilisation of waste environmental permission is generally required, if not otherwise stated. In addition, there are a number of substances that already are specially regulated, e.g. organic persistent pollutants (POP), or as more scientific evidence on potential impacts on health and the environment emerges – may be regulated in the future, i.e. nanoparticles, fine particles, odorous compounds, soluble compounds, to name a few, from which waste handlers should also be aware of. Furthermore, the interpretation of the European legislation related to the use of waste-derived products, like pyrolysis liquids, requires clarification.

Current recycling processes focus on separating single pure plastic fractions for further material use. The efficient recycling of plastics and other economically important compounds from multi-material wastes is also hampered by the fragmentation of recycling industry, where several players across the value chain are optimizing their own part. This leads to losses of valuables and weak profitability. It is therefore essential also to improve the recyclability of plastics-containing wastes by improving the economic viability of the whole recycling process chain and added-value products.





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