

# COMPARISON OF SOLVENT-BASED POST-CONSUMER PLASTICS DEPOLYMERIZATION TO STATE-OF-THE-ART TECHNOLOGIES

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## ABSTRACT

Chemical recycling of pure and mixed post-consumer plastics has undergone extensive research for decades. Decreasing available disposal capacities and political pressure towards reduction of landfilling, high crude oil and thus feedstock prices have always been economic and ecological incentives for the development of recycling technologies.

Major companies in chemical and oil and gas industry developed a range of different technologies. Complex and capital-intensive reactor designs, such as fluidized beds and rotary kilns were applied to overcome process difficulties originating from high viscosity and low thermal conductivity of polymer melts. High temperature applications and elaborated catalysts produced the favored products but also caused high operation costs. Simpler and more cost efficient designs led to poor and inconstant product qualities and low throughputs.

Early papers and articles written in the early 1990s have already described the challenge of making the technology cost effective. 20 years later, crude oil prices rose approximately five-fold, plastics world production increased by some 180% and landfill bans were put in place in various countries.

This set of changed economic conditions can finally lead to the economic viability of depolymerization technologies.

After intense literature studies and discontinuous laboratory tests a continuous bench-scale pilot plant was designed and constructed. The aim is to find process parameters for ideal cracking conditions into favorable products.

A moderate process temperature and pressure design favors energy efficient operation; the non-catalytic solvent based process avoids margin losses through catalyst regeneration or a spent-catalyst application.

The concept provides an economically viable solution for the chemical recycling of preferably polyolefins. The solvent-based technology enables an up-scalable reactor design and controllability of reaction and flow conditions throughout the cracking unit.

This work presents a process concept based on experimental results from performed pilot plant tests and compares the found conclusions to state-of-the-art technologies towards economic considerations assuming an up-scaling to a commercial size unit.

## INTRODUCTION

Feedstock recycling of post-consumer plastics has always been a diverse and wide field of research since polymers became an integral part of everyday material applications.

Economic and ecological incentives changed over the decades. Waste management being earlier driven by decreasing available disposal volumes and rising disposal costs, today especially the political pressure towards reduction of landfilling and increase of resource conservation raises recycling questions for the so-called 'hard-to-recycle fractions'. Additionally, energy crises, resulting supply shortages and peak hydrocarbon feedstock prices have always triggered development waves for recycling technologies.

And difficulties in implementation of those have been rather economical than technical.

One of the early newspaper articles, 'Plastics Reborn' (Shelley, Fouhy, & Moore, July 1995) quotes Mark Meszaros, Amoco Chemical Co., saying 'The challenge is making it cost effective'.

Economic feasibility of a recycling process is simplified determined from the feedstock price, the attainable product price and the average unit costs for processing.

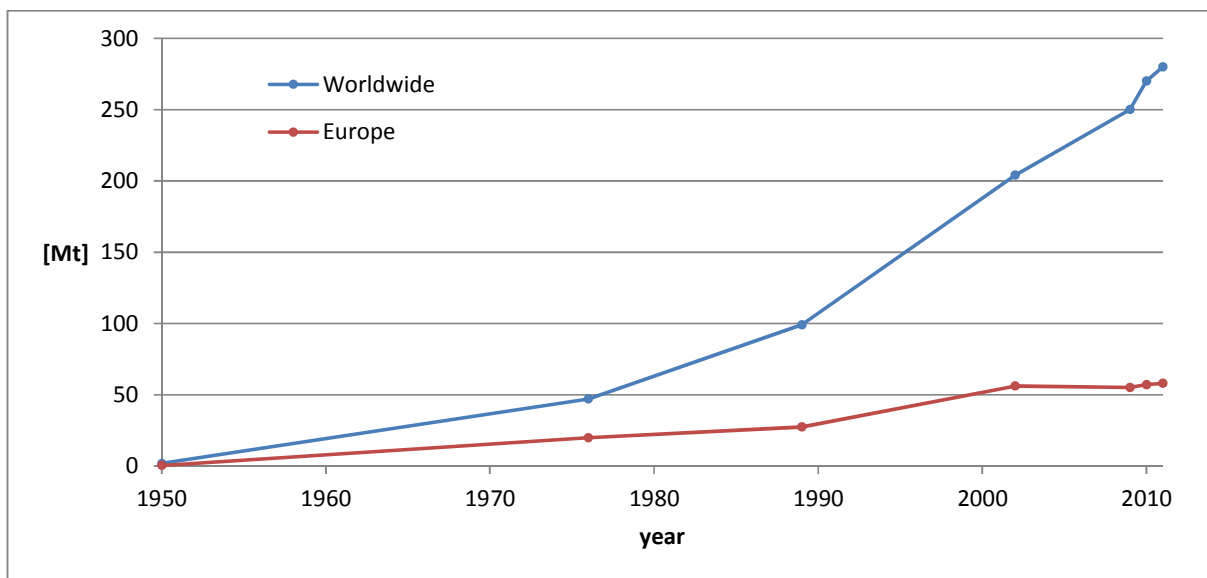
Feedstock prices and available amounts of post-consumer plastics depend on various influencing parameters and only partially follow price formation in free markets. Markets are usually regional due to high transport costs and often influenced by bilateral supply contracts. The amounts available in the market depend on consumer practice and regulations and commonly cannot be adjusted to demand.

Demands are mainly driven by legislation, for example required recycling rates and landfill bans, and economic incentives by processing secondary raw materials.

According to the Association of Plastics Manufacturers - Plastics Europe (Plastics Europe, 2012), the world plastics production has been steadily increasing over the last decades (Table 1). Since 1995, when ‘Plastics Reborn’ was published, production has been more than doubled (Figure 1).

**Table 1: Plastics production data** (Plastics Europe, 2012, p. 6)

		1950	1976	1989	2002	2009	2010	2011
<b>Worldwide</b>	[Mt]	1,7	47	99	204	250	270	280
<b>Europe</b>	[Mt]	0,35	19,8	27,4	56,1	55	57	58



**Figure 1: Plastics Production in Europe and Worldwide** (Plastics Europe, 2012, p. 6)

Generally and theoretically speaking, accessible amounts of post-consumer plastics for feedstock recycling are increasing. With this set of changed economic and legal conditions, depolymerization technologies could be proven to be finally economically viable.

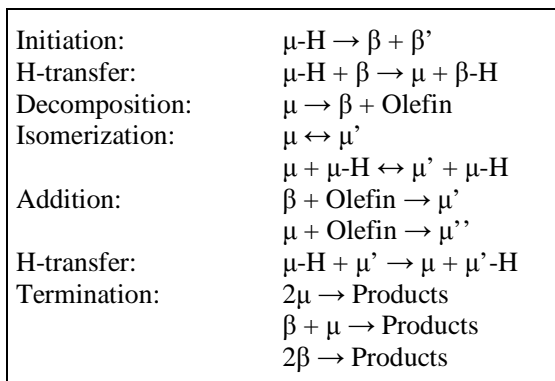
Detailed considerations of feedstock availability are mostly important for the economic feasibility and success. However, this work will further solely be focused on technical feasibility and process comparisons.

Extensive reflections on the feedstock situation towards quantities and qualities in the Austrian market are described by Bauer et al. (Bauer, 2013)’.

Target materials are pre-treated post-consumer fractions, which are typically available in highly developed waste management systems and currently mainly undergo the routes of thermal recovery as refuse-derived fuel fractions. Being primarily consisting of packaging wastes, those fractions show high ratios of polyolefins (polyethylene PE, polypropylene PP) and polystyrene (PS) with small admixtures of polyethylene terephthalate (PET) and polyvinylchloride (PVC). Plastics packaging wastes make up to approximately 22 % (Bauer, 2013) of post-consumer wastes, typically have a short life cycle time and are therefore available in large quantities – one of the main ideas for an economically feasible process development in terms of economy-of-scale.

## THERMAL DEPOLYMERIZATION OF POLYOLEFINS

Thermal cracking reactions of polyethylene and polypropylene follow free radical mechanisms. Buekens et al. (Buekens & Huang, 1998) propose a random-chain scission for both polymers. The polymer backbone breaks randomly into fragments of various length and leads to a wide, largely Gaussian product distribution. The cracking reactions can be simplified to the following scheme (Figure 2), wherein  $\beta$  is a reactive radical, mainly engaged in H-abstraction and  $\mu$  a larger, mainly decomposing radical (Buekens A. , 2006, p. 22):



**Figure 2: Free radical cracking reactions** (Buekens A. , 2006, p. 22)

Product distribution is depending on feedstock mixture and mainly influenced by reaction temperature and retention time. Product yields in thermal cracking of polyethylene and polypropylene has been extensively carried out in several pilot plants designs and batch reactors.

Kaminsky et al. (Kaminsky, Schlesselmann, & Simon, Olefins from polyolefins and mixed plastics by pyrolysis, 1995) examined cracking of several polymers in sand fluidized bed, called the Hamburg process (Kaminsky, Predel, & Sadiki, 2004). Williams et al. also studied pyrolysis behaviors in a fluidized bed reactor (Williams & Williams, 1997). Aguado et al. carried out thermal and catalytic cracking tests in a screw kiln reactor (Aguado, Serrano, Escola, & Garagorri, Catalytic conversion of low-density polyethylene using a continuous screw kiln reactor, 2002). Batch reactors and autoclaves were used by various working groups, especially with catalyst performance testing (Aguado, Serrano, Escola, Garagorri, & Fernandez, 2000). Several mixtures of polyolefins (Bockhorn, Hornung, Hornung, & Schawaller, 1999), (Ranzi, et al., 1997) and admixtures of polystyrene (Faravelli, Bozzano, Colombo, Ranzi, & Dente, 2003), polyethylene terephthalate (PET) and polyvinylchloride (PVC) (Bhaskar, et al., 2004) have been tested to observe the influencing effects on product yields and favored reaction routes.

Additionally, solvent effects need to be taken into account for thermal cracking mechanisms. Serrano et al. describe the effects of different solvents in the thermal degradation of HDPE (Serrano, Aguado, Vicente, & Sanchez, 2007). The differences in product yields with solvents having different hydrogen-donating abilities show the significant change in reaction mechanism. Highly hydrogen-donating solvents promote termination reactions, therefore lower conversion rates and shift the product ratio from olefinic to paraffinic products.

Those theoretical findings show the sensitivity of tertiary polymer recycling processes towards feedstock, reaction matrix and reactor temperatures. Product yields, although sophisticatedly elaborated and carried out in large variety, are mostly examined for discontinuous batch scale and therefore cannot take account of retention times in the process.

However, sharp retention time distributions are essential in thermal cracking processes in order to avoid over-cracking of the product. Free radical mechanisms form unstable primary products, such as olefins and dienes. Those are converted into more stable products and polymerized by secondary reactions. Together with aromatics and other coke precursors, over-cracking can lead to augmented coking and overall produce less valuable products. (Buekens A. , 2006, p. 15)

Therefore to establish a reliable database for up-scaling and process evaluation, it is most important to model the process in a pilot plant continuously. In order to maximize product values in a Gaussian product distribution, reactor temperature and retention time are the two main parameters to be varied.

## STATE-OF-THE-ART TECHNOLOGIES IN COMMERCIAL APPLICATIONS

In the realization of polymer thermal cracking processes, the core issues derive from material properties of the feedstock: polymer melts have high viscosities and show low thermal conductivities. Inconstant product qualities from high temperature gradients throughout the reactors, coking at heating surface due to overheating and additionally inhomogeneous feedstock qualities from waste are some reasons why feedstock recycling couldn't be proven to be feasible.

An enormous number of process concepts and variations were developed over the past decades to overcome those issues. In order to gain an evaluating overview, processes are principally sorted by process parameters and subsequently divided into groups of reactor designs.

The reaction atmosphere allows a first division into

- pyrolysis in inert atmosphere,
- gasification with oxygen or steam in controlled, sub-stoichiometric amounts in the atmosphere,
- hydrogenation/ hydrocracking in hydrogen atmosphere.

Hydrogenation produces high product qualities of gasoline and diesel. However, high pressure design reactors and hydrogen compression units sum up to high invest costs and hydrogen consumption push operating costs. Several hydrogenation processes were developed into pilot plant stadium but stopped due to unfeasibility, for instance the RWE hydrogenation Process, the Hiedrierwerke Process, the Freiberg Process, the Böhlen Process and the ITC Process (Tukker, de Groot, Simons, & Wiegersma, 1999). Solely the VCC (Veba Combi Cracking) Process was built in commercial scale of 90.000 t/a, but was shut down due to unfeasibility in 1999. Polyolefins are therein pretreated and subsequently hydrogenated at 400°C to 450°C and approximately 100 bar. (Tukker, de Groot, Simons, & Wiegersma, 1999)

Gasification is carried out at relatively high temperatures of 900°C to 1700°C and moderate pressures, typically to produce Syngas. Additionally to high invest and operating costs of a high temperature reactor, Syngas needs to be further processed into products, for instance by a Fischer-Tropsch synthesis. Some of the proposed process concepts were up-scaled to commercial size. The Thermosteact Process for residual wastes was implemented for 225.000 t/a in Germany and shut down in 2004 because of bankruptcy. Furthermore seven commercial scale plants were erected in Japan. (Thermosteact Sinerga SA). SVZ Schwarze Pumpe realized a fixed bed pressure gasification for 140.000 t/a of post-consumer plastics at 1000°C and 25bar. (Tukker, de Groot, Simons, & Wiegersma, 1999) The plant was shut after bankruptcy in 2010 (Lausitzer Rundschau, 2010; Nill Tech GmbH).

Pyrolysis processes can be conducted at different temperature levels, low temperature processes below 400°C, moderate temperature between 400°C and 600°C and high temperature above 600°C. Depending on the polymers contained in the feedstock mixture, the economic optimum is to be found with value and quality of the attained products and operating costs for the process.

Furthermore, pyrolysis processes are divided into catalytic and non-catalytic processes. Catalytic conversion enhances selectivity towards favored reaction routes and therefore product qualities and lowers reaction temperature. However, catalyst handling in processing of polymer melts, especially with post-consumer plastics, is challenging: Feedstock dispersion usually requires pretreatment due to the viscosity of polymer melts, for instance mixing with a solvent or pre-cracking and visbreaking. The catalyst needs to be continuously or periodically regenerated from the deactivating coke delayed on the catalyst surface during cracking. Furthermore, with processing waste materials, there is a high risk of catalyst contamination, e.g. with heavy metals. Catalyst aging or even poisoning can only be avoided by extensive pre-treatment and feedstock control measures. Due to those reasons, catalyst application with feedstock recycling is often applied in a form of catalytic upgrading after a thermal cracking step.

Generally speaking, feedstock pretreatment units, regenerators and catalytic upgrading sections will impact the overall invest costs massively and therefore need to be optimized with the attainable product quality.

Feedstock recycling processes can be furthermore categorized by their main reactor design into

- reactive extrusion designs,
- rotary kiln reactors,
- fluidized bed systems,
- stirred tank reactors,
- tube reactors.

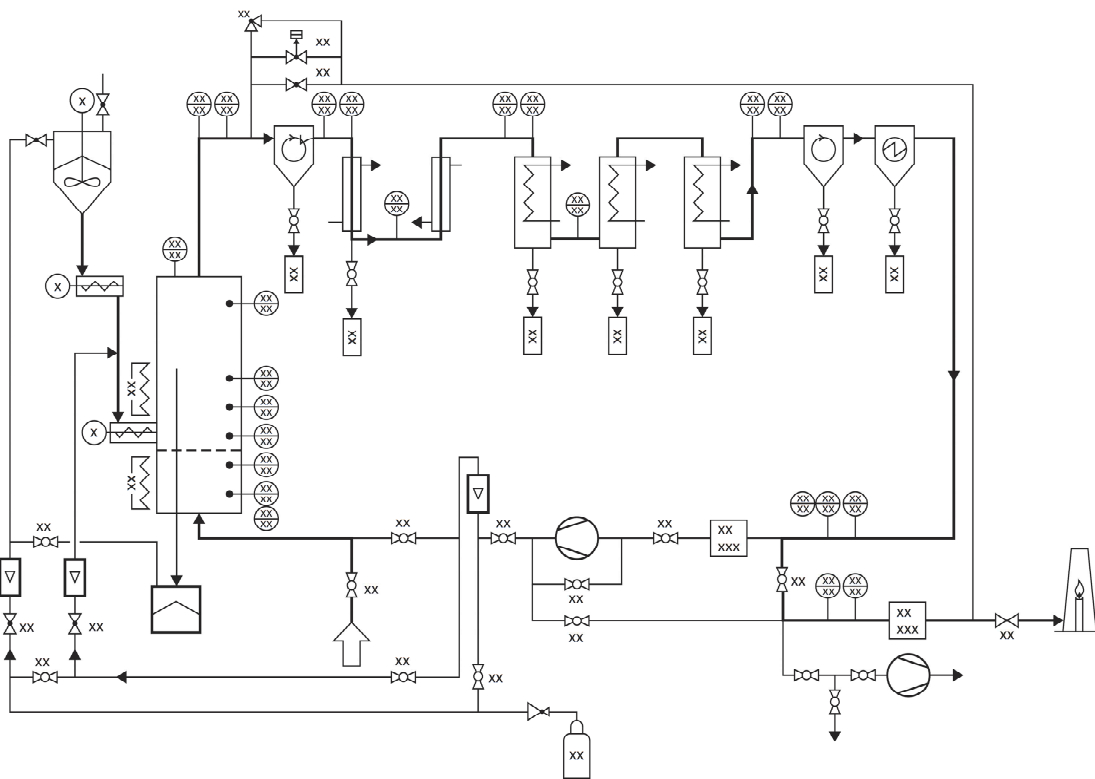
Reactive extrusion achieves constant and high product qualities due to good operability and controllability in the cracking process. However, up-scaling is limited with extruders and serial design of smaller extrusion units lead to high capital expenses. The mainly electrical screw heating systems comprise to high operating expenses. Reactive extrusion is predominantly used for visbreaking of polymer melts in low-temperature

application and was applied for instance in the IKV Extrusion Process, the Leuna and the Stahlwerke Bremen Degradative Extrusion Processes (Tukker, de Groot, Simons, & Wiegersma, 1999).

Rotary kiln designs were widely applied in different temperature ranges. High temperature applications of waste tires and waste electrical and electronic equipment (WEEE) are for instance the Veba Öl Process (Scheirs & Kaminsky, 2006, pp. 381-471).

Moderate-temperature processes for post-consumer plastics and polyolefins were realized e.g. in the Mitsui Process in several commercial scale plants in Japan (Scheirs & Kaminsky, 2006, p. 441) or the Toshiba Process built in demonstration plant size of 15.000 t/a (United Nations Environment Programme, 2009). Rotary kiln applications are unlimited in up-scaling and very suitable for Syngas and energy recovery, but face issues with retention times and liquid product discharge. Rotating reactors and gas handling comprise to relatively high invest costs while direct heating of the contacting atmosphere or indirect heating of the kiln with burners accumulate to moderate operating expenses.

Fluidized bed systems are highly elaborated reactor designs, combining low temperature gradients throughout the reactor and optimized heat transfer by the fluidized bed material consisting of sand or catalyst material. Therefore, design is well up-scalable at high controllability and homogeneous and high-quality products are achievable. However, fluidized bed reactors require a complex plant environment comprising compression and fluidizing units, regenerators and feedstock dispersion systems, which are demanding to implement for polymer melts. A typical and important process at moderate temperatures for polyolefins degradation is the Hamburg Process (Scheirs & Kaminsky, 2006, p. 476), which was realized in several plants approximately 5.000 t/a. Figure 3 shows a Piping and Instrumentation Diagram (P&ID) of the implemented process.



**Figure 3: The Hamburg Process** (Scheirs & Kaminsky, 2006, p. 89)

Liquid phase cracking processes are generally carried out in stirred tank reactors or tube reactors. Tank reactors are an inexpensive and simple design option, but originate difficulties in operability and product qualities. The ratio of heat transfer surface and reactor volume is limited by  $4/d_{\text{Reactor}}$  (reactor diameter) and the thermally low conductivity of the polymer feedstock leads to a large temperature gradient throughout the tank reactor. Additionally, retention time distribution is widely spread and therefore for cracking reactions mostly unfavorable. In summary, these conditions lead to over-cracking, less valuable and inhomogeneous product qualities and promote coking on the heating surface, which in turn leads to even lower heat transfer. A typical process for this kind of plant configuration is the Syntrol Process for the conversion of pre-treated

post-consumer plastics into heating oils, which was implemented at demonstration plant size of 4.500 t/a in Baar/Switzerland (Nil Tech GmbH).

Frequently, various catalysts are used in these processes to lower reaction temperature, consequently the energy amounts to be transferred and to enhance product qualities by selectivity of the reaction mechanism.

However, catalyst applications face the above mentioned difficulties in realization and thus often lead to economically inefficient spent-catalyst processes. The Gossler-Envitec Process is a catalytic-thermal pyrolysis process for the production of paraffins from polyolefins and was realized in mobile small scale of 1000 t/a (Gossler-Envitec GmbH). The Ozmotech Process combines moderate-temperature catalytic pyrolysis with a catalytic upgrading unit for polyolefins (Scheirs & Kaminsky, 2006, p. 724). Cynar Plc., the technology license holding company, plans to realize 10 plants of approximately 7.000 t/a (Waste Management World, 2012 ). Other examples for catalytic liquid reactor applications for post-consumer plastics are the Fuji Recycle Process and the Amoco Process (Scheirs & Kaminsky, 2006, pp. 438-440).

Tube reactor applications enable enlarged heat transfer surface to reactor volume ratios combined with distinct and sharp retention time distributions by ideally plug flow conditions through the reactor. The simple and thus relatively inexpensive reactor design is up-scalable in tube bundle reactors. The well-known BASF Process comprises a stirred reactor for dehalogenation and melting of the feedstock and a tube reactor for cracking of post-consumer plastics into typical hydrocarbon feedstock for refineries, such as dry gas, naphtha and gas oil cuts (Figure 4) (Stabel, Wörz, Kotkamp, & Fried, 1996). It was realized in demonstration plant scale of 15.000 t/a (Tukker, de Groot, Simons, & Wiegersma, 1999). However, commercial size implementation projects were stopped presumably due to a lack of feedstock in the 1990s.

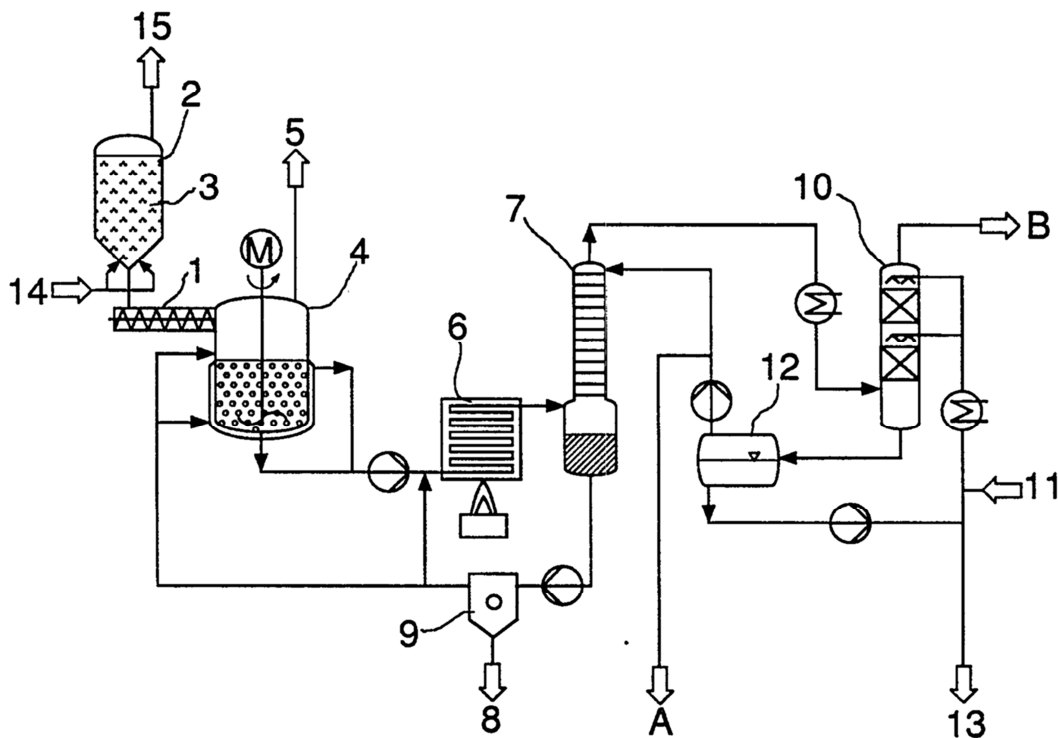


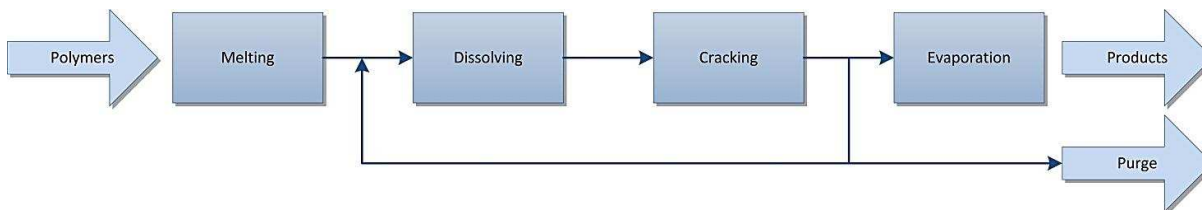
Figure 4: The BASF Process (Stabel, Wörz, Kotkamp, & Fried, 1996)

## PROCESS CONCEPT FOR SOLVENT-BASED DEPOLYMERIZATION

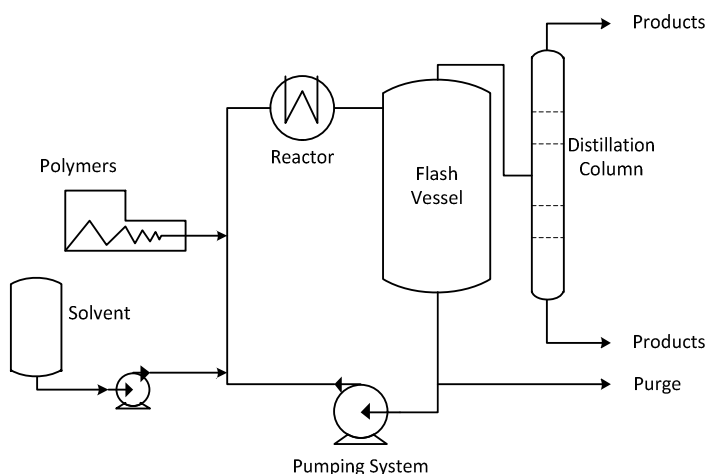
For the production of refinery feedstock products from post-consumer plastics, a liquid phase cracking process at moderate reaction temperatures realized in a tube reactor combines up-scaling possibility and enhanced operability for homogenous product qualities in a simple reactor design at moderate invest and operating costs.

Current weak points of the process can be ameliorated by incorporating a high-boiling solvent into the process. Viscosity reduction diminishes difficulties in the realization of the pumping system. Enhanced coking is inhibited by improved heat and mass transfer throughout the system.

Figure 5 shows the process flow chart and Figure 6 the pilot plant design as realized.



**Figure 5: Process steps of solvent-based depolymerization**



**Figure 6: Process Flow Diagram of the constructed pilot plant**

The pre-treated post-consumer plastic feedstock is dosed to the pump-around system in a molten stage. The polymer melt is dissolved in the hot solvent and is fed to the tube reactor section in a homogeneous flow. In a flash vessel products are separated from the pump-around medium comprising of the solvent and cracking residues. The attained products are rectified into favored distillation cuts. Residues are continuously removed by purge rejecting.

## CONCLUSION

In Table 2 the main parameters for process evaluation are summed up.

**Table 2: Process evaluation parameters**

Technology	Up-scaling	Operability	Product qualities	CAPEX	OPEX
Reactive Extrusion	Limited	Good	High	High	High
Rotary kiln	Unlimited	Average	Low	High	Average
Fluidized bed	Unlimited	Good	High	High	High
Stirred Reactor	Limited	Low	Low	Low	Low
Solvent-based	Unlimited	Good	Average	Low	Low

In order to evaluate processes for economic feasibility, solely up-scalable designs enabling a constant product quality can succeed. Elaborated and complex reactor systems facilitate those criteria, however, are often proven to be unfeasible due to large capital and operating expenses. In order to find an economic optimum between product values and expenses, solvent-based depolymerization can establish a viable process realizable in commercial size.

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