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Regional plastic waste recycling through pyrolysis – a techno-economic evaluation

Master's thesis in Sustainable Energy Systems (MPSES)

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Department of Space, Earth and Environment
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Abstract

The aim of this thesis was to investigate the economic feasibility of plastic waste recycling by pyrolysis-based processes on a regional scale. The Gothenburg region was used as a reference regarding the volumes of plastic waste flows. The initial part of the project was a mapping of the regional and national waste flows to see how the amounts of different polymers compare to each other, establishing the possibility of treating certain flows separately. Parallel to this, a literature study was performed to investigate the current processes for treating plastic polymers using pyrolysis.

Four different processes were modelled using the flow-sheeting software Aspen Plus in both regional and national scale; one process handling mixed plastics, one handling polyvinyl chloride (PVC) and two handling polystyrene (PS), the two latter being one simpler and one more complex, with different degrees of product separation. With the process layouts established, investment costs, revenues and running costs were calculated for both the regional and national scale plants. A cash flow analysis was conducted to assess the feasibility of regional plastic waste recycling by pyrolysis. The economic performance of regional scale plants was compared to the national scale plants.

The results show that economies of scale have a large impact on profitability and with the current price setting, only the national scale mixed process handling 320 kt/yr shows any potential to raise interest from investors, with a pay-back period (PBP) of seven years. The simpler PS process and the more complex PS process have a PBP of 15 and 17.5 years respectively, the difference mainly arising from the substantially higher investment cost for the more complex process which is not compensated by the extra revenue. The PVC process is nowhere near profitable in any of the cases, mainly due to the complexity of the process and the low value of the products. Even though the national scale mixed process is promising, one drawback is that it does not treat wastes containing PVC, hence leaving the waste management problem with PVC unresolved.

Keywords: Pyrolysis, PS, PVC, Mixed plastics, Recycling, Plastic waste, Fluidized bed reactor.

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Ivar Petersson & Andreas Svensson, Gothenburg, June 2019

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Nomenclature

Abbreviations

APEA	Aspen Process Economic Analyzer
BFB	Bubbling fluidized bed
CEPCI	Chemical Engineering Plant Cost Index
CHCl	Chlorinated hydrocarbons
CO	Carbon monoxide
CPI	Consumer Price Index
DFB	Dual fluidized bed
ELV:s	End-of-life vehicles
EPR	Extended producer responsibility
EPS	Expanded polystyrene
ESP	Electrostatic precipitator
FCOP	Fixed costs of production
FTI	Förpacknings- och tidningsinsamlingen
HCl	Hydrogen chloride
HETP	Height equivalent of a theoretical stage
HHC	Halogenated hydrocarbons
HP	High-pressure
ISBL	Inside battery limits
LHV	Lower heating value
LP	Low-pressure
MAPD	Methylacetylene and propadiene
MP	Medium-pressure
NPV	Net present value
OSBL	Outside battery limit
PBP	Payback period
PE-LD	Polyethylene - low density
PE-HD	Polyethylene - high density
PMMA	Poly(methyl methacrylate)
PP	Polypropene
PS	Polystyrene
PVC	Polyvinyl chloride
SCB	Statistiska Centralbyrån
VCOP	Variable costs of production
WEEE	Waste electric and electronic equipment
Re	Reynolds number
Ga	Galilei number

Greek Letters

μ	Dynamic viscosity	$Pa \cdot s$
ρ	Density	kg/m^3

Latin Letters

A	Area	m^2
a,b,c	Constants	
D	Diameter	m
d	Diameter	m
g	Acceleration due to gravitation	m/s^2
H	Height	m
h	Height	m
h	Enthalpy	J/kg
$\dot{m}$	Mass flow	kg/s
N_t	Number of theoretical stages	
P	Power	W
p	Pressure	bar
$\dot{Q}$	Heat flow	W
R	Reflux ratio	
r	Discount rate	
T	Temperature	K or $°C$
U	Velocity	m/s
V	Volume	m^3

Subscripts

ads	Adsorber
c	Column
cond	Condenser
cs	Cross-sectional area
feed	Feed of plastic waste
g	Gas
in	In to the system
mf	Minimum fluidization
out	Out of the system
p	Particle
pack	Packed distillation column
reboil	Reboiler
ref	Reference

1

Introduction

1.1 Background

Plastic materials have played a major role in society during the last century and are expected to do so in the future as well [1]. The world wide production of different plastics was close to 350 million tonnes in 2017 [2]. During their lifetime, plastics have been a substitute for other types of materials such as metals and ceramics, due to for example its low weight, ease of processing, corrosion resistance against most chemicals and its low cost [1]. However, the biodegradability of many plastics is practically none, making waste management important to prevent them from accumulating in nature. The plastic waste in marine environments is expected to increase and is of high concern because of its effect on the oceans and wildlife [3]. Moreover, most plastics are currently produced from fossil resources which is not sustainable. The waste management hierarchy is a way to order different steps of waste handling, and from most preferred to least preferred option they are: reduce, reuse, recycle, recover and landfill [4]. Today, a large part of plastic waste is incinerated or landfilled [2]. Landfilling means that the material is not utilized in any way. While incineration utilizes the energy bound in the material, it means the loss of a material that could be put to higher value if recycled. Another drawback is the generation of greenhouse gas emissions. There are thus good reasons to minimize the use of these methods. Directive (EU) 2018/852, amending directive 94/62/EC on packaging and packaging waste, states new targets for the recycling of packaging waste; 50 % of the plastics should be recycled by the year 2025, and 55 % by 2030 [5]. The member states are responsible for taking the necessary measures to attain the targets.

Since 1992, China has imported roughly 45 % of the plastic waste produced all over the world [6]. Stricter policies for waste imports has been implemented in China during the last decade [7]. In the end of 2017 import of nonindustrial plastic waste was banned completely. The new legislation has reinforced the urgency to find alternatives for plastics waste handling [6].

Recycling of plastics can be categorized into mechanical and chemical recycling [8]. Mechanical recycling simply means remolding the plastic into new products, preserving its chemical structure. This is a simple and efficient method, but it cannot be repeated indefinitely as the material degrades slightly over each cycle. Moreover, it requires high purity in the feedstock in order to achieve a material of good quality. Meanwhile, chemical recycling can convert the plastics into the compounds from which they are originally made, thus enabling a sustainable life cycle, and it can handle a feedstock consisting of a mixture of different plastics [1, 9]. Both pyrolysis and gasification are examples of thermo-chemical processes which can be utilized for chemical recycling of the aforementioned feedstock. Pyrolysis provides the opportunity to crack plastic polymers into their monomers, allowing repolymerization into new plastics in a more efficient and straightforward process than gasification. However, pyrolysis is less flexible towards mixtures of plastics and other materials [10].

Pyrolysis of mixed plastics to obtain pyrolysis oil, that can be distilled into different fractions and used as fuel or as raw material for other chemicals and materials, is well researched and companies are presently trying to commercialize the process [9, 11, 12, 13]. However, pyrolysis-based recycling can be implemented in many different ways. With different reactor conditions, pyrolysis of mixed plastics could yield light olefins for direct reprocessing into new polyolefins [14]. Moreover, several studies suggest that a more valuable product could be obtained by pyrolyzing certain polymers separately. Scott et al. found that pyrolysis of polystyrene (PS) can yield a monomer recovery of 76.2 % [15]. Kaminsky and Franck studied the pyrolysis of poly(methyl methacrylate) (PMMA), reporting a monomer recovery of 97.2 % [16]. This type of direct cracking into monomers for repolymerization allows for a less complex process. Other studies have focused on polyvinyl chloride (PVC), which is especially troublesome in the present waste management system [17, 18, 19]. Due to the long lifetime of PVC products, the PVC waste of today may contain additives that have been banned since it was produced [20]. If recycled mechanically, these additives would stay in the plastic, rendering it illegal for use in new products. Incineration is also undesirable due to the formation of highly corrosive hydrogen chloride (HCl) and increased emissions of dioxins and furans [17]. Several researchers have investigated the treatment of PVC by a low-temperature dehydrochlorination step followed by pyrolysis at a higher temperature, showing that this setup is an efficient way to remove up to 99.5 % of chlorine in a controlled manner [18, 19, 21].

The economic feasibility of a pyrolysis-based process will depend on how it is designed, as well as the scale of the plant. While a larger scale reduces specific investment costs, larger investments are more difficult to get in place, and shipping plastics over long distances requires more administration and increases operational costs. It is therefore of interest to investigate how a pyrolysis process can be designed to handle different types of plastic waste efficiently, and how large the plant would have to be to achieve economic feasibility. A plant for treating mixed plastics has the potential benefits of reducing or even eliminating the costs for sorting the waste, and a high amount of feed per uptake area. While PMMA constitutes less than one percent of the EU plastics market, both PVC and PS are present in substantial volumes [2]. For the reasons mentioned above, separate plants for PVC and PS treatment could thus also be of interest.

1.2 Aim

The aim of this thesis is to investigate the economic feasibility of pyrolysis-based recycling of plastic polymers into their monomers and other valuable chemicals on a regional level. The Gothenburg region is used as a reference regarding the volumes of plastic waste flows. Four different processes are examined; one treating mixed plastic waste, one treating waste PVC, and two different processes treating PS. The regional scale plants are compared to national scale plants. The possibility of using a flexible process, cycling between the different feedstocks over the year, is discussed in comparison to the modeled plants.

1.3 Boundaries

The thesis is restricted to pyrolysis-based processes, and covers modeling of the treatment and separation processes required to obtain monomers and other useful products from the pyrolysis gas. The pyrolysis reactor itself is not modeled, nor are any experiments conducted. Instead, data on the pyrolysis products resulting from different feedstocks are taken from experimental studies found in literature, forming the basis for mass and energy balances. The influence of any additives in the plastic material is not examined, due to the scarcity of literature describing experiments on such materials. Most literature referred to in this thesis has only studied the pyrolysis of pure polymers and their mixtures. The treatment and separation processes are chosen based on process heuristics and expert knowledge. Optimization in any wider sense is not performed.

The regional scale plants are based on waste volumes in the Gothenburg region, including the 13 municipalities that are part of the GR organization: Ale, Alingsås, Göteborg, Härryda, Kungsbacka, Kungälv, Lerum, Lilla Edet, Mölndal, Partille, Stenungsund, Tjörn, and Öckerö [22].

2

Methodological framework

This thesis involves a series of steps, where each forms the basis for the next, to fulfill the main aim of the study. The work flow is visualized in Figure 2.1.

Figure 2.1: The work flow of the thesis. Process modeling and economic evaluation are done in parallel for all four processes, symbolized by the layered arrows in the figure.

Initially, two parallel literature studies are made. One examines the waste flows available – the total volumes of plastic waste in the region, and its composition with respect to different polymers. To be able to compare the economics of plants at different scales, the waste volumes on a national level are also examined. An understanding of the current waste management system – how the plastic waste is currently treated, and whether it poses any specific challenges – is also established.

The other literature study examines experimental results from the pyrolysis of different plastics, including single polymers and mixtures. The purpose is partially to find what products can be obtained from mixed plastics through pyrolysis at different conditions, keeping in mind that recycling is often aimed at generating material of the same type as the waste – turning waste plastics into new plastics. The purpose is also to find what polymers, if any, could generate a higher value when pyrolyzed separately from others – predominantly through high monomer recovery.

A flowsheet describing the process modeling is presented in Figure 2.2. Having chosen what feedstocks and pyrolysis conditions to proceed with, processes to separate saleable fractions from the pyrolysis products are established. To some extent, this step involves continued literature studies, as conventional solutions to many of the problems and uncertainties that arise in the development of such processes have already been found. Where possible, process conditions are taken from literature and otherwise chosen so as to promote energy efficiency. By using the software Aspen Plus, the processes are modelled to give the size of the equipment, the consumption of different utilities and chemicals, and the volumes of separated products.

Figure 2.2: Method flowsheet of the process modeling.

From the models it is possible to estimate both investment and running costs. In cases where process units are not modelled in Aspen, their costs are estimated by other means. Based on product prices, revenues from product sales are calculated. Putting together the investment costs, running costs and revenues, the economic performance of each process is concluded. To make a more solid economic evaluation, a sensitivity analysis is conducted to see the impact of different parameters. By scaling the processes according to regional and national waste volumes, conclusions are drawn on the economic impact of the plant scale.

3

Review of plastic waste flows

To determine what pyrolysis processes are relevant to focus on and the potential scale of such processes, the total amount and composition of available plastic waste must be estimated. The estimation of the total amount is approached in two different ways: a) mapping each of the largest waste flows in the Gothenburg region, and b) scaling down based on national statistics. If all the relevant data can be found, the first option is likely to be more accurate. However, whether all data can be found is uncertain, and doing so is time demanding. By comparing the results and discussing the success of data acquisition, a conclusion is drawn on which estimate to use as basis for the process models.

To map the waste flows individually, an understanding of the organization of waste management is required. Different categories of waste are handled by different actors [23]:

- Extended producer responsibility (EPR) is applied to certain product categories. This means that the original producer of a product is responsible for its treatment at the end of its lifetime. The EPR categories that contain a significant portion of plastic volumes are packaging waste, end-of-life vehicles (ELV:s) and waste electric and electronic equipment (WEEE). Producers organize the collection of these wastes through commonly owned companies; Förpacknings- och tidningsinsamlingen (FTI) for packaging, BilRetur for ELV:s and El-Kretsen for WEEE [24, 25, 26].
- The municipalities are responsible for the collection and treatment of household waste that is not included in the EPR legislation, and “thereby comparable” waste from businesses. The plastics in this category is collected in the form of mixed combustible waste and as sorted fractions from recycling centres.
- For wastes not included in the categories above, the general principle is that the holder of a waste is responsible for its management. As a result, each business is responsible for the waste they generate in their operations. The responsibility transfers with the waste. Most commonly, businesses pay recycling companies to collect their waste. This waste can be collected as sorted fractions or as mixed garbage, determined by what fractions the recycling companies accept and at what prices. The recycling companies either sort the waste and pass it on to others who treat it, or conduct end treatment themselves.

In the current system, mixed residual combustible waste, after source separating of EPR plastics, is not subject to further sorting [Lia Detterfelt, Renova AB, oral communication, 2019-02-20]. The plastics in this waste are thus currently inaccessible to any material recycling strategies, and are assumed not to form any basis for a plastics pyrolysis plant in this study.

The results of the investigation of individual waste flows are shown in Table 3.1. Regarding packaging waste, statistics on the amount per capita of each waste material in each municipality is readily available on the FTI website [27]. For ELV:s and WEEE, no data on the overall amount of plastics in the collected waste can be found. Nor is there any systematic presentation of data on the amount of plastics collected at municipal recycling centres, however the amount collected in the Gothenburg municipality in 2016 is found in a report from IVL [28]. Regarding waste from businesses, four of the largest recycling companies are contacted and data for year 2018 is provided [29]. However, this data does not entirely correspond to the Gothenburg region, as the companies have different areas for administrative division. One of the companies gives a number referring to Västra Götaland County as a whole.

Table 3.1: Plastic waste flows in the Gothenburg region [t/a] [27, 28, 29].

Category	Plastic waste [t/a]
Packaging (FTI)	8 140
Gothenburg recycling centres	816
Businesses (four recycling companies)	11 080
Total	**20 040**

The other approach for estimating the waste amount is to use national statistics and scale the numbers down based on population. The most recent data at Statistics Sweden (Statistiska centralbyrån, SCB) is from 2016, and states that 316 130 tonnes of plastic waste was collected in Sweden that year [30]. According to the same authority, 1 028 000 of Sweden's 10 230 000 people live in the municipalities included in the Gothenburg region [31]. Assuming an even distribution among the population, this means a plastic waste amount of 31 770 tonnes per year in the Gothenburg region.

The result of the regional waste mapping can be seen as a confirmation that the estimated amount based on national statistics is reasonable. The difference can be explained by the omission of several waste flows from the regional investigation. The estimate from national statistics is therefore used as basis in this study.

The composition of different polymers in the plastic waste is rarely reported. While recycling companies often sort the plastics by polymer, they are seldom willing to share information about the composition. For an estimate on composition, data on the plastics put on the market is used instead. The trade organization Plastics Europe provides statistics on the total amount of plastic products sold in the European Union [2]. Assuming that the same distribution of polymers applies in the Gothenburg region, the rounded off estimate of 32 000 tonnes can be divided into the amounts shown in Table 3.2. These are the amounts that are used as basis for the processes examined in this study.

Table 3.2: Distribution of the amounts of different polymers in society [2].

Polymer	EU 2017 [%]	GR waste [t/a]
Polyethylene-LD (PE-LD)	17.6	5 600
Polyethylene-HD (PE-HD)	12.3	3 900
Polypropene (PP)	19.3	6 200
Polystyrene (PS)	3.7	1 200
Expanded PS (EPS)	2.9	900
Polyvinyl chloride (PVC)	10.2	3 300
Polyethylene terephthalate (PET)	7.4	2 400
ABS, ASA, SAN	2	600
Poly(methyl methacrylate) (PMMA)	0.6	200
Polyamide (PA) (Nylon)	2	600
Polycarbonate (PC)	1.6	500
Other thermoplastics	5.5	1 800
Polyurethane (PUR)	7.6	2 400
Other thermosets	7.6	2 400

4

Process modeling

This chapter describes the different processes and how they have been modeled, as well as the methods used for economic evaluation. Two different processes treating PS was modeled and these will be referred to as the original PS process and the simpler PS process, respectively.

4.1 Pyrolysis in fluidized bed reactors

To facilitate the comparison between modeled processes, and to increase the possibility of combination into a single plant, it is preferable to assume that the modeled processes operate with the same type of reactor. A popular choice for pyrolysis and gasification reactors is the bubbling fluidized bed (BFB), with benefits including high heat and mass transfer rates, uniform reactor conditions and good temperature control [1, 10]. The dual fluidized bed (DFB) concept consists of a bubbling fluidized bed pyrolysis reactor, combined with a circulating fluidized bed combustor [32]. By continuously cycling the bed material between the two, heat is transferred from the combustor to the pyrolysis reactor. The PS and mixed plastics plants are based on a DFB setup, however for the PVC plant a different reactor type is used due to difficulties in finding appropriate literature. The reactor type used in the PVC plant is presented in Section 4.6.

In a fluidized bed, a certain gas velocity is required to achieve fluidization. This is known as the minimum fluidization velocity, U_{mf}. A useful correlation for calculating U_{mf} has been given by Wen and Yu [33]. Using the Galilei and Reynolds numbers, equations 4.1 – 4.3 can be used to find U_{mf}, where d_p is the bed particle diameter, ρ is the density, g is the acceleration due to gravity and μ is the dynamic viscosity.

$$\mathrm{Ga} = \frac{d_p^3 \rho_g (\rho_p - \rho_g) g}{\mu_g^2} \tag{4.1}$$

$$\mathrm{Re}_{mf} = \sqrt{33.7^2 + 0.0408\mathrm{Ga}} - 33.7 \tag{4.2}$$

$$\mathrm{Re}_{mf} = \frac{U_{mf} d_p \rho_g}{\mu_g} \tag{4.3}$$

Index p and g denote bed particle and gas, respectively. The bed material is assumed to be silica sand, with a particle diameter of 420 µm, the smallest size of the particles used in [34], and a density of 2 650 kg/m^3 [35, 36]. To ensure good fluidization, a safe margin should be kept between U_{mf} and the real gas velocity U. From the gas velocity, the required volumetric flow rate can be calculated as $Q = UA_{cs}$ if the cross-sectional area A_{cs} of the reactor is known. To avoid making detailed calculations on plastics decomposition rate, a linear relationship between plastics feed rate and required cross-sectional reactor area is assumed. Reactor areas are extrapolated from a fluidized bed pyrolysis reactor in Ebenhausen, which has a diameter of 1.8 m and has been used for a feed rate of 800 kg/h [37]. Through this relationship, the volumetric input of fluidization medium in each model, as determined by the feed rate of plastics, is found.

The height of the fluidized bed reactors are not calculated. Instead, the equipment costs are estimated based on the output of pyrolysis products using relations from literature, as described in Appendix D.1.

4.2 Thermodynamic models and modeling assumptions

To supply the necessary heat for pyrolysis, some fuel for the combustor is required. Different fuels are used in each process, preferentially utilizing product streams that have a low value and/or are too small to be of interest to the market. The heat demand is calculated using enthalpies from Aspen, and heats of polymerization from literature [38]. The calculations are described in Appendix D.2.

The models in Aspen are based on the Peng-Robinson equation of state which is recommended when modeling petrochemical plants [39] and has been used to model pyrolysis-based recycling of PS previously [40]. All the modeled processes include equipment where assumptions are made regarding pressure drop and efficiencies. Compressors are assumed to operate with an isentropic efficiency of 85 % and total pump efficiency is taken to be 70 % [41]. If standard or pressurized conditions apply, the pressure drop in heat exchangers is assumed to be 0.1 bar and the pressure drop in distillation columns is 1 kPa per theoretical stage [42]. For vacuum operation the pressure drop is taken to be roughly 10 % of the inlet absolute pressure for heat exchangers and 1 % of the absolute condenser pressure per theoretical stage in a distillation column.

In case compounds are modelled which are not included in the Aspen compound data base, the structures of those are drawn in the software and Aspen is allowed to estimate the thermodynamic properties. These are validated by data found in literature, see Appendix I.

In the models, some heat integration is implemented manually, however, they are in no sense thermally optimal. Heat integration refers to the heat exchange between process streams to avoid excessive use of heating and cooling utilities. Pinch analysis is a method for finding the minimum amount of utilities that could be used, and Aspen has a built-in energy analyzer for doing such analysis. This could be used to make assumptions on a lower total utility cost than given by the model. However, due to heating and cooling utilities constituting only a small fraction of the running costs for all the modeled processes, no pinch analysis is performed in this study.

4.3 Mixed plastics process

There is extensive literature on experimental studies of the pyrolysis of mixed plastics, with different feed compositions and different pyrolysis conditions. When narrowing it down to studies using a feed roughly similar to the waste composition presented in Section 3, and with pyrolysis conditions resulting in a high recovery of light olefins, the literature is more limited. Few experiments have been done using actual waste plastics with a diverse composition. The process for mixed plastics is based on the product composition from a study by Kaminsky et al. [43]. The feed was taken from household plastic waste, and the authors used elementary analysis to determine its composition, shown in Table 4.1.

Table 4.1: Mixed plastics feed composition used by Kaminsky et al. [43].

Component	Amount [%]
Polyolefins (PE/PP)	73
Polystyrene	26
PVC	1

The authors conducted three experiments in a fluidized bed reactor at 700 °C, with different fluidization media: steam, nitrogen and a mixture of the two. For the present study, steam fluidization was chosen as basis for the product composition, mainly because the separation of nitrogen from light hydrocarbons would raise process costs considerably. The main components in the pyrolysis product are shown in Table 4.2.

Table 4.2: Mass balance of the mixed plastics pyrolysis, on total organic input basis [43].

Component	Amount [wt.%]
Gases	**51**
Hydrogen	0.6
Carbon monoxide	0.7
Carbon dioxide	2.8
Methane	6.4
Ethylene	19
Acetylene	0.2
Ethane	2
Propylene	11
Propane	0.09
C_4 olefins	7.8
Oil	**42**
Aliphatics	2.6
BTX-aromatics	10
Styrene	19
Other aromatics	9
Distillation residue	**5**
Solids	**1.3**

Most of the styrene is presumably a product of the polystyrene present in the feed. The output of styrene is thus expected to be much lower when pyrolyzing the mixture of polymers presented in Section 3. To avoid overestimating the revenues, styrene is not separated as a product, but taken out in a mixed gasoline-range fraction. It is uncertain what pyrolysis products would result from the other polymers present in the waste, but in lack of a better option, styrene is seen as a placeholder for these compounds. One could also suspect that the output of olefins would be somewhat lower with a lower fraction of polyolefins in the feed. However, since it is difficult to know what the resulting outputs would be, they are kept as given.

The article does not specify all components in the oil and in the distillation residue, both described as highly aromatic. For modeling in Aspen, some assumptions therefore had to be made regarding the heavier compounds in the pyrolysis product. Furthermore, the solid product was not included in the Aspen model. The full composition, as presented by Kaminsky et al., and the composition used in Aspen are shown in Appendix A.1 [43].

In the reported experiments, no chlorine removal strategies were used. The chlorine content of the oil was 70 ppm, and many times higher in the distillation residue – the content is not given in detail for each experiment, but it was between 0.3 and 7.4 % for all of them. Fluidizing with steam had a negative effect on oil chlorine, so a similar trend might apply for the distillation residue. Any presence of hydrogen chloride is not mentioned. In the model, the chlorine content is assumed to be zero. If PVC is present in the feed plastics, it would either have to be mechanically removed beforehand, or measures would have to be taken to reduce the chlorine amount in the product. A possible strategy is the addition of $CaCO_3$, $NaHCO_3$ or similar reagents in the reactor, to bind the released chlorine in salts [21].

Ethylene and propylene are commonly produced by steam cracking of saturated hydrocarbons such as liquefied petroleum gas, natural gas liquids or naphtha. Comparing the product composition from Table 4.2 to that of naphtha cracking, it is seen that they are similar. The process model is therefore based on the process used in naphtha cracking plants, which is well-described in literature. [44]

The process can be divided into five sections: pyrolysis, cooling, primary fractionation, compression and cryogenic separation. The front-end process, including the first four sections, is shown in Figure 4.1. Upon leaving the reactor, the first step is to rapidly cool the product gas in a heat exchanger to stop any reactions converting the desired olefins into aromatics. To avoid fouling from tar condensation in the heat exchanger, the outlet temperature is set to to 360 °C. Further cooling is done by quenching with recirculating oil. This is followed by separation of a pyrolysis fuel oil in a primary fractionator. The fuel oil is cooled to 45 °C and split into a product stream, a recirculation stream to the oil quench, and a recirculation stream to the fractionator. In the present model, the fractionator has 10 equilibrium stages. Product gas enters the column at the bottom (stage 10), cooled fuel oil enters at stage 6, and cooled gasoline from the subsequent water quench enters at the top.

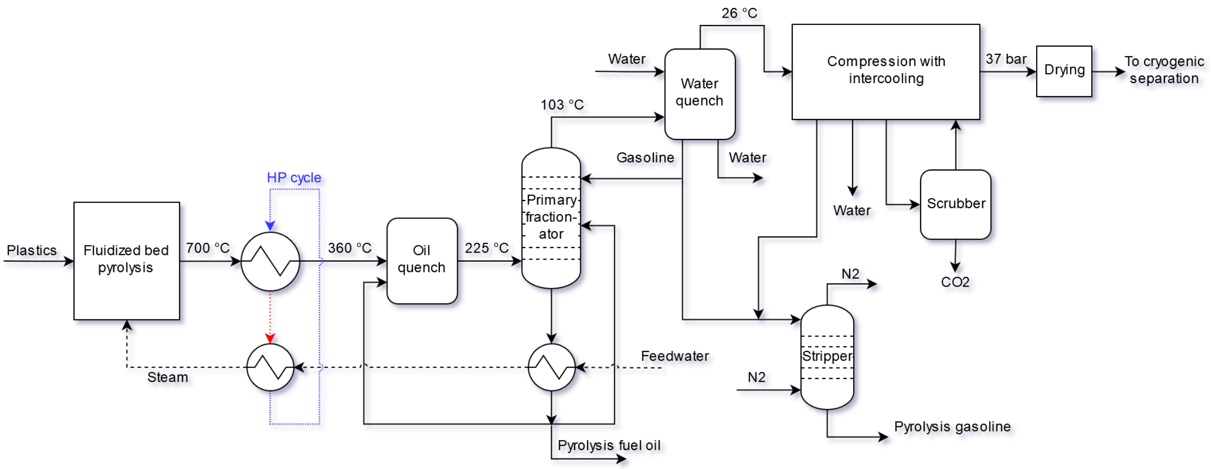

Figure 4.1: Flowsheet of the mixed plastics front-end process.

The setup of the primary fractionator may seem contradictory to traditional distillation principles. Conventional distillation columns have a condenser at the top and a reboiler at the bottom. The bottom stream is partially reboiled, with the vapor reentering the bottom stage of the column. This provides an extra equilibrium stage, and maximizes the separation efficiency of the column itself. The setup used here, where the bottom stream is cooled and then refluxed to an intermediate stage, lowers the separation efficiency. This setup is a tradeoff between the two purposes of the column: separation and cooling [44]. By supplying cooling via the already condensed hot fuel oil, suitable for heat exchange, heat integration is improved.

Some preheating of fluidization steam, shown as a dashed line in Figure 4.1, is achieved through heat integration. At near atmospheric pressure, feedwater is preheated and partially evaporated in the fuel oil cooler, and further evaporated by high-pressure steam (dotted red/blue) raised in the product gas cooler. HP steam is used as a heat medium to ensure good heat transfer in the product gas cooler.

The fractionator distillate enters a water quench tower, where it is cooled to 26 °C. A pyrolysis gasoline fraction condenses in the tower, and is collected at the bottom. Due to low miscibility, the gasoline can be separated from water by gravity in a subsequent decanter. Some gasoline is refluxed to the fractionator, and some is taken out as product.

To enable distillation at reasonable temperatures, the remaining gas is compressed to 37 bar. Due to the high reactivity of olefins, four compressor stages with intercooling between each are required, to keep the temperature below 100 °C at all points [44]. To reduce compression costs, a low pressure drop in the intercoolers is important, and is therefore assumed to be 0.05 bar in each. Small amounts of water and hydrocarbons are condensed in each intercooler. Condensed hydrocarbons from different stages are mixed into the gasoline product or routed towards the separation section depending on their composition. To reduce the vapor pressure of the gasoline, it is stripped of dissolved light gases using nitrogen.

Prior to the last compressor stage, carbon dioxide is removed in a caustic scrubber. In addition to the risk of freezing in the cryogenic section, carbon dioxide could contaminate the ethylene product. After compression, the gas is cooled to 35 °C. To avoid formation of hydrates, which takes place below 15 °C, the remaining moisture is removed by adsorption on molecular sieves. Four packed bed adsorbers are required: one for drying the gas stream, one for drying the condensed hydrocarbons that are also routed to the cryogenic section, and one copy of each for cycling. The adsorbers are sized for a 24-hour adsorption period before cycling. After drying, the products enter the cryogenic section.

A typical naphtha-based ethylene plant has six major distillation columns: demethanizer, deethanizer, depropanizer, debutanizer, and a splitter each for C_2 and C_3 compounds [44]. The first four are named after the heaviest distillate component; e.g. a depropanizer separates propane and lighter components from heavier components. There are several different commercially significant processing routes regarding these columns, but a configuration that is commonly found in modeling studies, and appears in an example model by Aspen, is a straight progression from demethanizer to debutanizer [45, 46]. To facilitate modeling setup, the same configuration is used for the present process. However, as the plant scale justified by regional or even national waste flows is far smaller than the typical scale of an ethylene plant, recovering and purifying the small amount of C_4 components present is assumed economically unfeasible. The debutanizer is thus omitted. The cryogenic separation section is shown in Figure 4.2.

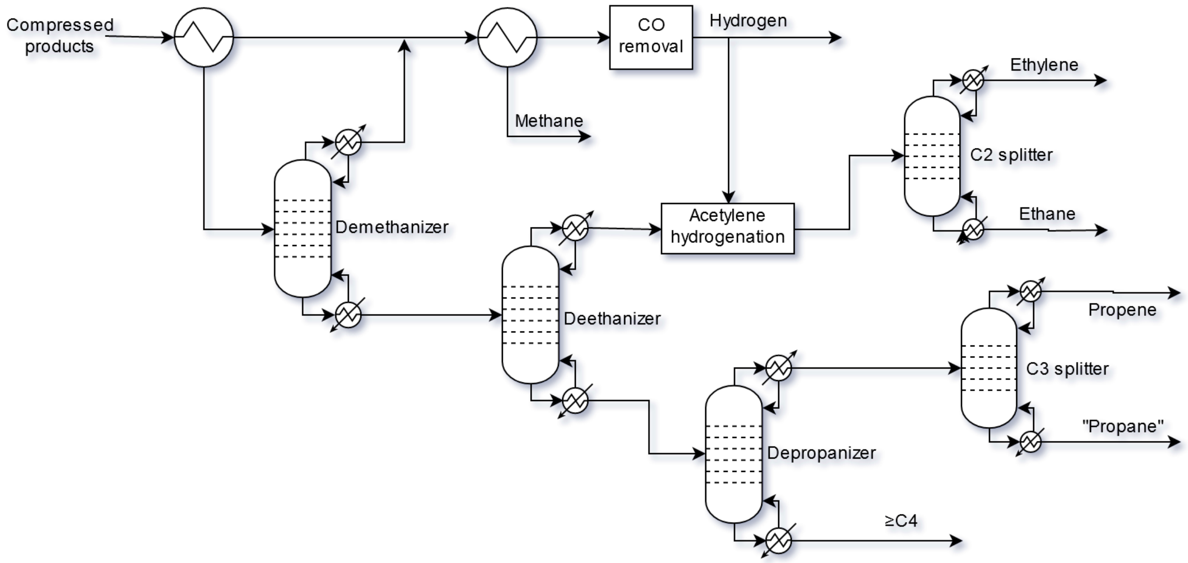

Figure 4.2: Flowsheet of the mixed plastics cryogenic separation section.

The dried feed is partially condensed in several stages at temperatures down to -125 °C, and the condensates are routed to different stages in the demethanizer. The remaining vapor as well as the demethanizer distillate are separated into hydrogen and methane, at temperatures down to -160 °C. The demethanizer bottom product is routed to the deethanizer.

The deethanizer distillate contains ethane, ethylene and small amounts of acetylene. In some ethylene plants, acetylene is recovered and sold, but more commonly it is hydrogenated into ethane and ethylene [44]. Ethylene specifications for polymerization allow a maximum acetylene content of 2 vol-ppm [47]. Given once again the small scale of the modeled process, the option of acetylene recovery is rejected. After addition of the necessary amount of hydrogen, acetylene is hydrogenated over a Pd/Al_2O_3 catalyst. The hydrogen required for this corresponds to less than 3 % of the hydrogen produced. Kinetic parameters are taken from Mostoufi et al. [48]. The resulting stream is then fractionated into polymer-grade ethylene (99.9 vol-%) and ethane [47].

The deethanizer bottom stream is fed to the depropanizer, where the C_3 content is separated from heavier compounds. In the subsequent C_3 splitter, propylene is purified to polymer grade (99.5 wt-%) [49]. Due to the small amount of propane and the level of C_4 contamination of the C_3 stream, the bottom “propane” stream from the splitter is actually a mixture of propane, butene and butadiene. The distillation columns and their operational conditions are summarized in Table 4.3. D is the column diameter, N_t is the number of theoretical stages, and R is the reflux ratio. As can be seen, due to the small flows the columns are all assigned the same diameter, which is the minimum diameter that Aspen can use in the economic evaluation. To some extent, the same situation occurs in the other process models as well.

Table 4.3: Distillation column data for the mixed plastics process.

Column	D [m]	N_t	R	$T_{condenser}$ [°C]	$T_{reboiler}$ [°C]	p [bar]
Demethanizer	0.457	47	0.7	-94	24	36
Deethanizer	0.457	50	0.81	-21	85	24
Depropanizer	0.457	50	1.1	12	81	8
C_2 splitter	0.457	50	4.98	-25	-2	22-23
C_3 splitter	0.457	60	7.25	34	58	14-15

In a typical ethylene plant, the C_3 stream contains small amounts of methylacetylene and propadiene (MAPD) which would also require hydrogenation before entering the splitter to achieve desired propylene purity [44]. The article from which the product composition was taken does not specify any MAPD content, so no MAPD hydrogenation step is included in the model [43]. However, it is possible that in reality, small MAPD amounts are present in the plastics pyrolysis gas. This would bring a small increase in equipment costs and hydrogen consumption.

Another caveat is the presence of carbon monoxide (CO) in the hydrogen and methane product streams, at 3.8 and 3.2 mol-% respectively. In the case of hydrogen, CO must be removed as it is a poison for all hydrogenation processes [44]. This is commonly done by CO adsorption or by methanation followed by adsorptive drying. For natural gas, specifications regarding CO are hard to come by. However, typical CO content in biogas is below 2 vol-% according to Nyns et al. [50]. For ordinary combustion purposes it is not a technical issue, but the toxicity of CO may cause concerns regarding the risk of leakage. Due to time constraints the removal of CO from these streams is not considered in this thesis. However, the costs for adding such units are assumed to be small compared to other process units in the plant.

Certain units in the process are difficult to model in Aspen. These are therefore excluded from the Aspen model and treated with other methods. As mentioned in Section 4.1, the flow of fluidization gas to the pyrolysis reactor is calculated using literature formulas and values. Using steam as fluidization gas, U_{mf} is found to be 0.071 m/s. To ensure good fluidization, a velocity of 0.2 m/s is assumed to be desirable, resulting in a steam flow of 0.866 kg per kg plastic. The total heat requirement for the pyrolysis reactor and its feeds, as described in Section 4.2, is then 4.76 MJ per kg plastic.

The caustic scrubber, present in the last intercooler of the compressor, is not modeled in Aspen. Its size and sodium hydroxide consumption are calculated by a simplified approach. According to Cuoq et al., ethylene plant scrubbers typically utilize a weak (1 wt-%) solution in combination with a stronger (5 – 10 wt-%) solution [51]. Furthermore, Maugans et al. mention that the scrubber typically has 3 – 4 stages [52]. It is assumed that caustic solutions of 1 wt-% and 7.5 wt-% are used, with equal amounts of CO_2 being absorbed in both. The scrubber is assumed to consume 1.5 moles of sodium hydroxide per mole of CO_2 absorbed. For scrubber sizing, only the more dilute solution is considered in order to simplify calculations. Dimensions are calculated in Aspen by feeding the cracked gas, and a water flow corresponding to the flow of dilute caustic, to a 4-stage column. The spent caustic is treated as a waste water stream, as described in Section 4.7.4.

The sizes of the adsorber units for drying the pyrolysis products (the last step of Figure

4.1) are calculated assuming that 3A zeolite, with properties given by Interra Global, is used [53]. It is assumed that cycling takes place when 70 % of the bed is saturated with water. The procedure for establishing the dimensions are given in Appendix E. The sizes are then entered into Aspen, where the vessel costs are calculated. The cost for zeolite is neglected. Assuming a zeolite cost of 500 USD/tonne, the cost for filling all four adsorbers is 10 700 SEK – less than 0.02 % of the annual operating costs.

4.4 Original polystyrene process

Processing of PS by pyrolysis is an efficient recycling method due to the high yield of styrene monomer, usually in the range of 55-79 % depending on process conditions [34, 40, 54]. The pyrolysis-based recycling of PS has been investigated for a long time and under different conditions, ranging from reactions catalyzed by solid acids and bases to non-catalytic reactions in fluidized beds using either nitrogen or steam as fluidization medium [34, 40, 54, 55].

The PS process modelled in this project is based on a study using a lab-scale fludized bed reactor with nitrogen as fluidization medium and quartz sand as bed material [34]. The experiments were run at different conditions with the highest yield of styrene obtained at 600°C. The distribution of products from the aforementioned pyrolysis experiment is presented in Table 4.4. Compared to other studies, the yield of styrene from these experiments was the highest found in literature and will therefore serve as a basis for the process modelling in Aspen [34, 40, 54]. Table 4.4 displays the composition of the liquid fraction (at ambient conditions), group G1-G3, of the product stream exiting the pyrolysis reactor. The compounds are grouped according to boiling points (b.p.). Each of the groups G1-G3 in the table includes a category named others. The exact boiling points and the properties of these compounds are unknown so assumptions are made that these are split between the remaining compounds in each respective group by a mass weighted fraction. A thorough description of this procedure and the calculations used to obtain the Aspen mass fraction input are presented in Appendix B. Moreover, the values obtained from the calculations, which are used in Aspen can be seen in Table B.1 in Appendix B together with the values from the experimental study. Regarding the solid coke, according to the study, the mass fraction was difficult to measure but it was estimated to be below 0.2 *wt*% [34]. In this study it is assumed to be 0.19 *wt*% and it is modelled as pure carbon in Aspen. Also, to simplify, the compound xylene is modelled as pure p-xylene.

Table 4.4: Products from pyrolysis of PS in a fludized bed reactor at 600°C.

Group	Compound	Mass fraction [wt%]
G1: b.p. < 200°C	Benzene	0.35
	Toluene	2.32
	Ethylbenzene	0.57
	Xylene	0.22
	Styrene (monomer)	78.70
	Alpha-methyl styrene	2.30
	Others	2.42
G2: 200<b.p.≤ 350°C	1,2-diphenyl ethane	2.21
	1,3-diphenyl propane	0.5
	2,4-diphenyl-1-butene (dimer)	3.9
	2,4-diphenyl-1-pentene	1.1
	Others	4.35
G3: b.p. > 350 °C	2,4,6-triphenyl-1-hexene (trimer)	0.11
	Others	0.11
	Cracking gas	0.65
	Coke (<0.2 wt%)	0.19
	Total	100

In a study by Bassil et al (2018) a techno-economic assessment was done on a pyrolysis-based plant for PS recycling. This study is used as a basis for building the PS process. However, the assumed pyrolysis product composition in this study is different than the one used in Bassil et al (2018) so the operating conditions of the downstream refining sections will differ. Based on the experimental data presented by Liu et al (2000), the fluidized bed reactor is chosen to operate at 600°C using nitrogen for fluidization. Nitrogen will serve as an inert in the pyrolysis and will not affect the product distribution. Also, it can be recovered downstream and recirculated to the reactor. The first section of the process is presented in Figure 4.3. The effluent gas leaving the reactor is separated from the solid and sand particles in a cyclone (not included in Figure 4.3). It is assumed that the cyclone removes all the solids and that no electrostatic precipitator (ESP) or filter is necessary further downstream of the process. The solids are sent to briquette manufacturers [40].

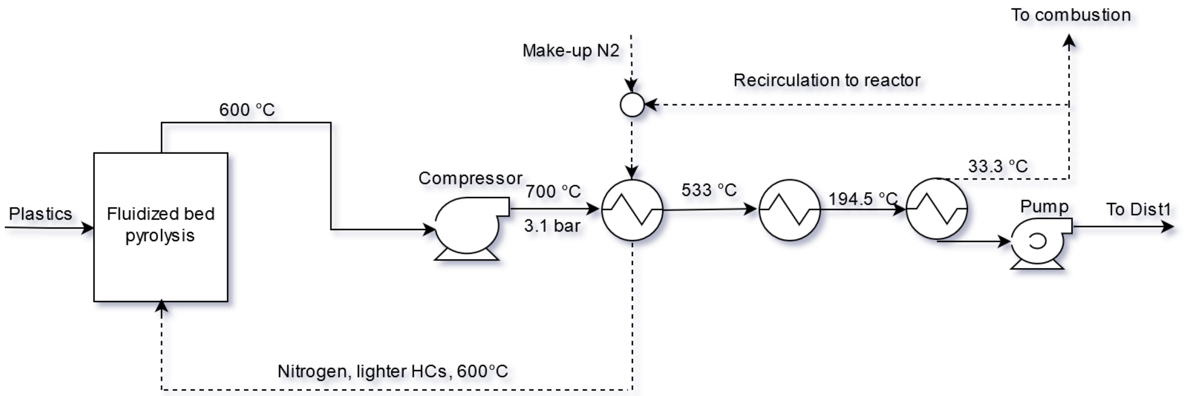

Figure 4.3: The first part of the original PS process.

After the cyclone, gases are fed to a compressor where the pressure is increased to 3.1 bar in order to effectively transport the gas through the process. This also serves the purpose of having a low loss of styrene in the downstream condensation. After compression the gas leaves at around 700°C and is cooled down and partially condensed in two separate heat exchangers. The first cooling is done by exchanging heat with the recirculated nitrogen on its way back to the reactor. The nitrogen stream is heated up to 600°C again. Downstream the pyrolysis gas is further cooled and partially condensed at around 30°C to obtain a coarse separation. Lighter hydrocarbons, nitrogen and small amounts of heavier hydrocarbons leave at the top. The loss of styrene in the top is roughly 1.9 wt% in this stage. The top stream from the flash is recirculated back to the reactor to fluidize the bed. The recycle is not pure nitrogen, but contains some lighter hydrocarbons. It is not recommended to recycle pyrolysis gases if the main products are olefins because this will cause undesired gas-phase reactions [21]. However, olefins are not the main product here and are also less than 1 *wt%* of the pyrolysis products so this gas recycling should not pose a major problem.

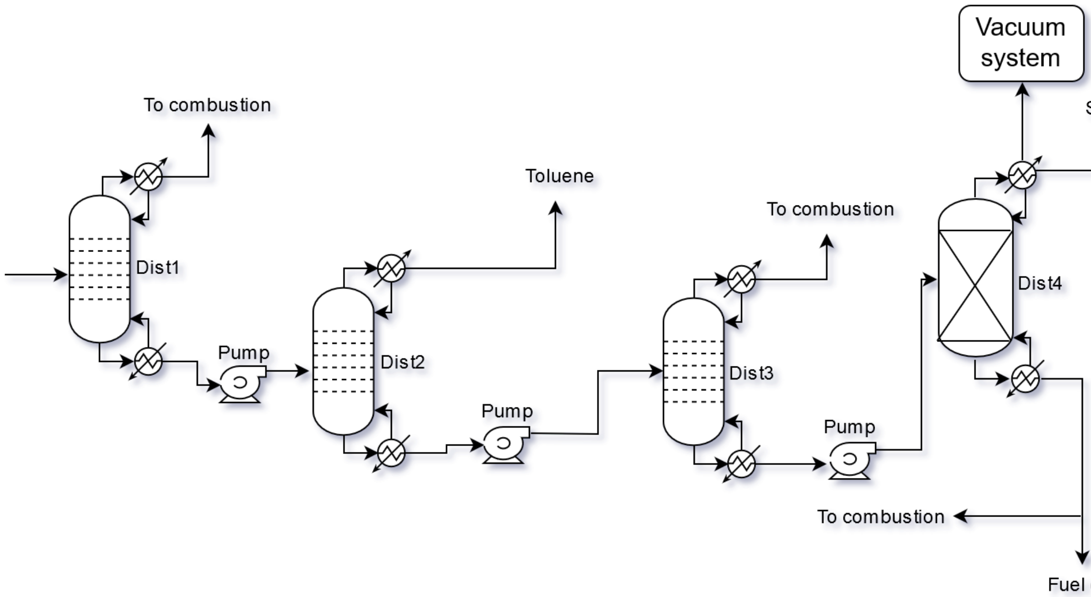

Figure 4.4: The second part of the original PS process.

The liquid stream from the condenser is fed to a distillation train where several products are extracted. Figure 4.4 displays the process layout of the distillation train. It should be noted that the first three columns are trayed columns while the last one is a packed column. The last column is operated under vacuum and in this type of operation, a low pressure drop is desired. A lower pressure drop is achieved when using a packed column instead of a trayed column [40]. The operating conditions for each distillation tower are presented in Table 4.5. The ranges of operating pressure are also included, the lowest being the condenser pressure and the highest being the inlet pressure to the column. Before the first distillation column the liquid stream is pumped to 4.5 bar. The first column extracts the remaining lighter hydrocarbons and benzene in the distillate. The bottom product is pumped to 5.5 bar and fed to the second column where toluene is taken out in the top at a purity of 99.5 *mol%*. The high-purity toluene can be sold.

The bottoms are again pumped to 4.5 bar and fed to the third column where both ethylbenzene and p-xylene are taken out in the top. This separation is difficult because the boiling points of ethylbenzene and styrene differ by only 9°C. This explains the large number of ideal stages (N_t) and the large reflux ratio (R) seen in Table 4.5. The final distillation tower is where the main product, styrene is taken out. To avoid the risk of spontaneous polymerization of styrene, this separation is performed under vacuum as it will lower the condenser and reboiler temperature significantly. The condenser is operated at a pressure of 6.89 kPa. The vacuum is achieved by a vacuum system connected to the condenser. This is not modelled in Aspen but a vacuum pump is added to estimate the cost. A brief description of how the vacuum pump dimensions are derived is found in Appendix F.

Before the fourth tower, a pump increases the pressure to 4.3 bar. The pressure of the bottom product from the third distillation column will be roughly 4.25 bar during continuous operation and since no real pressure increase is necessary here, the downstream pump will only be used during start-up. From the fourth tower styrene is taken out in the distillate stream with a purity of 99.6 $mol\%$. This purity is enough to produce new high-grade polystyrene [34]. From the pyrolysis reactor, the styrene amount was 0.787 kg/kg_{feed}. The amount of styrene from the distillation column is 0.784 kg/kg_{feed}. To further lower the risk of polymerization, an inhibitor should be added already in the tower where ethylbenzene and p-xylene are taken out, as well as in the styrene distillation column [40]. In the experimental study by Liu et al (2000) $2,4$-dinitrophenol is used for this purpose but no amounts are mentioned and therefore the inhibitor addition is not modelled in Aspen. Moreover, the inhibitor cost is not included. The bottom product from the last column consists of hydrocarbons heavier than styrene and these can be sold as fuel oil. The rather high boiling point of this stream will cause it to end up in the diesel range of fuels.

Table 4.5: Data for the distillation columns in the original PS process.

Column	D [m]	N_t	R	$T_{condenser}$ [°C]	$T_{reboiler}$ [°C]	p[bar]
Dist1	0.457	30	0.24	123.6	214.6	4.1-4.5
Dist2	0.457	50	31.9	152	201.1	2.7-5.5
Dist3	0.457	150	380	171.8	214.9	2.7-4.5
Dist4	0.914	20	1.8	65.5	112.6	0.069-4.3

The mass flow of the recirculated nitrogen stream is higher than the necessary fluidization mass flow so this stream is split up in two. The larger part, roughly 97.6 % is recirculated and downstream combined with a feed of fresh nitrogen. Together, these two streams add up to the necessary fluidization mass flow. The smaller part of the split stream is fed to the furnace for combustion. Further, the remaining lighter hydrocarbons and benzene from the first distillation column and the distillate from column three are all fed to the furnace to be combusted. This is however not enough to satisfy the demand of the pyrolysis reactor of 155.5 kW. Thus, a part of the fuel oil from column four, roughly 28.7 % is fed to the furnace.

There is a necessity of fluidization nitrogen in the reactor as mentioned before. The required amount of nitrogen is calculated by the procedure in Section 4.1. A minimum fluidization velocity of 0.071 m/s is found and to have some margin, the actual velocity is set to 0.2 m/s. This gives a nitrogen flow rate of 2.59 kg per kg plastic.

4.5 Simpler polystyrene process

Considering the moderate complexity of the previously discussed PS process, it is interesting to compare the complexity and in the end the cost of a process which is built up in a similar way but with only styrene separation. This plant is assumed to operate exactly as the former PS plant with the modification starting after the partial condensation and subsequent separation. The first part of the process is given in Figure 4.3. The distillation section is given in Figure 4.5 and the column operating conditions are given in Table 4.6. The liquid stream from the flash is now pumped to 3.45 bar and fed to the first distillation tower where the compounds lighter than styrene are taken out in the distillate. The distillate is then fed to the furnace to be combusted while the bottom product is pumped to the next tower. The pressure is increased to 3.5 bar but because the bottoms from distillation tower one are at roughly 3.35 bar and no real pressure increase is necessary, this pump is only used during start-up. Again, the styrene is separated under vacuum in a packed column with a condenser pressure of 6.89 kPa. The achieved purity is 99.6 $mol\%$ which is enough to produce new high-grade PS [34]. The amount of styrene from the pyrolysis reactor is still 0.787 kg/kg_{feed} but the styrene leaving the vacuum column is in this case 0.781 kg/kg_{feed}. The bottom product from the second column is split up in two where the first part, roughly 8.3 % is sent to the furnace and the rest is sold as diesel range fuel.

Table 4.6: Operating conditions for distillation columns used in the simpler PS process.

Column	D [m]	N$_t$	R	T$_{condenser}$ [°C]	T$_{reboiler}$ [°C]	p[bar]
Dist1	0.457	60	42.1	149.9	202.4	2.76-3.45
Dist2	0.914	20	4.6	65.5	111.4	0.069-3.50

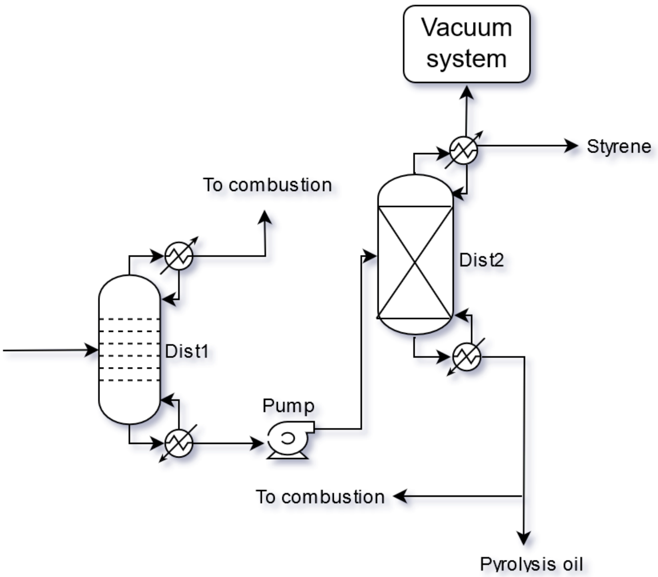

Figure 4.5: The second part of the simpler PS process.

4.6 PVC process

Few studies have been done on how to recycle PVC plastics by pyrolysis, both pure and in a combination with other types of plastic waste [17, 18, 19, 21, 56]. The PVC recycling is problematic because of the high chlorine content. The chlorine acts as a precursor to corrosive HCl and chlorinated hydrocarbons (HCs). A pyrolysis-process handling PVC is operated in two stages where the main part of the HCl and small amounts of HCs are removed in the first step at moderate temperatures, up to to 360°C. The remaining plastic structure from the PVC is further heated up to temperatures around 500°C in a second reactor where the main pyrolysis takes place [18]. The process modelled here is assumed to utilize this procedure.

There are even fewer studies on pure PVC than on PVC in combination with other polymers and most often the final product distribution is only presented in terms of HCl, other gases, liquid and solid residue [54, 57]. To the best of our knowledge only one study is found which gives a full final product distribution and in the study they performed lab-scale experiments in a batch reactor under vacuum at a pressure of 2 kPa [18]. The products in this study are also presented as HCl, other gases, light and heavy liquid and solid residue but with a full list of the belonging compounds in each respective group. In their experiments, the residence time in the reactor was at least 40 min and it was operated at different conditions. The full product composition given in the study is used in this project as input to the Aspen model after some simplifications [18]. A rigorous explanation about assumptions and calculations to find the input mass fractions used in Aspen can be seen in Appendix C. The experiments performed by Miranda et al (1999) were run at both 320°C and 520°C. The process modelled in this project is assumed to operate with two reactors at 320 and 520°C respectively with the associated products as in the study by Miranda et al (1999). From the experimental study the distribution of products at 320 and 520°C split into categories are found in Table C.7 in Appendix C. The products leaving the batch reactor at 520°C in the study by Miranda et al (1999) is the assumed actual product distribution leaving the second reactor here. One major assumption though is that the fractional amount of each category (HCl, light liquid, heavy liquid, other gases) in the experiments at 320 compared to 520°C as indicated in the third row in Table C.7 is driven off in the first reactor of our process. This means that 98.8 % of the HCl, 11.7 % of the other gases and 21.1% and 5.1% of the light and heavy liquid respectively, leave the first reactor as pyrolysis products. The remaining amounts of these compounds and the solid residue are assumed to be the products from the second reactor where the remaining plastic structure is cracked at 520°C.

The layout of the modelled PVC process is found in Figure 4.6-4.7. The main idea with the design is to keep the released HCl away from any water to prevent formation of the highly corrosive hydrochloric acid. Also, the chlorinated HCs are closely monitored so they do not accumulate in the system and the mass fractions are kept below 10 ppm in each product to satisfy the limit set by the industry [21].

The reactor in the study by Miranda et al (1999) is of batch-type and therefore only one is necessary. But to easier compare the modelled plants in this project, it is assumed that this process operates as two continuous reactors at different temperatures and achieves the same products as earlier mentioned. Both reactors are assumed to have a residence time of 40 min to mimic the experimental study by Miranda et al (1999). The PVC is fed to the first reactor where dehydrochlorination occurs at a temperature of 320°C and a pressure of 2 kPa. In the first stage 98.8% of the total HCl is released alongside small amounts of HCs and chlorinated HCs making up 343 ppm of the gas stream. This is beyond the 10 ppm limit set by the industry [21]. To counter this, the HCl must be separated from these and other HCs to make it more valuable as a product.

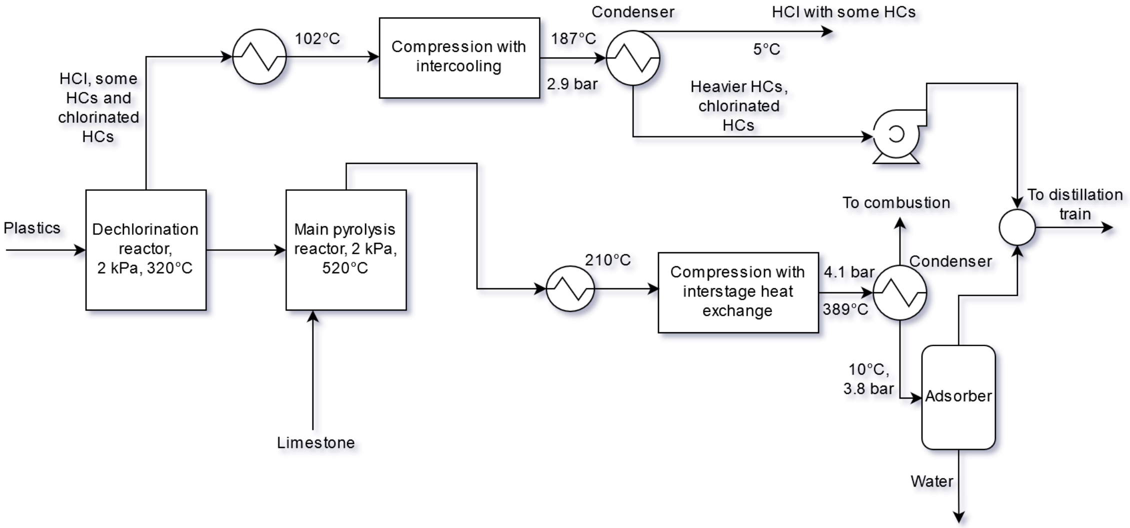

Figure 4.6: The first part of the PVC process.

The released gas from the first reactor is cooled down and fed to a three-stage compression train with interstage cooling. Dry HCl is not as corrosive compared to hydrochloric acid and the common materials can handle the former within the given temperature limits. The compressors and subsequent intercoolers are operated with a maximum temperature of 390°C to have some margin and to be within the tubes/internals temperature limit of 400°C for Nickel 201 [58]. The intercoolers exchange heat so that the gas is superheated by 20°C before the next compressor. The last compressor in the train is operated so that the subsequent condensation step at 5°C will reduce the amount of chlorinated HCs to 10 ppm in the gas stream. The achieved discharge pressure is 3 bar. The gas stream contains some HCs but the achieved purity of HCl is 99.3 *mol*%. This product can be sold and used in the industry. The condensate from the HCl separation consists mainly of HCs, small amounts of HCl and the remaining chlorinated HCs.

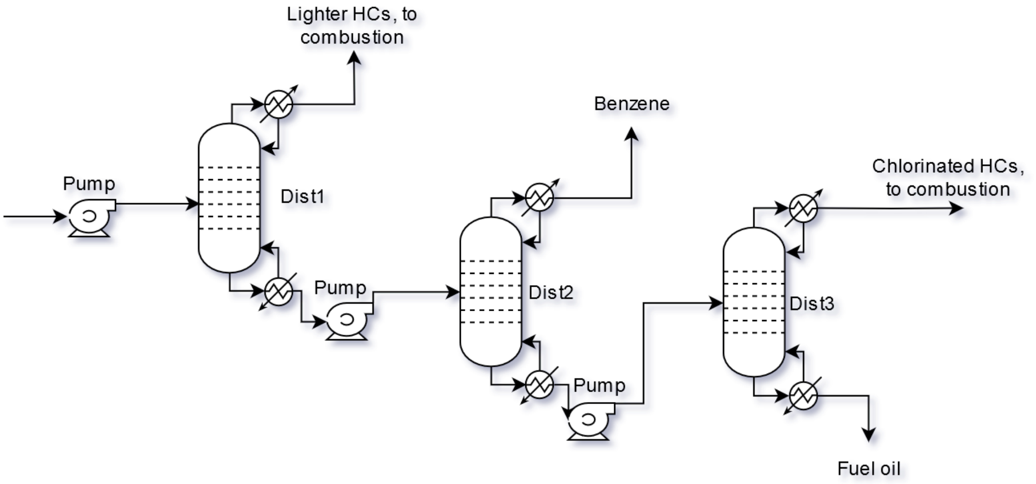

Figure 4.7: The second part of the PVC process.

The main pyrolysis takes place in the second reactor which also operates at a pressure of 2 kPa but with a temperature of 520°C. The remaining products from the study at 520°C by Miranda et al (1999) is now assumed to be released. The small amount of remaining HCl (1.2 wt%) is simultaneously removed in the reactor by adding limestone ($CaCO_3$) [21]. This will cause an exothermic reaction according to Equation 4.4. Injection of limestone is only modelled in Aspen as a feed stream in to a stoichiometric reactor in stoichiometric amounts with a given conversion of 100 %.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2 \tag{4.4}$$

The gas leaving the reactor is separated from the solid residue which consists of carbon and $CaCl_2$ (not shown in Figure 4.6). To simplify, no further refining of the solids is done, and these are sent to briquette manufacturers like in the PS case. After the solids separation, the gas is cooled down to 210°C as indicated in Figure 4.6. Downstream the gas is fed to a two-stage compression train with interstage heat exchange. The first compressor discharges the gas at a pressure of 0.35 bar and a temperature of 277°C. To prevent condensation in the next compressor, the gas is superheated by 60°C up to 327°C. The final compressor is again operated to keep the chlorinated HCs below 10 ppm in the gas from the subsequent condensation and the discharge conditions are 389°C and 4.1 bar. The downstream condenser separates mostly light HCs. This stream is sent to combustion. The condensate consists of heavier HCs and the chlorinated HCs. Before the mixing point shown in Figure 4.6, the liquid stream is fed to an adsorber for water removal. The water comes from the reaction presented in Equation 4.4. Water is removed in this stage to prevent any production of highly corrosive hydrochloric acid. The sizes of the adsorber units for water removal are calculated assuming that 3A zeolite, with properties given by Interra Global, is used [53]. It is assumed that cycling takes place when 70 % of the bed is saturated with water. The procedure for establishing the dimensions is given in Appendix E. These sizes are entered into Aspen, where the software estimates the vessel cost. The cost of zeolite is neglected. Assuming a zeolite price of 500 USD, the cost for filling both adsorbers is 10800 SEK - less than 0.19 % of the annual operating costs. The water-free liquid is fed to the mixing point where it is combined with the liquid from the HCl condenser and fed to the distillation train.

Table 4.7: Operating conditions for the distillation columns in the PVC process.

Column	D [m]	N$_t$	R	T$_{condenser}$ [°C]	T$_{reboiler}$ [°C]	p[bar]
Dist1	0.457	12	0.55	32.4	201.84	5.0-5.2
Dist2	0.457	15	3.75	79.8	188.9	1.0-5.11
Dist3	0.457	10	4.13	133.2	306.2	1.0-1.15

The remaining part of the process is used to extract useful products while keeping track of the chlorinated HCs and HCl, the two latter being sent to combustion and subsequent flue gas treatment. Operating conditions for the distillation columns are given in Table 4.7 and the process layout is found in Figure 4.7. The mixed stream is pumped to 5.2 bar and fed to the first distillation tower. Condenser pressure is chosen so that it will operate at a temperature appropriate for heat exchange with cooling water. Remaining lighter hydrocarbons and HCl are extracted as distillate and sent to combustion. The bottoms are pumped to the second tower but since the pressure out is 5.11 bar and no pressure increase is necessary, the pump is only used during start-up.

In the second tower benzene is taken out in the top at a purity of 99.5 $mol\%$. This product can be sold. The bottom is at a pressure of 1.15 bar and this is enough for feeding it to the final column. Again the subsequent pump is only necessary during start-up. The final column serves as a separator of chlorinated HCs and fuel oil where the former is taken out in the top and the mass fraction is kept below 10 ppm in the bottom fuel oil. Chlorinated HCs are sent to combustion and subsequent flue gas treatment. Streams sent to combustion are split to satisfy the individual heat demand of each reactor.

The heat duty is calculated with the assumption that the reaction goes to completion in the first reactor and the remaining products are only heated to a temperature of 520°C in the second reactor. This assumption will give the correct total demand of both reactors but the distribution will probably be different in a real process since a part of the reaction also occurs in the second reactor. The procedure for calculating the heat demand is given in Appendix D.2. The first reactor has a demand of 178.86 kW and the second reactor a demand of 22.05 kW. The fuel sent to combustion is more than enough to satisfy the total heat demand of 200.9 kW but because they contain corrosive HCl and chlorinated HCs, they are not split up. Reactor 1 is fed with exact amount of fuel to satisfy the heat demand. On the other hand, the remaining fuel sent to combustion to satisfy the second reactor yields a duty of 50.37 kW. This heat demand is enough to satisfy the second reactor as well as the reboilers on Dist2 and Dist3 which needs 9.70 and 17.98 kW respectively. No rigorous heat integration was made, and only the excess heat from combustion off-gases was matched as previously described.

The chemistry related to combustion of halogenated hydrocarbons (HHC) is complex but can be examined with Equation 4.5 [59]. For chlorinated HCs the term Hl = Cl.

$$C_xH_yHl_z + \left(x + \frac{y-z}{4}\right)O_2 \rightarrow xCO_2 + zHHl + \frac{y-z}{2}H_2O \tag{4.5}$$

The list of chlorinated HCs from the experiments by Miranda et al (1999) was long and here it is assumed that only the two major compounds are present as described in Appendix C. The considered compounds are chlorobenzene (C_6H_5Cl) and benzylchloride

(C_7H_7Cl). Applying the reaction in Equation 4.5 to the compounds, the result is:

$$\begin{aligned} C_6H_5Cl + 7O_2 &\rightarrow 6CO_2 + HCl + 2H_2O \\ C_7H_7Cl + 8.5O_2 &\rightarrow 7CO_2 + HCl + 3H_2O \end{aligned} \tag{4.6}$$

For HHC compounds with y<z, the following reaction also needs to be considered:

$$C_xH_yHl_z + xO_2 \rightarrow xCO_2 + yHHl + \left(\frac{z-y}{2}\right)Hl_2 \tag{4.7}$$

For both the compounds considered here y>z so the reaction in Equation 4.7 can be neglected. Combustion of chlorinated HCs comes with the risk of dioxins formation [59]. These toxic compounds can cause endocrine disruption [60]. Because of the complexity of the dioxins formation [59], only the reactions in Equation 4.6 was considered in this project. However, if dioxins are produced in the process these can be removed either by a catalytic reaction or by a filter [61].

4.7 Economic analysis

Each process has a number of investment costs, variable operation costs, fixed operation costs, and revenues. To be regarded as economically feasible, any project must have the prospect of generating enough net profit to outweigh the risk of investment, as judged by the investors. This can be measured in different ways.

4.7.1 NPV and cash flow analysis

In this thesis, process economics are judged by their payback period (PBP) and their net present value (NPV) at the end of their lifetime. The PBP is here defined as the time it takes for the NPV to change from negative to positive. Given a discount rate r, the NPV of a project is the sum of the present values of the future cash flows calculated by Equation 4.8 where C is the cash flow in year n and t is the project life time in years [62].

$$\text{NPV} = \sum_{n=1}^{n=t} \frac{C}{(1+r)^n} \tag{4.8}$$

The economic assessment has been based on general economic project evaluations for chemical processes given in [62]. The fixed capital investment of a project consists of the inside battery limit (ISBL) investment and the outside battery limit (OSBL). ISBL is the cost of the plant itself and OSBL is the addition of costs for modifications to the site infrastructure. OSBL is typically taken as $30-50\%$ of ISBL [62]. Moreover, the fixed capital investment includes both engineering and construction costs and contingency charges. Engineering and construction costs relates to the costs ranging from design of the equipment and the plant to construction supervision and administrative charges including project management. Contingency charges are included in the budget to compensate for variations in the cost estimation. Working capital is another type of investment which is necessary in addition to the fixed capital investment to initiate the production and keep it running [62]. This capital is invested when the plant starts running and is recovered at the end of the project life time. The working capital is taken as 15% of the total fixed capital cost (OSBL included).

When the investment cost is found, a cash flow analysis is done to find the NPV of the plant for each year. Recommended average values are taken to split up the fixed capital investment and the working capital according to Table 4.8 [62]. The investment is done over three years with the largest part in project year 1. The working capital is invested in project year 2 when the plant starts running and is recovered at the end of the final project year.

Table 4.8: Investment costs and variable costs split over the project life time.

Project year	Fixed capital investment	Working capital	FCOP	VCOP
0	30%	-	-	-
1	50%	-	-	-
2	20%	100%	100%	30%
3	-	-	100%	70%
4	-	-	100%	100%
.				
.	-	-	100%	100%
.				
n	-	-100%	100%	100%

The plant will also have running costs categorized as either fixed or variable. The fixed costs of production (FCOP) do not vary with the production. These include for example labor costs and maintenance. Variable costs of production (VCOP) are related to e.g. feedstock material and utilities which vary with the production. If the plant is not running, these costs are 0. FCOP and VCOP are split by recommended values according to Table 4.8 [62]. The FCOP starts at 100% in project year 2 and will be present at full rate until the plant is shut down in the end of the life time. The VCOP starts with 30% in project year 2 and continues at a rate of 70% in project year 3. Finally, the production is assumed to run at full capacity from project year 4 until the end of the life time. The revenues of the process will follow the production capacity in the same manner as the VCOP with 30% in project year 2, 70% in year 3 and 100% from year 4 on wards. The modelled processes are assumed to have a project life time of 30 years.

The cash flow analysis is realized using a number of equations which are described below. The FCOP and VCOP are combined as one annual cost. The annual gross profit is found by subtracting the costs from the revenues, according to:

$$\text{Gross profit} = \text{Revenues} - \text{Costs} \tag{4.9}$$

The investment is assumed to be depreciated over the years of production and will be split using a straight line depreciation with the same amount depreciated in each year. The taxable income is calculated by Equation 4.10:

$$\text{Taxable income} = \text{Gross profit} - \text{Depreciation charge} \tag{4.10}$$

The tax of year n is paid based on the taxable income of year $n-1$. For taxable incomes ≤ 0 the tax is 0. With the Swedish company tax of 20.6% from 2021 on wards, the paid tax is found by:

$$\text{Tax(n)} = 0.206 \cdot \text{Taxable income(n-1)}, \tag{4.11}$$

The cash flow of year n is calculated by the following expression:

$$C = \text{Gross profit} - \text{Investment} - \text{Working capital} - \text{Tax} \tag{4.12}$$

The interest rate is taken to be 6.25%, average of the two mid-points used in [63], and the final NPV for the project is calculated with Equation 4.8.

4.7.2 Aspen Process Economic Analyzer (APEA)

With all the plant layouts established, the cost of each process is estimated using the built in Aspen Process Economic Analyzer (APEA). APEA estimates the capital investment, fixed operation costs and costs for electricity, heating utilities and cooling utilities. Process units for which the cost cannot be properly estimated in Aspen are unmapped from the Economic Analyzer, and their costs calculated outside the software. APEA will give the total capital investment excluding OSBL [64]. To compensate for this, the OSBL was taken as 40% of ISBL and added to find the total fixed capital investment of the process.

4.7.3 Taylor process step scoring method

The process step scoring method is a neat way of doing capital estimations of a chemical process [65]. The method uses a procedure which is described briefly: First the flow sheet is drawn, indicating the main process steps of the plant and showing the operating conditions for each step. This includes for example relative throughputs (ton/ton product), pressures, temperatures and reaction times. Secondly, the significant process steps are listed, such as evaporation, chemical reactions and compression. Each significant step is scored based on the above operating conditions. For N process steps the score (S) is summed to find the costliness index (I) by Equation 4.13:

$$I = \sum_{1}^{N} (1.3)^S \tag{4.13}$$

The capital investment is found by the expression below:

$$\text{Capital in k£} = 42 \cdot I \cdot (\text{Capacity in 1000 tons})^{0.39} \tag{4.14}$$

This value is in $k£$ of 1977. The value is recalculated in the same way as in [66], using the British consumer price index (CPI) of 1977 and 2018 [67].

4.7.4 Other cost estimation tools

For all processes, the cost of the pyrolysis reactors are calculated outside Aspen, as they are not modeled. Where the dual fluidized bed reactor is used, economic parameters are taken from Alamia et al. [68]. The vacuum reactors in the PVC process have been cost estimated with the Taylor method as described in Section 4.7.3. The calculations are described in Appendix C. The calculations for fluidized bed reactor costs are shown in Appendix D.1. Operation costs related to flue gas treatment and waste water treatment are calculated using models by Papadokonstantakis et al. [69]. The models include annualized investment costs. As the investment for flue gas treatment is already accounted for, this cost is removed from the model.

4.7.5 Economic data

The exchange rates presented in Table 4.9 are used to convert costs and revenues to SEK.

Table 4.9: Exchange rates used in the thesis.

	1 US$	1 £	1 €
SEK	9.3	11.6	10.5

Various types of utilities which are used in the different processes are presented in Table 4.10. The costs for electricity, cooling water and refrigerants are taken directly from Aspen. The main reason being that the default cost of electricity in Aspen is found to be similar to the Swedish cost of electricity [70]. Moreover, the cost of refrigeration and cooling water are assumed to correlate to the electricity price and these are kept as default in Aspen. The cost of steam is highly dependent on how it is produced and since Aspen is developed in the U.S., these prices are assumed to be based on the current mixture of fuels used there, mainly fossil fuels with natural gas being the predominant [71]. In Sweden, the mixture is somewhat different with biomass being the dominating fuel [72]. With this in mind, the steam costs are estimated using the procedure described in Appendix H.

Table 4.10: Different utilities used in the plants and their individual costs.

Utility	Cost	Unit	Reference
Electricity	0.72	SEK/kWh	[73]
Cooling water	$1.97 \cdot 10^{-6}$	SEK/kJ	[73]
LP steam	0.259	SEK/kWh	-
MP steam	0.379	SEK/kWh	-
HP steam	0.498	SEK/kWh	-
Refrigerant 1 (-25 to -24 °C)	$2.55 \cdot 10^{-5}$	SEK/kJ	[73]
Refrigerant 2 (-40 to -39 °C)	$3.12 \cdot 10^{-5}$	SEK/kJ	[73]
Refrigerant 3 (-65 to -64 °C)	$5.47 \cdot 10^{-5}$	SEK/kJ	[73]
Refrigerant 4 (-103 to -102 °C)	$7.93 \cdot 10^{-5}$	SEK/kJ	[73]
Very low temperature refrigeration (-170 to -169 °C)	$8.28 \cdot 10^{-5}$	SEK/kJ	[73]

Prices of products, feed plastics and used chemicals are presented in Table 4.11 together with references to each of them. The revenue from sold fuel oil and gasoline is calculated based on the lower heating value (LHV) of diesel and gasoline [74, 75]. The LHV together with the average cost of diesel and gasoline is used to calculate a price in SEK/MJ as indicated by fuel oil and gasoline in Table 4.11. This price is used to calculate revenues in SEK/kg based on the estimated LHV of the streams in Aspen. Since hydrogen is most commonly produced by steam methane reforming, its price is highly dependent on the natural gas price and is therefore calculated based on the relation between them [76, 77].

Table 4.11: Material prices.

Material	Price	Unit	Reference
Mixed waste plastics	0	SEK/kg	[20]
Waste PS	6.15	SEK/kg	[40]
Waste PVC	0	SEK/kg	[20]
Fuel oil	0.185	SEK/MJ	[78, 74]
Gasoline	0.166	SEK/MJ	[78, 75]
Methane	190	SEK/MWh	[77]
Ethylene	9.95	SEK/kg	[79]
Propylene	8.56	SEK/kg	[80]
Benzene	7.44	SEK/kg	[81]
Toluene	9.47	SEK/kg	[81]
Styrene	10.4	SEK/kg	[82]
Hydrogen	11.7	SEK/kg	[76, 77]
Nitrogen	9.95	SEK/kg	[83]
Sodium hydroxide	4.65	SEK/kg (dry)	[84]
HCl	0.465	SEK/kg	[85]

Costs for transportation of products and waste plastics are not considered. Product storage costs are not examined either.

4.8 Sensitivity analysis

The profitability of each plant depends on a large set of parameters. Some of these, such as the prices of petroleum products, can exhibit large variations that are hard to predict. Others, such as the investment costs, are uncertain due to the level of detail in the modeling. To estimate the uncertainty range of each plant's calculated NPV, Monte Carlo simulations are done. In Monte Carlo simulations, a set of parameters are given randomized values according to a given distribution [86]. By running a large number of simulations, a statistically significant distribution of results are obtained. To obtain meaningful results, it is important to account for any correlations between parameters.

In this thesis, all examined parameters are given a uniform distribution within specified ranges. For all plants, the investment cost and the electricity price have been varied by ± 30 %, and the discount rate by ± 50 %. The costs of refrigerants and cooling water are assumed to depend only on the costs for compression/pumping, and are thus varied according to the electricity price. Another parameter examined in all cases is the crude oil price. The prices for the fuel oil and gasoline fractions are based on diesel and gasoline fuel trading prices, respectively. However, the fractions produced in the plants are heavily aromatic. EU specifications restrict the aromatics content in gasoline to 35 vol-%, and polycyclic aromatics in diesel to 8 mass-% [87]. The produced fractions could thus be used merely for blending in motor fuel, hydrogenated to conform to the specifications, or used for other purposes – in the worst case, burnt for steam or electricity generation. These options give reason to suspect that the real value of the streams may be lower than assumed. Therefore, while other petrochemical prices (excluding styrene) are varied by ± 30 %, the fuel oil and gasoline fractions' prices are varied from -50 % to +25 %. All petrochemical product prices – not including methane and hydrogen – are assumed to correlate completely. All parameters examined in the Monte Carlo simulations are presented in Table 4.12, together with their ranges.

As a comparison, the modeled plants are scaled up to represent processes handling the national waste flows. Thus, the sensitivity analysis is conducted for all the modeled plants in both regional and national scale.

Table 4.12: Parameters examined in the Monte Carlo analysis.

Parameter	Associated plant	Range
Interest rate	All plants	± 50 %
Total investment cost	All plants	± 30 %
Electricity price	All plants	± 30 %
Mixed waste plastics price	Mix	-1.050 – 1.575 SEK/kg
Waste PS price	PS orig. & simple	0 – 10.25 SEK/kg
Waste PVC price	PVC	-1.89 – 0.945 SEK/kg
Styrene price	PS orig. & PS simple	10.4-18.6 SEK/kg
Prices following petroleum index:		
Fuel oil	All plants	0.0925 – 0.231 SEK/MJ
Gasoline	Mix	0.0832 – 0.208 SEK/MJ
Ethylene, propylene	Mix	± 30 %
Benzene	PVC	± 30 %
Toluene	PS orig.	± 30 %

5

Results

In this section the main results are presented. The first section presents the main product flows of each process, their revenues and the running costs and investment costs. Meanwhile, the subsequent section gives the economic performance of the plants. In the final sections the results of the Monte Carlo analysis for the regional and national scale plants are compared to each other and a comparison is made with other previous studies. Lastly, the possibility of using a flexible process is discussed.

5.1 Distribution of revenues and costs

Table 5.1 presents the streams that are sold in the mixed plastics plant, showing that gasoline and ethylene are the largest streams and the ones that contribute most to the revenue.

Table 5.1: Output streams from the mixed plastics process and their generated revenue.

Product	Amount [kg/kg$_{feed}$]	Price [SEK/kg]	Revenue [MSEK/yr]
Ethylene	0.197	9.95	62.61
Propylene	0.110	8.56	30.24
H_2 (excl. impurities)	0.0060	11.70	2.23
Methane	0.068	4.00	8.74
Gasoline	0.327	6.59	68.97
Fuel oil	0.096	7.18	21.93
Total revenue			**192.49**

Table 5.2 summarizes the running costs for the mixed plastics process. The largest waste water stream is that from the water quench tower, at 43 tonnes/h. The spent caustic also adds somewhat to the same cost category.

Table 5.2: Running costs for the mixed plastics process.

Category	Cost [MSEK/yr]
Running cost excluding utilities, Aspen	31.51
Energy utilities	5.27
Nitrogen	2.23
Sodium hydroxide	5.85
Waste water treatment	12.40
Flue gas treatment	12.90
Total running costs	**70.16**

The distribution of capital investment costs in the mixed plastics process, between different types of equipment and other cost categories, is shown in Table 5.3. The costs regarding equipment refer to the total installation costs for those units.

Table 5.3: Capital investment costs for the mixed plastics process.

Category	Cost [MSEK]
Fuel feeding	147.7
Reactor & combustor	230.0
Flue gas train	139.1
Distillation columns	87.3
Compressors	37.1
Heat exchangers	16.6
Flash separators	11.9
Other units*	13.4
Administration, contingencies etc.	202.5
OSBL	354.2
Total capital investment	**1239.8**

* Including pumps, adsorbers, decanters, acetylene hydrogenation reactor, water quench, scrubber and gasoline stripper.

The main product flows of the PS process and their associated revenues are presented in Table 5.4. The revenue from styrene is by far the largest contributor to the total revenues.

Table 5.4: Output streams from the PS process and their generated revenue.

Product	Amount [kg/kg$_{feed}$]	Price [SEK/kg]	Revenue [MSEK/yr]
Toluene	0.0303	9.47	0.60
Styrene	0.784	10.4	17.12
Fuel oil	0.113	3.3	0.78
Total revenue			**18.50**

The running costs of the PS process are summarized in Table 5.5. The cost of PS waste is the largest category, roughly 46% of the running costs. Comparing the revenues and the running costs, there is a possibility of substantially increasing the economic performance by lowering the cost of PS waste.

Table 5.5: Running costs for the PS process.

Category	Cost [MSEK/yr]
Running costs excluding utilities, Aspen	12.05
PS waste	12.92
Energy utilities	1.33
Nitrogen	0.36
Flue gas treatment	1.54
Total running costs	**28.2**

The capital investment costs for the PS process, divided into different types of equipment and other categories, are given in Table 5.6.

Table 5.6: Capital investment costs for the PS process.

Category	Cost [MSEK]
Fuel feeding	25.0
Reactor & combustor	23.2
Flue gas train	28.8
Distillation columns	46.4
Compressor	7.0
Heat exchangers	1.6
Pumps	1.8
Flash separation	0.9
Administration, contingencies etc.	102.4
OSBL	94.8
Total capital investment	**331.8**

Products from the simpler PS process are summarized in Table 5.7. The major revenue is from styrene, though slightly lower than in the original PS process.

Table 5.7: Output streams from the simpler PS process and their generated revenue.

Product	Amount [kg/kg$_{feed}$]	Price [SEK/kg]	Revenue [MSEK/yr]
Styrene	0.781	10.4	17.05
Fuel oil	0.147	3.32	1.02
Total revenue			**18.07**

The running costs of the simpler PS process are given in Table 5.8. Again, a major cost is for the PS waste. Comparing the running costs for the original and the simpler PS processes, Table 5.5 and 5.8 respectively, it is seen that both the cost of utilities and running costs from Aspen are substantially lower in the simpler PS process.

Table 5.8: Running costs for the simpler PS process.

Category	Cost [MSEK/yr]
Running costs excluding utilities, Aspen	8.76
PS waste	12.92
Energy utilities	0.54
Nitrogen	0.36
Flue gas treatment	1.54
Total running costs	**24.12**

The capital investment cost for the PS process, divided into different types of equipment and other categories, is given in Table 5.9.

Table 5.9: Capital investment costs for the simpler PS process.

Category	Cost [MSEK]
Fuel feeding	25.0
Reactor & combustor	23.2
Flue gas train	28.8
Distillation columns	16.7
Compressor	7.0
Heat exchangers	1.8
Pumps	1.3
Flash separation	0.9
Administration, contingencies etc.	34.0
OSBL	55.4
Total capital investment	**194.1**

It can be pointed out that the reactor and combustor, together with fuel handling and flue gas cleaning, constitute a large portion of investment costs for the mixed plastics and PS processes. The method by which these costs are estimated is rough, and it may thus be a significant source of error in the total investment costs.

The product flows of the PVC process are presented in Table 5.10 with their revenues. The largest flow is assigned to HCl, however, the largest revenue comes from benzene. The running costs of the PVC process are presented in Table 5.11.

Table 5.10: Output streams from the PVC process and their generated revenue.

Product	Amount [kg/kg$_{feed}$]	Price [SEK/kg]	Revenue [MSEK/yr]
HCl	0.5847	0.47	0.90
Benzene	0.0568	7.44	1.40
Fuel oil	0.2060	1.71	1.16
Total revenue			**3.46**

Table 5.11: Running costs for the PVC process.

Category	Cost [MSEK/yr]
Running costs excluding utilities, Aspen	15.04
Energy utilities	0.95
$CaCO_3$	0.02
Flue gas treatment	0.23
Total running costs	**16.24**

The distribution of capital investment costs in the PVC process, between different types of equipment and other cost categories, is shown in Table 5.12. The costs regarding equipment refer to the total installation costs for those units. For the PVC process, total reactor costs and total compressor costs constitute a major part of the total installed cost, roughly 40 % each.

Table 5.12: Capital investment costs for the PVC process.

Category	Cost [MSEK]
Fuel feeding	13.0
Reactor & combustor	28.6
Flue gas train	16.1
Distillation columns	11.6
Compressors	61.2
Heat exchangers	9.6
Other units*	9.9
Administration, contingencies etc.	179.4
OSBL	131.7
Total capital investment	**461.1**

* Including pumps, adsorbers and separation equipment.

5.2 Economic performance

Figure 5.1 shows the costs and revenues for each regional-scale plant.

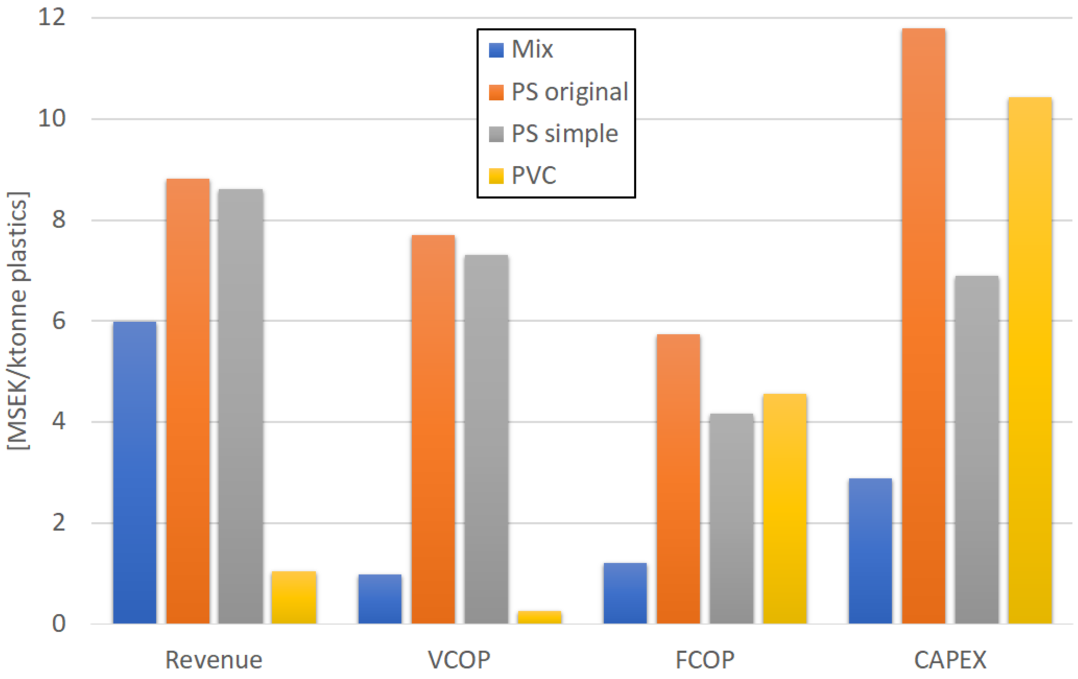

Figure 5.1: Summary of costs and revenues for the reference cases.

Comparing the results for mixed plastics and PS, the chart clearly illustrates a tradeoff: with the possibility of high monomer recovery, treating polymers separately can generate a higher revenue. On the other hand, the larger volumes in a process for mixed plastics decrease the specific investment cost and fixed production costs despite a more complicated process layout. Plastic waste sorted by polymer is typically also more expensive. Due to the low value of the products from the PVC plant, its revenue is by far the lowest.

The FCOP, unlike the revenues and VCOP, do not depend linearly on the plant scale. Therefore, with sufficiently large scale, the PS and PVC plants could still reach a positive cash flow. Nonetheless, the margins between revenues and VCOP for these plants are small, and much larger plants would be required to achieve an acceptable return on investment, if at all possible.

The decreased specific investment cost for the mixed plastics process is also evident in Figure 5.2 where the reference NPV of each plant is scaled by their fixed investment cost.

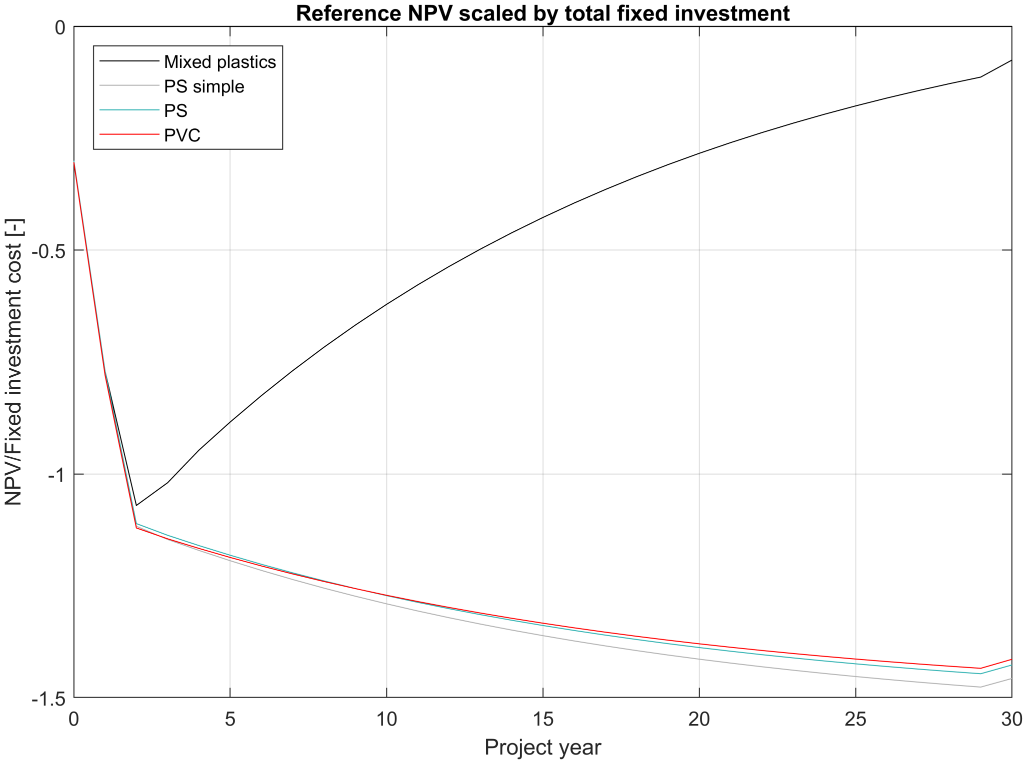

Figure 5.2: The reference economic performance of each plant scaled by their individual fixed investment cost.

5.3 Sensitivity analysis

Figure 5.3 shows the results of the sensitivity analysis for the mixed plastics process, for the regional and the national scale plants.

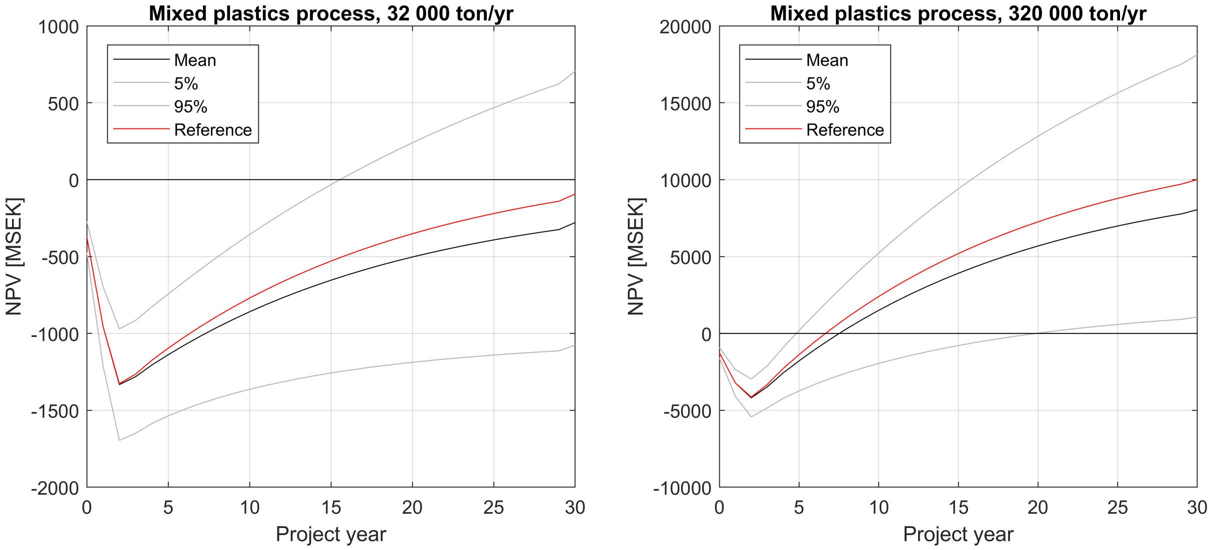

Figure 5.3: NPV curves of the Monte Carlo analysis for regional (left) and national (right) scale mixed plastics plant.

Comparing the two, a clear improvement is seen when scaling up. The annual profit is higher in relation to the investment cost, resulting in a PBP of seven years in the reference case. Within the whole 90 % confidence interval, profit is reached over the project lifetime. Although transportation costs are not accounted for and would have some impact on the results, a drastic change is assumed to be unlikely. However, an expected PBP of seven years may still be too long to raise interest from investors.

As can be seen in the figure, the mean curve in the sensitivity analysis deviates from the reference curve. The same applies for the other processes, as shown further down. The reason for this is that some values used in the reference cases are not at the center of the ranges used in the sensitivity analysis, i.e. the mean values for these parameters are not the same as the reference values. In the case of the mixed plastics process, the reference prices for the feed plastics and the fuel oil and gasoline are off-center, resulting in a lower mean curve in the sensitivity analysis.

The results of the Monte Carlo analysis for the PS process are presented in Figure 5.4. The left and the right figure shows the regional and national scale, respectively. It can be seen in both cases that the mean and reference curve differ significantly, mainly because the PS waste price, styrene price and fuel oil prices are not varied over a symmetrical interval. As the styrene price is varied according to the interval in Table 4.12 with the reference value being the lowest, it has the largest impact and explains why the mean curve is above the reference curve. The investment cost for the base scale PS process is high per ton processed waste, as evident from Figure 5.1. The left graph in Figure 5.4 shows a situation where the process will never be profitable over a life time of 30 years. The mean curve shows a down-going trend meaning the costs exceed the revenues with a resulting negative gross profit. The high investment cost per ton plastic waste and the negative gross profit over the majority of the project life time indicates that the plant is too small and needs to be scaled up.

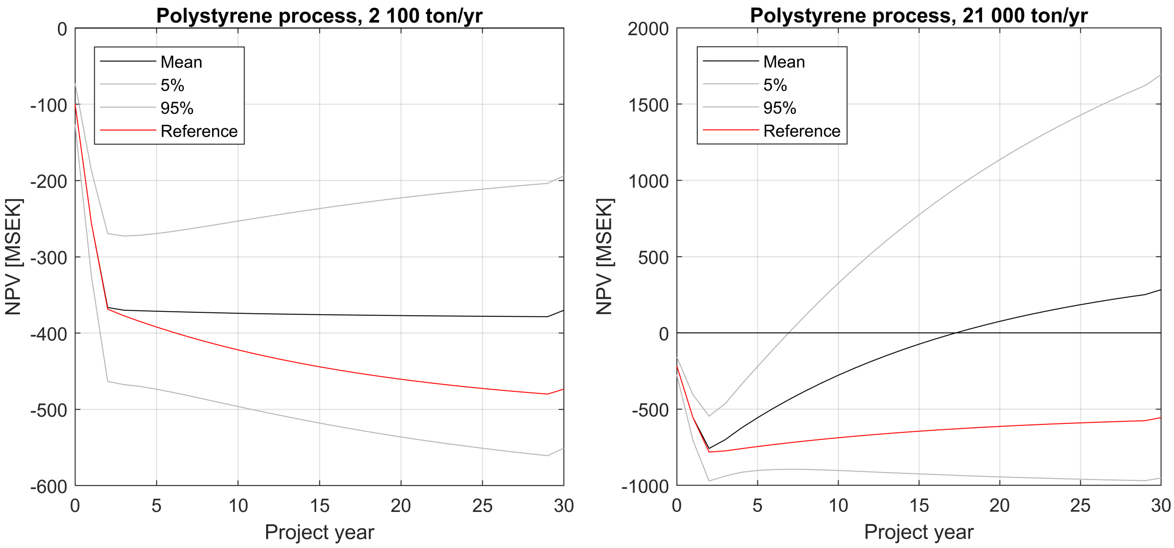

Figure 5.4: NPV curves of the Monte Carlo analysis for regional (left) and national (right) scale PS plant.

The result of the Monte Carlo analysis for the scaled-up PS process is seen to the right in Figure 5.4. Now the situation is different with a mean curve crossing the point of break-even after 17.5 years. The grey lines representing lower and upper limits show that the uncertainty is high. In a best-case scenario the PBP is 7 years and the worst-case represents a situation where the plant will never be profitable over the expected life time. However, the mean PBP of 17.5 years for the national scale PS process is to long to be considered profitable.

The results from the Monte Carlo analysis for the simpler PS process are presented in Figure 5.5. Again, some of the varied parameters in the PS processes are not changed symmetrically and this explains the difference in the mean and reference curve. The styrene price is most significant and causes the mean curve to be above the reference curve. The investment cost per ton plastic waste is considerably lower than for the original PS process, seen in Figure 5.1. In contrast to the original PS process, the simpler one has a positive mean gross profit, indicated by the mean curve to the left in Figure 5.5. For the simpler scaled-up process, the Monte Carlo results are seen to the right in Figure 5.5. The performance is better than the small scale version but the PBP is still too long, 15 years indicated by the mean curve. Also for the simpler PS process the lower and upper limits show a high uncertainty where the best-case scenario has a PBP of 6.5 years and the worst-case scenario never crosses break-even. The results show that even the simpler process cannot be considered profitable.

The original PS process showed a down-going trend for the mean curve in the base case, seen to the left in Figure 5.4. On the other hand, the graph to the left in Figure 5.5 shows that the simpler PS process has a positive mean gross profit. The main reason is the lower FCOP and the lower cost of utilities for the simpler process. FCOP for the original process are roughly 38 % higher than for the simpler PS process, meanwhile the VCOP are 32% higher. These differences are evened out for the national scale processes. However, the investment costs are substantially different, with the original process having a higher investment, though compensated by a slightly higher annual revenue. This, in the end, explains the relatively small difference between the mean PBP for the two processes. Nevertheless, the results show that the increased complexity of the original PS process, the associated increased investment and slightly higher running costs are not compensated by the extra revenue from the process.

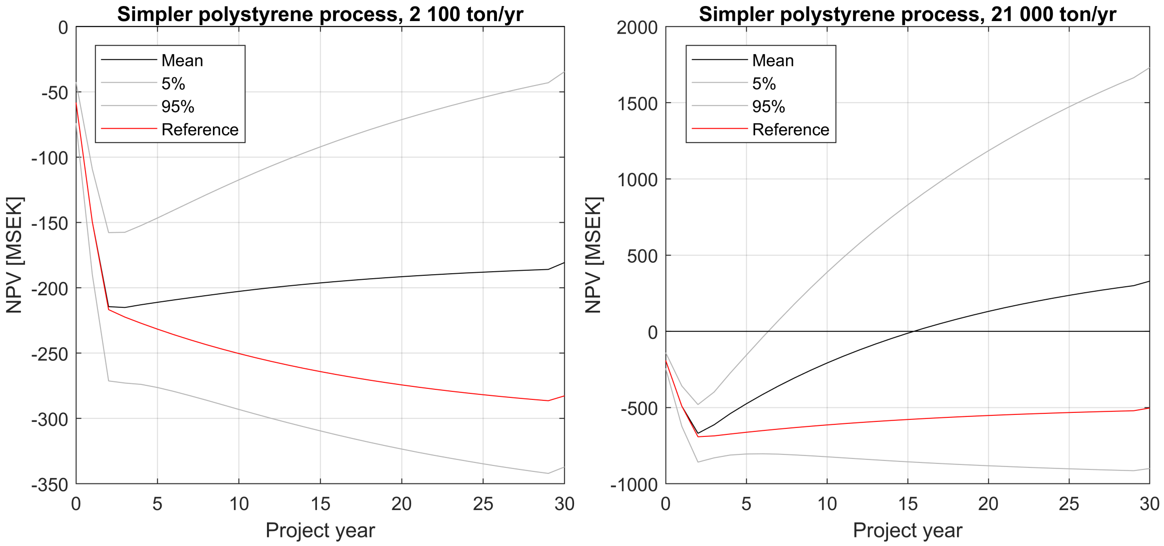

Figure 5.5: NPV curves of the Monte Carlo analysis for regional (left) and national (right) scale of the simpler PS plant.

The performance of the PVC process over the project life time is presented in Figure 5.6, with the difference between reference and mean curve caused mainly by the PVC waste price which is not varied symmetrically. The trend is clear with the plants being nowhere near profitable over the project life time of 30 years. The scaled-up process has a mean curve which shows a positive trend but it is not enough to make it profitable over the expected life time of 30 years. The main issue is the low value of the products shown in Table 5.10 combined with the high complexity of the process and the associated high investment cost due to vacuum operation of the reactors. The subsequent compressors used to pressurize the streams for further refining constitutes 41% of the total installed cost in the regional scaled process.

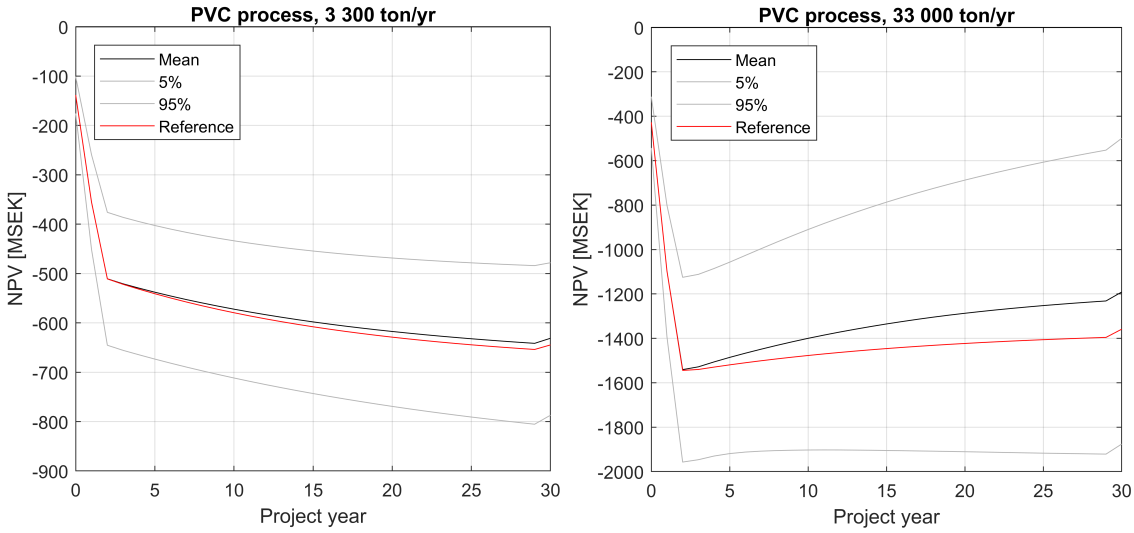

Figure 5.6: NPV curves of the Monte Carlo analysis for regional (left) and national (right) scale of the PVC plant.

To summarize, both for regional and national scale plants, the mixed plastics process shows the most promising economic results. The national scale mixed plastics plant is the only one that is close to being of interest from an investor's point of view in the present price situation. However, it may be seen as a drawback of the process that only 31 % of the plastic is converted into monomer for new plastics – the remainder is converted into compounds that are combusted in the plant or sold as fuels. Furthermore, the mixed plastics process modeled in this study provides no solution for treating PVC. It is assumed that if PVC is present in the waste, it is removed before feeding the waste to the reactor. By implementing measures for dealing with chlorine, PVC could be treated in the same process, but this would add to the costs.

5.4 Comparison with previous studies

The results can be compared to those found by Fivga and Dimitriou, who conducted a techno-economic assessment of the pyrolysis of household plastic waste, assumed to consist of polyethylene, polypropene and polystyrene, for the production of a heavy fuel substitute [11]. Their study, published in 2018, was set in the UK and evaluated the process for four different capacities, with plastic feed rates of 100, 1 000, 10 000 and 100 000 kg/h. The fuel production rate was 0.858 kg per kg of plastics. While the smallest plant never achieved a positive NPV, the others recovered the investment after 3.62, 1.23 and <1 year of operation, respectively. For the 10 000 kg/h plant, the NPV at year 20 (the assumed plant lifetime) was roughly 220 M£, compared to a total investment cost of 9.35 M£. Comparing with the 4 000 kg/h regional mixed plastics process examined in this study, the results are on a completely different magnitude. The comparison suggests that the production of a heavy fuel substitute is a far more viable option, assuming that it is seen as an acceptable path of material recovery. One could argue that if the product is used as a fuel, it should be regarded as energy recovery, which according to the waste management hierarchy is less preferable than material recycling. With raised recycling goals, policy will be aimed at making recycling the more viable option. On the other hand, the heavy fuel product could be used as a raw material for petroleum-based materials such as plastics.

The results from the PS processes in this study can be compared with the results found by Bassil et al (2018) in their techno-economic evaluation of a PS process. Here, the PS processes are based on the study by Bassil et al (2018) but with slight modifications. The original PS process has the same separation equipment but different operating conditions, such as the number of distillation column equilibrium stages and inlet pressures, the main reason being differences in the assumed pyrolysis product distribution. In the simpler PS process, the same type of separation equipment is also used but it operates substantially different since only styrene and fuel oil are taken out as products. Another distinction is that the two PS processes here operates with fluidized bed reactors, while the process in Bassil et al (2018) uses a rotary kiln reactor. Also, the rotary kiln reactor operates with a PS inflow of 3780 kg/h compared to the national scale PS processes in this study operating at 2625 kg/h. In the study by Bassil et al (2018), the reference case PBP is 12 years and can be compared with the mean PBP here of 15 and 17.5 years for the simpler and the original PS processes, respectively. Considering the distinctions in operation, the revenues and costs differ between these processes, but the main factor being the used styrene prices and the reactor investment cost. Styrene reference price in the study by Bassil et al (2018) was 18.6 SEK/kg and here 10.4 SEK/kg, the latter taken from a more recent source [82]. In the study, the rotary kiln reactor cost was found to be 68 MSEK for the design size of 3780 kg/h but it was pointed out that this cost was difficult to estimate [40]. This can be compared with the total reactor cost of 353 MSEK in this study for the national scale processes handling 2625 kg/h. This is an appreciable difference. However, the reactor cost estimates in this study are based on a fluidized bed gasifier for methane production [68], and the accuracy of this method might be a bit off. Still, the major differences between the studies are highlighted and this explain the distinctions in the PBP.

5.5 Feasibility of a flexible process

As previously mentioned, an important tradeoff between the examined plants is the higher product value in a process recovering a large amount of monomer from a single polymer, versus the economies of scale in a plant treating all or nearly all plastic waste. To reap the benefits of both, a flexible plant able to shift between different types of feedstock would be required. By treating, for example, the annual amount of polystyrene waste in a few weeks or months and treating other plastics for the rest of the year, high flow rates in the plant could be maintained. However, to avoid excessive investment costs, it is important that most of the equipment can be utilized in all operation modes.

As the pyrolysis reactor stands for a significant part of the investment costs in all the examined processes, a reasonable prerequisite for a flexible plant is the utilization of the same reactor regardless of the feed. This, along with the low product value from the PVC process, implies that the PVC process examined here is not feasible for combination with the others. The remaining option is then a plant which cycles between PS and mixed plastics. Given the available waste flows, such a plant would be treating mixed plastics for most of the year, and PS for a small portion of it – 6.6 % of the operation time if ratios from Table 3.2 apply. The equipment required for treating mixed plastics would thus have a high degree of utilization either way. The question is then if the extra equipment required for treating PS would pay off.

Comparing the process flowsheets of the mixed plastics process and the PS process (Figures 4.1 – 4.4), it is seen that much of the same types of equipment is present in both processes. They both share the same reactor type and a number of heat exchangers and distillation columns. Distinctive to the PS process is a 150-stage distillation column, a packed distillation column, and a vacuum system. These are the units that, in a flexible plant, may have a low degree of utilization if they cannot replace units in the mixed plastics process. This, along with the added downtime and costs to readjust the process when changing feedstocks, is what speaks against the feasibility of a flexible plant. It is also uncertain how adaptable the remaining process equipment is. A more detailed study would be required to reach an estimate on the economics of the situation, but given the relatively small difference between the revenues in Figure 5.1, there is not much economic leeway.

6

Conclusion

In this study, different processes for treating plastic wastes by pyrolysis and obtaining valuable products are modeled, with the aim of investigating the economic feasibility of pyrolysis-based recycling on a regional level. Separate processes for treating polystyrene and PVC are compared to a process for treating a mixture of different plastics. The economics of regional-scale plants are also compared to national-scale plants.

The results indicate that economies of scale have a major influence on the profitability of the examined plants, favoring the mixed plastics process over the others. Upscaling the plants to match national waste flows results in a substantial improvement in profitability. Transportation costs are not included in the evaluation, but assuming these costs are small compared to the total revenues, the conclusion that national-scale plants are more profitable is still valid.

The main conclusion of the study is that, out of the modeled plants, in the present system, the national-scale mixed plastics plant is the preferred option from a profitability point of view. However, with a payback period of seven years, it is highly debatable whether such a plant can be regarded as economically feasible.

The outlook for pyrolysis-based recycling strategies is largely dependent on the price development for plastic waste, and on the volumes of waste that are made available. Improved separation of the plastics that currently end up in municipal solid waste has the potential to dramatically increase the amount of plastics available for recycling, allowing for larger, more economical recycling plants. Policy makers have an important role in creating incentives to reduce the amount of plastics that is incinerated, and steering consumer behavior towards improved recycling.

6.1 Future work

The processes examined in this study are only four out of a seemingly endless number of possible pyrolysis-based recycling processes. Techno-economic studies of other processes have been made, but many more remain. An interesting concept is the two-step approach investigated by Artetxe et al., where low-temperature pyrolysis is used to yield waxes and oils, followed by cracking into light olefins at higher temperatures in a second reactor [88]. Simple, regional pyrolysis plants could then be used to turn the plastics into liquid, for transportation to a larger, centralized cracker.

In the main conclusion, the national-scale mixed plastics plant is the recommended option from an economic point of view, though taking into account the PBP of seven years. However, the process feedstock is simplified to neglect the presence of chlorine in the products. Considering the concluded low economic feasibility of individually handling PVC and the problems with other recycling methods, a pyrolysis-process neglecting the PVC would leave a gap in the current plastic waste management system. A process handling PVC mixed with other polymers has been investigated before [21], and it could be of interest to see the techno-economic feasibility of a similar process in the current system.

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A

Mixed plastics process data

A.1 Pyrolysis gas composition

Table A.1 shows the composition of pyrolysis products from mixed plastics as presented by Kaminsky et al. and the composition used in the Aspen model [43].

Table A.1: Composition of the mixed plastics pyrolysis product [43].

Component	Reported [wt.%]	Model component	Model flow [wt.%]
Gases	**51**		
Hydrogen	0.6	”	0.62
Carbon monoxide	0.7	”	0.72
Carbon dioxide	2.8	”	2.89
Methane	6.4	”	6.61
Ethylene	19	”	19.63
Acetylene	0.2	”	0.21
Ethane	2.0	”	2.07
Propylene	11	”	11.36
Propane	0.09	”	0.09
n/i-Butene	2.7	1-Butene	3.20
cis/trans-Butene	0.4		
Butadiene	4.7	1,3-Butadiene	4.86
Aliphatics	**2.6**		
C5-hydrocarbons	2.6	Cyclopentadiene	1.34
		2-Methyl-1-Butene	1.34
C6-hydrocarbons	0.4	2-Methyl-1-Pentene	0.41
BTX-aromatics	**10**		
Benzene	5.5	”	5.68
Toluene	4.0	”	4.13
Xylene	0.7	p-Xylene	0.72
Other aromatics	**28**		
Styrene	19	”	19.63
Indene	1.0	”	1.03
Naphthalene	2.2	”	2.27
		Ethylbenzene	3.02
		1-Methylnaphthalene	2.10
		Biphenyl	0.88
Distillation residue	**5.0**		
		Fluorene	0.65
		Anthracene	2.58
		1-Phenylnaphthalene	1.29
		Fluoranthene	0.65
Solids	**1.3**	**”**	**0**

A.2 Revenues and costs

The mixed plastics process produces a number of output streams, of which some are combusted to supply heat for pyrolysis and for preheating fluidization steam. A summary of the products and their generated revenue is shown in Table A.2.

Table A.2: Output streams from the mixed plastics process and their generated revenue.

Product	Amount [kg/h]	Price [SEK/kg]	Revenue [MSEK/yr]
Ethylene	786.5	9.95	62.61
Propylene	441.7	8.56	30.24
Hydrogen (excl. impurities)	23.8	11.70	2.23
Methane	273.0	4.00	8.74
Ethane	86.6	Combusted	
C_3 - C_4 fraction	7.09	Combusted	
C_4 - C_6 fraction	550.9	Combusted	
Gasoline	1308.3	6.59	68.97
Fuel oil	382.1	7.18	21.93
Total revenue			**192.49**

Table A.3 summarizes the running costs for the mixed plastics process.

Table A.3: Running costs for the mixed plastics process.

Category	Cost [MSEK/yr]
Running cost excluding utilities, Aspen	31.51
Energy utilities	5.27
Nitrogen	2.23
Sodium hydroxide	5.85
Waste water treatment	12.40
Flue gas treatment	12.90
Total running costs	**70.16**

Table A.4 summarizes the investment costs for the mixed plastics process.

Table A.4: Investment costs for the mixed plastics process.

Category	Cost [MSEK]
Investment cost, Aspen	368.81
DFB and flue gas train	377.68
Total ISBL investment cost	**885.56**
Total ISBL & OSBL investment cost	**1239.79**

A.3 Aspen data

Tables A.5 – A.18 show the model summary.

Table A.5: Heater blocks in the mixed plastics process.

Name	C1-HX	C2-HX	C2F-HX	C3-HX	C4-HX	CRY-HX1	CRY-HX2	CRY-HX3
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3	3	3	3	3
Specified pressure [bar]	-0,05	-0,05	-0,1	-0,05	-0,05	-0,1	-0,1	-0,1
Specified temperature [C]	45	45	10	45	35	-35	-95	-125
Calculated pressure [bar]	3,85	8,55	23,3	18,35	36,95	36,85	36,75	36,65
Calculated temperature [C]	45	45	10	45	35	-35	-95	-125
Calculated vapor fraction	0,99529788	0,965591198	1	0,969816134	0,921510048	0,425082927	0,598338953	0,820185355
Calculated heat duty [cal/sec]	-16418,8334	-22732,0616	-5423,05479	-19984,8136	-23902,4788	-47365,6405	-13332,7404	-3119,00235
Net duty [cal/sec]	-16418,8334	-22732,0616	-5423,05479	-19984,8136	-23902,4788	-47365,6405	-13332,7404	-3119,00235
First liquid / total liquid	1	0,708873287		0,866685897	0,973913994	1	1	1
Total feed stream CO2e flow [kg/hr]	6725,38553	6725,03253	3,13047475	6720,69412	6593,25854	6605,43605	4636,01105	2811,78963
Total product stream CO2e flow [kg/hr]	6725,38553	6725,03253	3,13047475	6720,69412	6593,25854	6605,43605	4636,01105	2811,78963

Name	ETAN-HX	ETOP-HX	G-HX	HSEP-HX	MET-HX1	MET-HX2	MTOP-HX	PPAN-HX
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3	3	3	3	3
Specified pressure [bar]	-0,1	-0,1	-0,1	-0,1	-0,1	-0,1	-0,1	-0,1
Specified temperature [C]	15	25	45	-160	-110	5	-110	15
Calculated pressure [bar]	1	23,4	1,22	35,8	35,7	35,6	35,9	1
Calculated temperature [C]	15	25	45	-160	-110	5	-110	15
Calculated vapor fraction	1	1	0	0,718074541	0,0418453001	1	0,0995395427	1
Calculated heat duty [cal/sec]	2302,52733	5167,85989	-24981,9913	-3598,88479	1116,92099	10639,4498	-3948,69677	128,097401
Net duty [cal/sec]	2302,52733	5167,85989	-24981,9913	-3598,88479	1116,92099	10639,4498	-3948,69677	128,097401
First liquid / total liquid			1	1	1		1	
Total feed stream CO2e flow [kg/hr]	0	3,13047475	8,21893155	2092,89765	1826,42991	6335,83784	4837,35451	0
Total product stream CO2e flow [kg/hr]	0	3,13047475	8,21893155	2092,89765	1826,42991	6335,83784	4837,35451	0

Table A.6: HeatX blocks in the mixed plastics process.

Name	BOT-HX	DS-GEN	TLE
Hot side property method	PENG-ROB	PENG-ROB	PENG-ROB
Hot side use true species approach for electrolytes	YES	YES	YES
Hot side free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA
Hot side water solubility method	3	3	3
Cold side property method	PENG-ROB	PENG-ROB	PENG-ROB
Cold side use true species approach for electrolytes	YES	YES	YES
Cold side free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA
Cold side water solubility method	3	3	3
Exchanger specification	45	0	360
Units of exchanger specification	C		C
Minimum temperature approach [C]	10	10	1
Hot side outlet pressure [bar]	-0,1	-0,1	-0,1
Cold side outlet pressure [bar]	-0,1	-0,1	-0,1
Inlet hot stream temperature [C]	186,343974	249,810236	699,999609
Inlet hot stream pressure [bar]	1,44	39,9	1,6
Inlet hot stream vapor fraction	0	1	1
Outlet hot stream temperature [C]	45	249,647247	360
Outlet hot stream pressure [bar]	1,34	39,8	1,5
Outlet hot stream vapor fraction	0	0	1
Inlet cold stream temperature [C]	20,0094816	118,517854	249,941035
Inlet cold stream pressure [bar]	1,9	1,8	40
Inlet cold stream vapor fraction	0	0,0373131794	0
Outlet cold stream temperature [C]	118,517854	116,787255	249,810236
Outlet cold stream pressure [bar]	1,8	1,7	39,9
Outlet cold stream vapor fraction	0,0373131794	0,846287064	1
Heat duty [cal/sec]	122725,927	424700,406	424297,048
Calculated heat duty [cal/sec]	122725,927	424700,406	424297,048
Required exchanger area [sqm]	16,1706433	15,839041	8,65548824
Actual exchanger area [sqm]	16,1706433	15,839041	8,65548824
Average U (Dirty) [cal/sec-sqcm-K]	0,0203019012	0,0203019012	0,0203019012
Average U (Clean)			
UA [cal/sec-K]	3282,94802	3215,62645	1757,22867
LMTD (Corrected) [C]	37,3828419	132,073925	241,458072
LMTD correction factor	1	1	1
Number of shells in series	1	1	1
Total feed stream CO2e flow [kg/hr]	2,49429716	0	6727,96774
Total product stream CO2e flow [kg/hr]	2,49429716	0	6727,96774

Table A.7: Flash2 blocks in the mixed plastics process.

Name	C1-FL	C2-FL	C3-FL	C4-FL	CRY-FL1	CRY-FL2	CRY-FL3	HSEP1	HSEP2
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES	YES	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3	3	3	3	3	3
Temperature [C]	45	45							
Pressure [bar]	0	0	0	0	0	0	0	0	0
Specified heat duty [cal/sec]	0	0	0	0	0	0	0	0	0
Outlet temperature [C]	44,9999084	45,0000061	45,0291134	35,0000101	-34,9998763	-94,9999985	-124,999997	-110,000252	-159,999935
Outlet pressure [bar]	3,85	8,55	18,35	36,95	36,85	36,75	36,65	35,9	35,8
Vapor fraction	0,995298027	0,965591183	0,967048139	0,921510255	0,425084023	0,598338966	0,820185518	0,0995368787	0,718074023
Heat duty [cal/sec]	0	0	0	0	0	0	0	0	0
Net duty [cal/sec]	0	0	0	0	0	0	0	0	0
First liquid / total liquid	1	0,708873293	0,870545071	0,973914957	1	1	1	1	1
Total feed stream CO2e flow [kg/hr]	6725,38553	6725,03253	6605,43752	6593,25854	6605,43605	4636,01105	2811,78963	4837,35451	2092,89765
Total product stream CO2e flow [kg/hr]	6725,38553	6725,03253	6605,43752	6593,25854	6605,43605	4636,01105	2811,78963	4837,35451	2092,89765

Table A.8: Decanter blocks in the mixed plastics process.

Name	C2-DEC	C3-DEC	C4-DEC	WQ-DEC
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3
Pressure [bar]	0	0	0	0
Specified heat duty [cal/sec]	0	0	0	0
Outlet temperature [C]	45,0000061	45,0291134	35,0000101	82,0057469
Outlet pressure [bar]	8,55	18,35	36,95	1,32
Calculated heat duty [cal/sec]	-0,805869649	-0,331234366	-0,17239483	-525,986049
Net duty [cal/sec]	0	0	0	0
First liquid / total liquid	0,708966015	0,870594578	0,973926569	0,0254242304
First liquid / total liquid	0,708966015	0,870594578	0,973926569	0,0254242304
Total feed stream CO2e flow [kg/hr]	4,33840828	12,1789803	96,4595987	8,83923858
Total product stream CO2e flow [kg/hr]	4,33840845	12,1789804	96,4595977	8,83924553

Table A.9: Separator blocks in the mixed plastics process.

Name	ADSDRY-1	ADSDRY-2	SCRUBBER
Property method	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3
Inlet flash pressure [bar]	0	0	0
Heat duty [cal/sec]	-424,633175	-270,925131	-231,393229
Total feed stream CO2e flow [kg/hr]	6496,79895	108,637103	6720,69412
Total product stream CO2e flow [kg/hr]	6496,79895	108,637103	6720,69412

Table A.10: Pump blocks in the mixed plastics process.

Name	FW-PUMP	HC3-PMP	HP-PUMP	WAT-PUMP
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3
Specified discharge pressure [bar]	1,9	36,95	40	1,35
Pump efficiencies	0,7	0,7	0,7	0,7
Fluid power [kW]	0,0866067683	0,104656138	0,0272103738	0,383875789
Calculated brake power [kW]	0,123723955	0,149508768	0,0388719625	0,548393984
Electricity [kW]	0,123723955	0,149508768	0,0388719625	0,548393984
Volumetric flow rate [l/min]	57,7378456	3,37600444	81,6311213	658,07278
Calculated discharge pressure [bar]	1,9	36,95	40	1,35
Calculated pressure change [bar]	0,9	18,6	0,2	0,35
NPSH available [m-kgf/kg]	10,0171164	0	0	10,0171164
Head developed [m-kgf/kg]	9,18877378	267,006702	2,77724963	3,57341203
Pump efficiency used	0,7	0,7	0,7	0,7
Net work required [kW]	0,123723955	0,149508768	0,0388719625	0,548393984

Table A.11: Compressor blocks in the mixed plastics process.

Name	COMP1	COMP2	COMP3	COMP4	PROPCOMP
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3	3
Model Type	ISENTROPIC	ISENTROPIC	ISENTROPIC	ISENTROPIC	ISENTROPIC
Specified discharge pressure [bar]	3,9	8,6	18,4	37	15,5
Isentropic efficiency	0,85	0,85	0,85	0,85	0,85
Indicated horsepower [kW]	84,6784108	62,9555777	56,531452	46,1376276	4,68441494
Calculated brake horsepower [kW]	84,6784108	62,9555777	56,531452	46,1376276	4,68441494
Net work required [kW]	84,6784108	62,9555777	56,531452	46,1376276	4,68441494
Power loss [kW]	0	0	0	0	0
Efficiency (polytropic / isentropic) used	0,85	0,85	0,85	0,85	0,85
Calculated discharge pressure [bar]	3,9	8,6	18,4	37	15,5
Calculated pressure change [bar]	2,6	4,75	9,85	18,65	7,5
Calculated pressure ratio	3	2,23376623	2,15204678	2,01634877	1,9375
Outlet temperature [C]	95,7786216	97,560801	97,1256566	95,0055849	46,7173551
Isentropic outlet temperature [C]	86,2261662	90,5204182	90,624147	89,5559043	43,7764641
Vapor fraction	1	1	1	1	1
Head developed [m-kgf/kg]	10458,5754	7879,71947	7588,34529	6991,31033	3256,78549
Isentropic power requirement [kW]	71,9766492	53,512241	48,0517342	39,2169835	3,9817527
Inlet heat capacity ratio	1,21778094	1,21939373	1,24426915	1,29444521	1,25870275
Inlet volumetric flow rate [l/min]	27590,8329	9736,06499	4142,61167	1731,50613	447,39006
Outlet volumetric flow rate [l/min]	11280,024	5038,86989	2211,24603	976,308929	237,928851
Inlet compressibility factor	0,99163303	0,979602803	0,958640638	0,917855481	0,852032193
Outlet compressibility factor	0,986790078	0,971931602	0,946184402	0,901869016	0,781928135
Total feed stream CO2e flow [kg/hr]	6725,38553	6725,03253	6720,69412	6593,25854	0
Total product stream CO2e flow [kg/hr]	6725,38553	6725,03253	6720,69412	6593,25854	0

Table A.12: Valve blocks in the mixed plastics process.

Name	EBOT-VLV	ETAN-VLV	HC1-VLV	HC2-VLV	PBOT-VLV	PPAN-VLV
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3	3	3
Specified outlet pressure [bar]	9	1,1	1,25	1,25	1,1	1,1
Calculation type	ADIAB-FLASH	ADIAB-FLASH	ADIAB-FLASH	ADIAB-FLASH	ADIAB-FLASH	ADIAB-FLASH
Valve pressure specification (design mode)	P-OUT	P-OUT	P-OUT	P-OUT	P-OUT	P-OUT
Valve pressure specification (rating mode)	VAL-POSN	VAL-POSN	VAL-POSN	VAL-POSN	VAL-POSN	VAL-POSN
Calculated outlet pressure [bar]	9	1,1	1,25	1,25	1,1	1,1
Calculated pressure drop [bar]	14,99	21,59	2,6	7,3	7,39	13,69
Piping geometry factor	1	1	1	1	1	1

Table A.13: RadFrac blocks in the mixed plastics process.

Name	C2SPLIT	C3SPLIT	DEETH	DEMETH	DEPROP	G-STRIP	PRIFRAC	SCRUBCOL	W-QUENCH
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES	YES	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3	3	3	3	3	3
Number of stages	50	60	50	47	50	5	10	4	3
Condenser	PARTIAL-V	PARTIAL-V	PARTIAL-V	PARTIAL-V	PARTIAL-V	NONE	NONE	NONE	NONE
Reboiler	KETTLE	KETTLE	KETTLE	KETTLE	KETTLE	NONE	NONE	NONE	NONE
Number of phases	2	2	2	2	2	2	2	2	3
Free-water	NO	NO	NO	NO	NO	NO	NO	NO	DIRTY
Top stage pressure [bar]	22,2	14,2	23,5	36	8	1,1	1,35	18,3	1,3
Specified reflux ratio	6	10	0,81	0,7	1,1				
Calculated molar reflux ratio	4,95574809	7,40253239	0,81	0,7	1,1	8,43215136	0,141050145	5,26033673	15,2076809
Calculated bottoms rate [kmol/hr]	2,85779327	0,145776193	19,4882748	50,3833371	8,84767676	14,2934199	48,612706	438,956912	2439,61402
Calculated boilup rate [kmol/hr]	120,929165	69,080379	38,9297037	45,2765112	12,0314582	1,23168941	328,066953	83,3609557	163,30855
Calculated distillate rate [kmol/hr]	28,0372691	10,4948218	30,8950623	13,1597794	10,640598	1,74839965	337,803558	83,3662699	87,2030152
Condenser / top stage temperature [C]	-25,0844989	33,5657095	-20,5225078	-94,6045077	11,7406971	42,8458276	102,991952	44,9844483	26,1796029
Condenser / top stage pressure [bar]	22,2	14,2	23,5	36	8	1,1	1,35	18,3	1,3
Condenser / top stage heat duty [cal/sec]	-80122,3715	-69283,9411	-14420,0557	-2356,82157	-11991,1326	0	0	0	0
Condenser / top stage reflux rate [kmol/hr]	138,945642	77,6882586	25,0250005	9,21184561	11,7046578	14,7427705	47,6472409	438,534652	1326,15563
Reboiler pressure [bar]	22,69	14,79	23,99	36,46	8,49	1,14	1,44	18,33	1,32
Reboiler temperature [C]	-2,03790723	57,6726833	85,4237355	24,3373982	81,1890742	38,0285389	186,343974	43,9992993	82,0057469
Reboiler heat duty [cal/sec]	74825,117	68551,6557	34768,8868	26439,2019	16186,5457	0	0	0	0
Total feed stream CO2e flow [kg/hr]	3,13047475	0	3,13047475	4840,48498	0	6,34854943	6736,89667	6720,69412	6734,40238
Total product stream CO2e flow [kg/hr]	3,13047475	0	3,13047475	4840,48498	0	6,34854943	6736,89667	6720,69412	6734,22477
Basis for specified distillate to feed ratio	MOLE	MOLE	MOLE	MOLE	MOLE	MOLE	MOLE	MOLE	MOLE
Specified distillate to feed ratio			0,6132	0,2071	0,546				
Basis for specified bottoms to feed ratio	MOLE	MOLE	MOLE	MOLE	MOLE	MOLE	MOLE	MOLE	MOLE
Specified bottoms to feed ratio	0,0925	0,0137							
Calculated molar boilup ratio	42,3155748	473,879703	1,9975962	0,898640578	1,35984378				
Calculated mass boilup ratio	42,0605088	449,937815	1,78113505	0,738281807	1,23360073	0,0293881365	1,6320209	0,292927625	0,112051672

Table A.14: RPlug blocks in the mixed plastics process.

Name	ACETRX
Process stream property method	PENG-ROB
Process stream use true species approach for electrolytes	YES
Process stream free-water phase properties method	STEAM-TA
Process stream water solubility method	3
Thermal fluid property method	PENG-ROB
Thermal fluid use true species approach for electrolytes	YES
Thermal fluid free-water phase properties method	STEAM-TA
Thermal fluid water solubility method	3
Reactor dimensions length [meter]	2,5
Reactor dimensions diameter [meter]	0,4
Pressure at reactor inlet: process stream [bar]	0
Heat duty [cal/sec]	0
Minimum reactor temperature [C]	24,6919536
Maximum reactor temperature [C]	60,4145415
Residence time [hr]	0,00392278914
Total feed stream CO2e flow [kg/hr]	3,13047475
Total product stream CO2e flow [kg/hr]	3,13047475

Table A.15: Mixer blocks in the mixed plastics process.

Name	ACETMIX	COMBMIX	DRYMIX	G-MIX	HC-MIX
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3	3
Specified pressure [bar]	0	0	0	1,2	0
Outlet temperature [C]	24,6919505	0,191306714	37,1169915	44,687884	38,7393603
Calculated outlet pressure [bar]	23,4	1	36,95	1,2	36,95
Vapor fraction	1	0,67375049	0,888655062	0,00453670269	0
First liquid /Total liquid	1	1	1	1	1
Total feed stream CO2e flow [kg/hr]	3,13047475	6,34851583	6605,43605	6,34854943	108,637103
Total product stream CO2e flow [kg/hr]	3,13047475	6,34851583	6605,43605	6,34854943	108,637103

Name	HSEP-MIX	MET-MIX	MIX1	O-QUENCH
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3
Specified pressure [bar]	0	0	0	0
Outlet temperature [C]	-124,374892	-109,979974	699,999609	225,000302
Calculated outlet pressure [bar]	35,9	35,7	1,6	1,5
Vapor fraction	0,999960132	0,0120802079	1	0,99693271
First liquid /Total liquid	1	1	1	1
Total feed stream CO2e flow [kg/hr]	2092,89765	6335,83784	6727,96774	6729,08087
Total product stream CO2e flow [kg/hr]	2092,89765	6335,83784	6727,96774	6729,08087

Table A.16: FSplit blocks in the mixed plastics process.

Name	GSPLIT	OILSPLIT	QW-SPLIT	RETSPLIT
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3
First outlet stream			0,6	0,47
First specified split fraction			0,6	0,47
First calculated split fraction	0,201764509	0,949537256	0,6	0,47
Second calculated split fraction	0,798235491	0,0504627435	0,4	0,53
Total feed stream CO2e flow [kg/hr]	8,21893155	2,49429716	0	2,3683684
Total product stream CO2e flow [kg/hr]	8,21893155	2,49429716	0	2,3683684

Table A.17: Design spec blocks in the mixed plastics process.

Name	GR-CTRL	HPCTRL	OQ-CTRL	QW-CTRL
Specification	TPTOP	S2ENTAL	TOQ	TWQBOT
Specification target	103	-3129.18169818962	225	82
Specification tolerance	0.1	0.001	0.1	0.1
Lower bound	1000	1	100	20000
Upper bound	10000	5000	20000	100000
Comment	Vary gasoline reflux mass flow to reach primary fractionator distillate temperature of 103 °C.	Vary HP feedwater mole flow so that it leaves the product gas cooler as saturated vapor.	Vary fuel oil reflux mass flow to reach oil quench temperature of 225 °C.	Vary quench water mass flow to reach water quench bottoms temperature of 82 °C.

Table A.18: Aspen data for utilities in the mixed plastics process.

Name	C-WATER2	ELEC2	H-WATER2	HP-STM2	LOW-T2	LP-STM2	MP-STM2
Utility type	WATER	ELECTRICITY	WATER	STEAM	GENERAL	STEAM	STEAM
Specified cooling value [cal/gm]					-0,3202923474		
Specified electricity price [$/kWhr]		0,0775					
Specified energy price [$/cal]	8,876016E-10	8,876016E-10	6,238332E-08	3,726252E-08	3,2405832E-08	4,731084E-08	1,1471832E-08
Specified inlet pressure [bar]	1,01325		1,01325				
Specified outlet pressure [bar]	1,01325		1,01325				
Specified inlet temperature [C]	20	20	250	-180	125	175	-25
Specified outlet temperature [C]	25	15	249	-179	124	174	-24
Specified inlet vapor fraction				1		1	1
Specified outlet vapor fraction				0		0	0
Specified CO2 emission factor [kg/cal]		2,34E-07		2,34E-07	2,34E-07	2,34E-07	2,34E-07
Specified CO2 energy source efficiency factor	1	0,58	1	0,85	1	0,85	0,85
Calculated heating/cooling value [cal/gm]	-4,98608987		4,990215	410,653413	-0,320292347	523,521299	485,99208
Calculated inlet enthalpy [cal/gm]	-3794,46615		-3794,46615	-3145,94169		-3166,7851	-3152,79571
Calculated outlet enthalpy [cal/gm]	-3789,48006		-3799,45636	-3556,59511		-3690,30639	-3638,78779
Calculated inlet pressure [bar]	1,01325		1,01325	39,7537159		2,32178779	8,92539509
Calculated outlet pressure [bar]	1,01325		1,01325	39,0866691		2,25120518	8,7169648
Calculated inlet temperature [C]	20		20	250	-180	125	175
Calculated outlet temperature [C]	25		15	249	-179	124	174
Calculated inlet vapor fraction	0		0	1		1	1
Calculated outlet vapor fraction	0		0	0		0	0
Calculated purchase price [$/cal]			8,876016E-10		3,726252E-08		
Calculated total cost [$/hr]	0	0	0,27309055	0	1,43086967	0	0
Calculated total usage rate [kg/hr]	0	0	61655,1472	0	119889,54	0	0
Calculated CO2 emission factor [kg/cal]		2,34E-07		2,34E-07	2,34E-07	2,34E-07	2,34E-07
Calculated CO2 emission rate [kg/hr]					8,98553028		

Name	REFR1-2	REFR1G-2	REFR2-2	REFR2G-2	REFR3-2	REFR3G-2	REFR4-2	REFR4G-2
Utility type	REFRIGERATIO	REFRIGERATIO	REFRIGERATIO	REFRIGERATIO	REFRIGERATIO	REFRIGERATIO	REFRIGERATIO	REFRIGERATIO
Specified cooling value [cal/gm]	-0,9553835865	0,9553835865	-0,3202923474	0,3202923474	-0,3202923474	0,3202923474	-0,3202923474	0,3202923474
Specified energy price [$/cal]	-1,1346228E-08	1,4067648E-08	-1,3942044E-08	2,4618384E-08	-2,4367176E-08	3,5713404E-08	-3,537846E-08	
Specified inlet temperature [C]	-24	-40	-39	-65	-64	-103	-102	
Specified outlet temperature [C]	-25	-39	-40	-64	-65	-102	-103	
Specified CO2 emission factor [kg/cal]	2,34E-07	2,34E-07	2,34E-07	2,34E-07	2,34E-07	2,34E-07	2,34E-07	2,34E-07
Specified CO2 energy source efficiency factor	1	-1	1	-1	1	-1	1	-1
Calculated heating/cooling value [cal/gm]	-0,955383587	0,955383587	-0,320292347	0,320292347	-0,320292347	0,320292347	-0,320292347	0,320292347
Calculated inlet temperature [C]	-25	-24	-40	-39	-65	-64	-103	-102
Calculated outlet temperature [C]	-24	-25	-39	-40	-64	-65	-102	-103
Calculated total cost [$/hr]	0	0	0	0	0	0	0	0
Calculated total usage rate [kg/hr]	0	0	0	0	0	0	0	0
Calculated CO2 emission factor [kg/cal]	2,34E-07	2,34E-07	2,34E-07	2,34E-07	2,34E-07	2,34E-07	2,34E-07	2,34E-07

Figures A.1 – A.2 show the full model flowsheet.

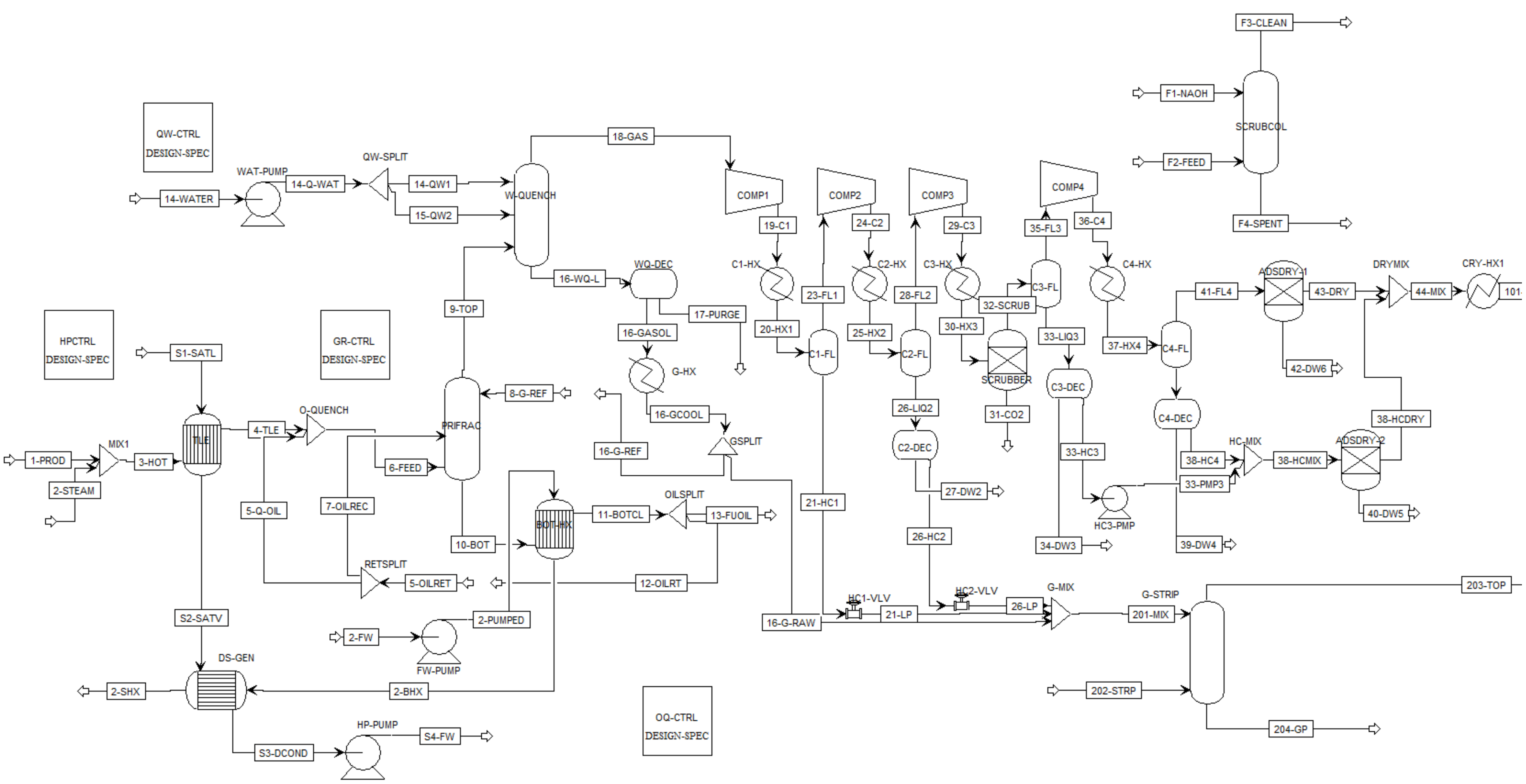


Figure A.1: Aspen flowsheet of the mixed plastics process, part 1.

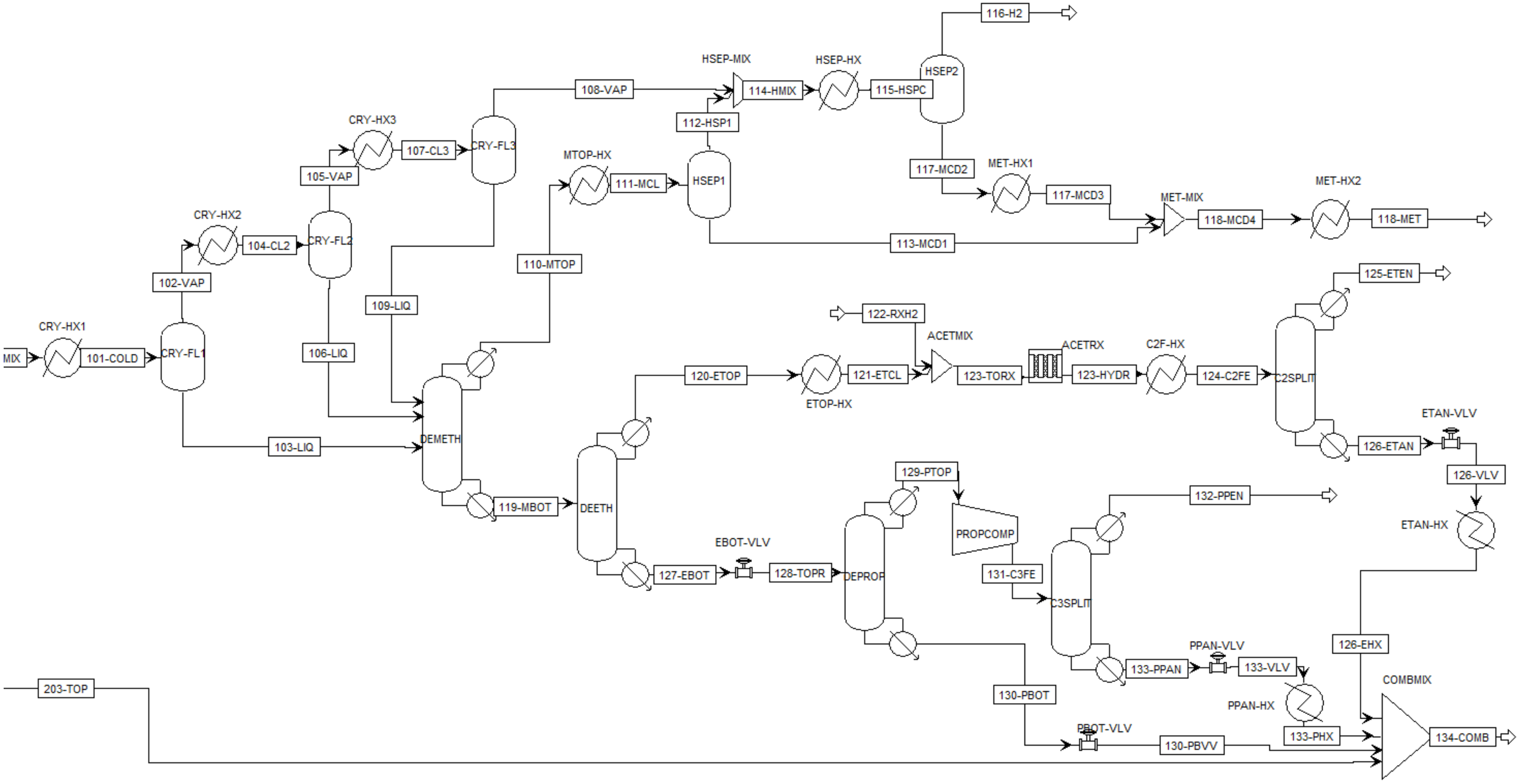


Figure A.2: Aspen flowsheet of the mixed plastics process, part 2.

B

Polystyrene process data

B.1 Gas composition

Table B.1 shows the composition of pyrolysis products from the polystyrene pyrolysis as presented by Liu et al. (2000) and the composition used in the Aspen model.

Table B.1: Product distribution from experiment by Liu et al run at 600°C in a fludized bed reactor. Also the distribution used in the Aspen model.

Group	Compound	[wt%]	Mass fraction used in Aspen [wt%]
G1	Benzene	0.35	0.497
	Toluene	2.32	3.295
	Ethylbenzene	0.57	0.8095
	Xylene	0.22	0.312
	Styrene (monomer)	78.7	78.7
	Alpha-methyl styrene	2.30	3.266
	Others	2.42	0
G2	1,2-diphenyl ethane	2.21	3.457
	1,3-diphenyl propane	0.5	0.782
	2,4-diphenyl-1-butene (dimer)	3.9	6.100
	2,4-diphenyl-1-pentene	1.1	1.721
	Others	4.35	0
G3	2,4,6-triphenyl-1-hexene (trimer)	0.11	0.22
	Others	0.11	0
	Cracking gas Ethylene	0.5	0.5
	Propylene	0.15	0.15
	Coke (<0.2 wt%)	0.191	0.191
	Total	100	100

B.2 Calculation of product input to Aspen

The groups G1-G3 are used to categorize the compounds according to their boiling points. Each group includes the category others. Since these compounds are unknown, they cannot be input in Aspen. Therefore the category others in each group were split between the compounds in the same group by a weighted average. In group G1 others are split up between the compounds excluding styrene. This is to make the yield of the main product as reasonable as possible and to not overestimate the pyrolysis yield. For G2 and G3 the compounds are just split between all components. By adding the mass fractions in group

G1 (excluding others and styrene) you get 5.76. Now take the old fraction of benzene, calculate the fraction of it in these 5.76 and to find the new benzene fraction, use Eq. B.1:

$$\text{New benzene fraction} = \text{Old benzene fraction} + \frac{\text{Old benzene fraction}}{(\sum G1) - \text{others} - \text{styrene}} \cdot others(G1) \tag{B.1}$$

and with numbers it turns out to be:

$$\text{New benzene fraction} = 0.35 + \left(\frac{0.35}{5.76}\right) \cdot 2.42 = 0.497 \tag{B.2}$$

If this is done for all compounds in the same manner and all categories others are assigned to 0, the result is the fourth column in Table B.1.

B.3 Revenues and costs, original PS process

The products from the PS process and their generated revenues are presented in Table B.2.

Table B.2: Annual production capacity and potential income from the PS process.

Product	Amount [t/yr]	Price [SEK/kg]	Revenue [MSEK/yr]
Toluene	63.67	9.47	0.60
Styrene	1646.6	10.4	17.12
Fuel oil	236.7	3.3	0.78
C_7-C_8 fraction	24.64	Combusted	
C_8-C_{24} fraction	95.52	Combusted	
C_2-C_9 fraction	20.88	Combusted	
C_2-C_9 fraction	43.97	Combusted	
Total revenue			18.50

The running costs for the PS process are given in Table B.3.

Table B.3: Running costs for the PS process.

Category	Cost [MSEK/yr]
Running costs excluding utilities, Aspen	12.05
PS waste	12.92
Energy utilities	1.33
Nitrogen	0.36
Flue gas treatment	1.54
Total running costs	28.2

Below is the investment cost from Aspen and for the reactor, see Table B.4.

Table B.4: Investment costs for the PS process.

Category	Cost [MSEK]
Investment cost, Aspen (MSEK)	160.03
DFB and flue gas train (MSEK)	76.99
Total ISBL investment cost (MSEK)	237.02
Total ISBL & OSBL investment cost (MSEK)	331.83

B.4 Revenues and costs, Simpler PS process

The products from the simpler PS process and their generated revenues are presented in Table B.5.

Table B.5: Annual production capacity and potential income from the simpler PS process.

Product	Amount [t/yr]	Price [SEK/kg]	Revenue [MSEK/yr]
Styrene	1640.05	10.4	17.05
Fuel oil	308.37	3.32	1.02
C_2-C_8 fraction	111.72	Combusted	
C_2-C_9 fraction	43.91	Combusted	
C_8-C_{24} fraction	27.94	Combusted	
Total revenue			18.07

The running costs for the PS process are given in Table 5.8.

Table B.6: Running costs for the simpler PS process.

Category	Cost [MSEK/yr]
Running costs excluding utilities, Aspen	8.76
PS waste	12.92
Energy utilities	0.54
Nitrogen	0.36
Flue gas treatment	1.54
Total running costs	24.12

Below is the investment cost from Aspen and for the reactor, see Table B.7.

Table B.7: Investment cost for the simpler PS process.

Category	Cost [MSEK]
Investment cost, Aspen (MSEK)	61.60
DFB and flue gas train (MSEK)	76.99
Total ISBL investment cost (MSEK)	138.59
Total ISBL & OSBL investment cost (MSEK)	194.03

B.5 Aspen data, original PS process

The extracted Aspen components data can be found in Table B.8-B.20.

Table B.8: Aspen data of heat exchangers (type Heater in Aspen) for the original PS process.

Name	COND	COOLER1
Property method	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA
Water solubility method	3	3
Specified pressure [bar]	-0,1	-0,1
Specified temperature [C]	33,5	
Specified vapor fraction	0,577	1
Calculated pressure [bar]	2,80264078	2,90264078
Calculated temperature [C]	33,5	194,497902
Calculated vapor fraction	0,768178326	1
Calculated heat duty [Watt]	-58058,117	-82980,8766
Net duty [Watt]	-58058,117	-82980,8766
First liquid / total liquid	1	

Table B.9: Aspen data of heat exchanger (type HeatX in Aspen) for the original PS process.

Name	N2HEATER
Hot side property method	PENG-ROB
Hot side use true species approach for electrolytes	YES
Hot side free-water phase properties method	STEAM-TA
Hot side water solubility method	3
Cold side property method	PENG-ROB
Cold side use true species approach for electrolytes	YES
Cold side free-water phase properties method	STEAM-TA
Cold side water solubility method	3
Exchanger specification	600
Units of exchanger specification	C
Minimum temperature approach [C]	1
Hot side outlet pressure [bar]	-0,1
Cold side outlet pressure [bar]	-0,1
Inlet hot stream temperature [C]	699,124275
Inlet hot stream pressure [bar]	3,10264078
Inlet hot stream vapor fraction	1
Outlet hot stream temperature [C]	532,746844
Outlet hot stream pressure [bar]	3,00264078
Outlet hot stream vapor fraction	1
Inlet cold stream temperature [C]	32,5094458
Inlet cold stream pressure [bar]	1,1
Inlet cold stream vapor fraction	1
Outlet cold stream temperature [C]	600
Outlet cold stream pressure [bar]	1
Outlet cold stream vapor fraction	1
Heat duty [Watt]	47808,9265
Calculated heat duty [Watt]	47808,9265
Required exchanger area [sqm]	0,22698221
Actual exchanger area [sqm]	0,22698221
Average U (Dirty) [Watt/sqm-K]	850
UA [J/sec-K]	192,934879
LMTD (Corrected) [C]	247,798256
LMTD correction factor	1
Number of shells in series	1

Table B.10: Aspen data for the flash in the original PS process.

Property method	PENG-ROB
Henry’s component list ID	
Electrolyte chemistry ID	
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
Temperature [C]	33,25
Pressure [bar]	2,7
Specified vapor fraction	0,03
Specified heat duty [Watt]	
EO Model components	
Outlet temperature [C]	33,25
Outlet pressure [bar]	2,7
Vapor fraction	0,768377087
Heat duty [Watt]	-30,2364426
Net duty [Watt]	-30,2364426
First liquid / total liquid	1

Table B.11: Aspen data for separator in the original PS process.

Name	SEP1
Property method	PENG-ROB
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
Inlet flash pressure [bar]	0
Heat duty [Watt]	-1,45519152E-09

Table B.12: Aspen data for the pumps in the original PS process.

Name	PUMP1	PUMP2	PUMP3	PUMP4	PUMP5	PUMP6
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3	3	3
Specified discharge pressure [bar]	4,5	5,51580584	4,5	4,3	1,01325	1,01325
Pump efficiencies	0,7	0,7	0,7	0,7	0,7	0,7
Fluid power [Watt]	14,5739317	10,7959118	11,3731166	0,492575336	1,16915347	6,25661866
Calculated brake power [Watt]	20,8199024	15,4227312	16,2473094	0,703679051	1,67021924	8,93802666
Electricity [Watt]	20,8199024	15,4227312	16,2473094	0,703679051	1,67021924	8,93802666
Volumetric flow rate [cum/hr]	0,291478633	0,356905555	0,337788287	0,340378234	0,0451991161	0,238523449
Calculated discharge pressure [bar]	4,5	5,51580584	4,5	4,3	1,01325	1,01325
Calculated pressure change [bar]	1,8	1,08895146	1,21209708	0,05209708	0,931202388	0,944302427
Head developed [J/kg]	201,010153	150,406082	163,482833	7,16869783	101,341759	109,428835
Pump efficiency used	0,7	0,7	0,7	0,7	0,7	0,7
Net work required [Watt]	20,8199024	15,4227312	16,2473094	0,703679051	1,67021924	8,93802666

Table B.13: Aspen data for the compressor in the original PS process.

Name	COMP1
Property method	PENG-ROB
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
Model Type	ISENTROPIC
Specified discharge pressure [bar]	3,10264078
Isentropic efficiency	0,85
Indicated horsepower [Watt]	28924,9647
Calculated brake horsepower [Watt]	28924,9647
Net work required [Watt]	28924,9647
Power loss [Watt]	0
Efficiency (polytropic / isentropic) used	0,85
Calculated discharge pressure [bar]	3,10264078
Calculated pressure change [bar]	2,10264078
Calculated pressure ratio	3,10264078
Outlet temperature [C]	699,124275
Isentropic outlet temperature [C]	684,520224
Vapor fraction	1
Head developed [J/kg]	181571,308
Isentropic power requirement [Watt]	24586,22
Inlet heat capacity ratio	1,09106242
Inlet volumetric flow rate [cum/hr]	745,714349
Outlet volumetric flow rate [cum/hr]	267,84526
Inlet compressibility factor	1,00014671
Outlet compressibility factor	1,00076136

Table B.14: Aspen data for the valve in the original PS process.

Name	VALVE1
Property method	PENG-ROB
Henry's component list ID	YES
Electrolyte chemistry ID	STEAM-TA
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
Specified outlet pressure [bar]	1,1
Specified pressure drop [bar]	28924,9647
Valve operating specification: % operating	28924,9647
Valve operating specification: flow coef	28924,9647
Cv at 100% opening	0
Valve pressure drop ratio factor	0,85
Valve pressure recovery factor	3,10264078
Valve inlet diameter [meter]	2,10264078
Calculation type	ADIAB-FLASH
Valve pressure specification (design mode)	P-OUT
EO Model components	684,520224
Valve pressure specification (rating mode)	VAL-POSN
Calculated outlet pressure [bar]	1,1
Calculated pressure drop [bar]	1,6
Calculated valve % operating	1,09106242
Checked outlet pressure	745,714349
Cavitation index	267,84526
Pressure drop ratio factor	1,00014671
Pressure recovery factor	1,00076136
Piping geometry factor	1

Table B.15: Aspen data for the distillation column (type RadFrac in Aspen) in the original PS process.

Name	DIST1	DIST2	DIST3	DIST4
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3
Number of stages	30	54	150	20
Condenser	PARTIAL-V	TOTAL	TOTAL	TOTAL
Reboiler	KETTLE	KETTLE	KETTLE	KETTLE
Number of phases	2	2	2	2
Free-water	NO	NO	NO	NO
Top stage pressure [bar]	4,13685438	2,75790292	2,75790292	0,0689475727
Specified reflux ratio	1,5	10	380	10
Calculated molar reflux ratio	0,242713877	31,8883722	380	1,80372665
Calculated bottoms rate [kmol/hr]	2,33118773	2,24482295	2,21496797	0,239295631
Calculated boilup rate [kmol/hr]	2,78766176	2,29888394	11,4854353	3,19569082
Calculated distillate rate [kmol/hr]	0,0481188289	0,0863647822	0,0298549714	1,97567234
Condenser / top stage temperature [C]	123,634157	152,034749	171,777717	65,4959274
Condenser / top stage pressure [bar]	4,13685438	2,75790292	2,75790292	0,0689475727
Condenser / top stage heat duty [Watt]	-134,167627	-24512,1235	-104924,519	-62613,096
Condenser / top stage subcooled duty [Watt]	-13,4272792			
Condenser / top stage reflux rate [kmol/hr]	0,0116791075	2,75403232	11,3448891	3,56357286
Reboiler pressure [bar]	4,42685438	3,28790292	4,24790292	0,0820476116
Reboiler temperature [C]	214,598522	201,133476	214,87806	112,597547
Reboiler heat duty [Watt]	25978,63	22026,1146	107022,652	42803,0743
Basis for specified distillate to feed ratio	MASS	MASS	MASS	MASS
Specified distillate to feed ratio	0,01	0,0308	0,0123	0,8321
Basis for specified bottoms to feed ratio	MASS	MASS	MASS	MASS
Basis for specified boilup ratio	MASS	MASS	MASS	MASS
Calculated molar boilup ratio	1,19581179	1,02408252	5,1853731	13,3545724
Calculated mass boilup ratio	1,1200416	0,960592582	4,86405494	8,95965078

Table B.16: Aspen data for the reactor unit (type RStoich in Aspen) in the original PS process.

Name	FURNACE
Property method	PENG-ROB
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
Specified pressure [bar]	1,01325
Specified temperature [C]	600
Specified heat duty [Watt]	-548000
Outlet temperature [C]	600
Outlet pressure [bar]	1,01325
Calculated heat duty [Watt]	-155471,913
Net heat duty [Watt]	-155471,913
Calculated vapor fraction	1
Total feed stream CO2e flow [kg/hr]	0
Total product stream CO2e flow [kg/hr]	62,2043244
Net stream CO2e production [kg/hr]	62,2043244
Utility CO2e production [kg/hr]	0
Total CO2e production [kg/hr]	62,2043244

Table B.17: Aspen data for the mixers in the original PS process.

Property method	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3
Specified pressure [bar]	0	0	0
Outlet temperature [C]	599,846794	93,2783325	32,5094458
Calculated outlet pressure [bar]	1	1	1,1
Vapor fraction	0,995952812	0,747493746	1
First liquid /Total liquid	1	1	1

Table B.18: Aspen data for the splitters in the original PS process.

Name	B6	SPLIT
Property method	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA
Water solubility method	3	3
First calculated split fraction	0,0242695	0,712527
Second outlet stream	0,9757305	0,287473
Second specified split fraction	0,9757305	0,287473
Second calculated split fraction	0,9757305	0,287473

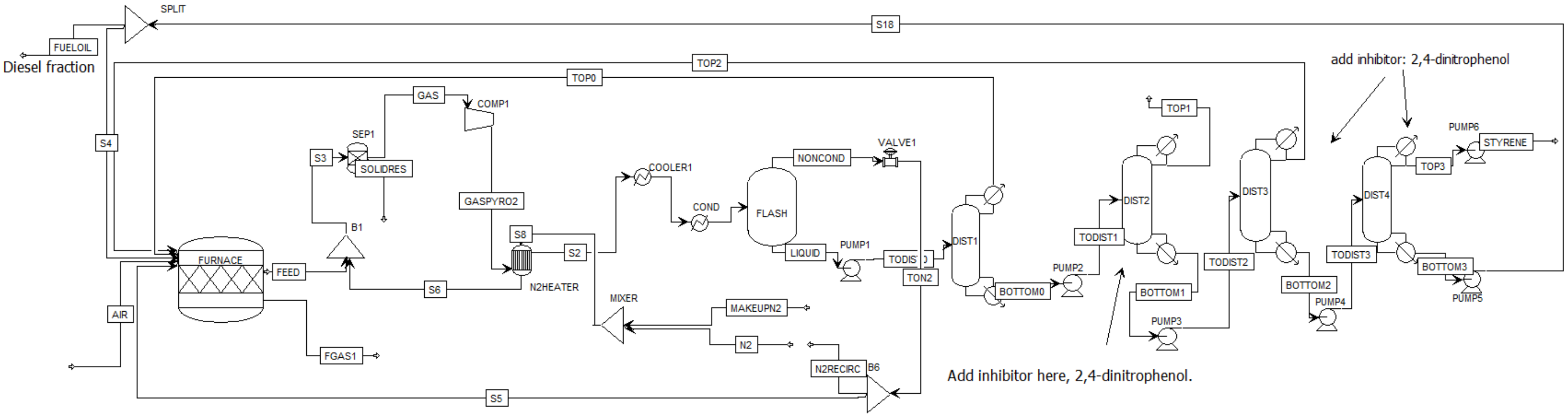
Table B.19: Aspen design specifications in the original PS process.

Name	DS-1	DSAIR	DSOIL
Specification	STYRENE	FO2IN/FO2OUT	QREAC
Specification target	0.005	6	-155.472
Specification tolerance	0.001	0.01	0.01
Lower bound	25	0.001	0.1
Upper bound	200	1000000	1
Comment	A maximum of 0.5 mol% of styrene in gas from condenser. This is achieved by varying the flash temperature.	Air to fuel ratio of 1.2. Varying the inlet mole flow of air.	Split fuel so heat in reactor is satisfied. Varying the oil split ratio so enough fuel is fed to the furnace.

Table B.20: Aspen data for utilities in the original PS process.

Name	CW	HPSGEN	HPSTEAM	LPSGEN	LPSTEAM	MPSGEN	MPSTEAM
Utility type	WATER	STEAM	STEAM	STEAM	STEAM	STEAM	STEAM
Specified energy price [$/kJ]	2,12E-07	-1,48867E-05	1,48867E-05	-7,73841E-06	7,73841E-06	-1,13126E-05	1,13126E-05
Specified inlet pressure [atm]	1						
Specified outlet pressure [atm]	1						
Specified inlet temperature [C]	20	249	250	124	125	174	175
Specified outlet temperature [C]	25	250	249	125	124	175	174
Specified inlet vapor fraction	0	1	0	1	0	1	
Specified outlet vapor fraction	1	0	1	0	1	0	
Specified CO2 emission factor [kg/J]	5,589E-08	5,589E-08	5,589E-08	5,589E-08	5,589E-08	5,589E-08	
Specified CO2 energy source efficiency factor	1	-0,85	0,85	-0,85	0,85	-0,85	0,85
Calculated heating/cooling value [J/kg]	-20875,7611	-1719323,71	1719323,71	-2191878,97	2191878,97	-2034751,64	2034751,64
Calculated inlet enthalpy [J/kg]	-15886670,9	-14890752,4	-13171428,7	-15450574,8	-13258695,8	-15234876,7	-13200125,1
Calculated outlet enthalpy [J/kg]	-15865795,1	-13171428,7	-14890752,4	-13258695,8	-15450574,8	-13200125,1	-15234876,7
Calculated inlet pressure [bar]	1,01325	39,0866691	39,7537159	2,25120518	2,32178779	8,7169648	8,92539509
Calculated outlet pressure [bar]	1,01325	39,7537159	39,0866691	2,32178779	2,25120518	8,92539509	8,7169648
Calculated inlet temperature [C]	20	249	250	124	125	174	175
Calculated outlet temperature [C]	25	250	249	125	124	175	174
Calculated inlet vapor fraction	0	0	1	0	1	0	1
Calculated outlet vapor fraction	0	1	0	1	0	1	0
Calculated CO2 emission factor [kg/J]	5,589E-08	5,589E-08	5,589E-08	5,589E-08	5,589E-08	5,589E-08	

Figure B.1 show the full model flowsheet of the original PS process.



Diesel fraction

add inhibitor: 2,4-dinitrophenol

Add inhibitor here, 2,4-dinitrophenol.

Figure B.1: Aspen flowsheet of the original PS process.

B.6 Aspen data, simpler PS process

The extracted Aspen model data can be found in Table B.21-B.33.

Table B.21: Aspen data for heat exchangers (type Heater in Aspen) for the simpler PS process.

Name	COND	COOLER1
Property method	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA
Water solubility method	3	3
Specified pressure [bar]	-0,1	-0,1
Specified temperature [C]	33,5	
Specified vapor fraction	0,577	1
Calculated pressure [bar]	2,80264078	2,90264078
Calculated temperature [C]	33,5	194,50077
Calculated vapor fraction	0,768150487	1
Calculated heat duty [Watt]	-58057,788	-82979,5748
Net duty [Watt]	-58057,788	-82979,5748
First liquid / total liquid	1	
Utility CO2e production [kg/hr]	0	-19,642144
Total CO2e production [kg/hr]	0	-19,642144
Utility usage [kg/hr]	10011,996	146,812251
Utility cost [$/sec]	1,23082511E-05	-0,000938714738
Utility ID	CW	MPSGEN

Table B.22: Aspen data of heat exchanger (type HeatX in Aspen) for the simpler PS process.

Name	N2HEATER
Hot side property method	PENG-ROB
Hot side use true species approach for electrolytes	YES
Hot side free-water phase properties method	STEAM-TA
Hot side water solubility method	3
Cold side property method	PENG-ROB
Cold side use true species approach for electrolytes	YES
Cold side free-water phase properties method	STEAM-TA
Cold side water solubility method	3
Exchanger specification	600
Units of exchanger specification	C
Minimum temperature approach [C]	1
Hot side outlet pressure [bar]	-0,1
Cold side outlet pressure [bar]	-0,1
Inlet hot stream temperature [C]	699,125088
Inlet hot stream pressure [bar]	3,10264078

Continued on next page

Table B.22 – continued from previous page

Inlet hot stream vapor fraction	1
Outlet hot stream temperature [C]	532,768608
Outlet hot stream pressure [bar]	3,00264078
Outlet hot stream vapor fraction	1
Inlet cold stream temperature [C]	32,5096294
Inlet cold stream pressure [bar]	1,1
Inlet cold stream vapor fraction	1
Outlet cold stream temperature [C]	600
Outlet cold stream pressure [bar]	1
Outlet cold stream vapor fraction	1
Heat duty [Watt]	47798,8119
Calculated heat duty [Watt]	47798,8119
Required exchanger area [sqm]	0,226927338
Actual exchanger area [sqm]	0,226927338
Average U (Dirty) [Watt/sqm-K]	850
UA [J/sec-K]	192,888237
LMTD (Corrected) [C]	247,805737
LMTD correction factor	1
Number of shells in series	1

Table B.23: Aspen data for flash in the simpler PS process.

Name	FLASH
Property method	PENG-ROB
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
Temperature [C]	33,25
Pressure [bar]	2,7
Specified vapor fraction	0,03
Specified heat duty [Watt]	0
Outlet temperature [C]	33,25
Outlet pressure [bar]	2,7
Vapor fraction	0,768349358
Heat duty [Watt]	-30,2303775
Net duty [Watt]	-30,2303775
First liquid / total liquid	1
Utility usage [kg/hr]	5,2131924
Utility cost [$/sec]	6,40884003E-09
Utility ID	CW

Table B.24: Aspen data for separator in the simpler PS process.

Name	SEP1
Property method	PENG-ROB
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
Inlet flash pressure [bar]	0
Heat duty [Watt]	-2,61934474E-09

Table B.25: Aspen data for pumps in the simpler PS process.

Name	PUMP1	PUMP2	PUMP3	PUMP4
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3
Specified discharge pressure [bar]	3,447378647	3,5	2,75790292	1,01325
Pump efficiencies	0,7	0,7	0,7	0,7
Fluid power [Watt]	6,05143664	1,4091247	3,39190806	6,23179376
Calculated brake power [Watt]	8,64490948	2,01303529	4,84558295	8,90256251
Electricity [Watt]	8,64490948	2,01303529	4,84558295	8,90256251
Volumetric flow rate [cum/hr]	0,291487748	0,333527042	0,0456335176	0,23757704
Calculated discharge pressure [bar]	3,44737865	3,5	2,75790292	1,01325
Calculated pressure change [bar]	0,747378647	0,15209708	2,67585531	0,944302427
NPSH available [J/kg]	0	0	0	0
Head developed [J/kg]	83,4618561	20,5332814	290,397884	109,433067
Pump efficiency used	0,7	0,7	0,7	0,7
Net work required [Watt]	8,64490948	2,01303529	4,84558295	8,90256251

Table B.26: Aspen data for the compressor in the simpler PS process.

Property method	PENG-ROB
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
Model Type	ISENTROPIC
Specified discharge pressure [bar]	3,10264078
Isentropic efficiency	0,85
Indicated horsepower [Watt]	28922,554
Calculated brake horsepower [Watt]	28922,554
Net work required [Watt]	28922,554
Power loss [Watt]	0
Efficiency (polytropic / isentropic) used	0,85
Calculated discharge pressure [bar]	3,10264078
Calculated pressure change [bar]	2,10264078
Calculated pressure ratio	3,10264078
Outlet temperature [C]	699,125088
Isentropic outlet temperature [C]	684,5209
Vapor fraction	1
Head developed [J/kg]	181556,047
Isentropic power requirement [Watt]	24584,1709
Inlet heat capacity ratio	1,09106312
Inlet volumetric flow rate [cum/hr]	745,651991
Outlet volumetric flow rate [cum/hr]	267,823111
Inlet compressibility factor	1,00014675
Outlet compressibility factor	1,00076147

Table B.27: Aspen data for the valve in the simpler PS process.

Name	VALVE1
Property method	PENG-ROB
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
Specified outlet pressure [bar]	1,1
Calculation type	ADIAB-FLASH
Valve pressure specification (design mode)	P-OUT
Valve pressure specification (rating mode)	VAL-POSN
Calculated outlet pressure [bar]	1,1
Calculated pressure drop [bar]	1,6
Piping geometry factor	1
Total feed stream CO2e flow [kg/hr]	0
Total product stream CO2e flow [kg/hr]	0
Net stream CO2e production [kg/hr]	0

Table B.28: Aspen data for RadFrac units (distillation towers) in the simpler PS process.

Name	DIST1	DIST2
Property method	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA
Water solubility method	3	3
Number of stages	60	20
Condenser	PARTIAL-V	TOTAL
Reboiler	KETTLE	KETTLE
Number of phases	2	2
Free-water	NO	NO
Top stage pressure [bar]	2,75790292	0,0689475729
Specified reflux ratio	50	10
Calculated molar reflux ratio	42,131694	4,57918994
Calculated bottoms rate [kmol/hr]	2,21194463	0,243805699
Calculated boilup rate [kmol/hr]	9,67884628	8,01779971
Calculated distillate rate [kmol/hr]	0,167447734	1,96813893
Condenser / top stage temperature [C]	149,870768	65,4599214
Condenser / top stage pressure [bar]	2,75790292	0,0689475729
Condenser / top stage heat duty [Watt]	-67883,0483	-124097,665
Condenser / top stage reflux rate [kmol/hr]	7,05485669	9,01248201
Reboiler pressure [bar]	3,34790292	0,0820476118
Reboiler temperature [C]	202,386913	111,404887
Reboiler heat duty [Watt]	92426,3654	106268,528
Utility CO2e production [kg/hr]	5,80966302	25,1548857
Total CO2e production [kg/hr]	5,80966302	25,1548857
Condenser utility usage [kg/hr]	111,492914	21400,4936
Condenser utility cost [$/sec]	-0,00052530686	2,63087049E-05
Condenser utility ID	LPSGEN	CW
Reboiler utility usage [kg/hr]	193,526625	174,53824
Reboiler utility cost [$/sec]	0,00137592357	0,000822349437
Reboiler utility ID	HPSTEAM	LPSTEAM
Basis for specified distillate to feed ratio	MASS	MASS
Specified distillate to feed ratio	0,0535	0,8298
Basis for specified bottoms to feed ratio	MASS	MASS
Basis for specified boilup ratio	MASS	MASS
Calculated molar boilup ratio	4,37571816	32,8860225
Calculated mass boilup ratio	4,10222443	22,1556848

Table B.29: Aspen data for the furnace component (type RStoic in Aspen) in the simpler PS process.

Name	FURNACE
Property method	PENG-ROB
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
Specified pressure [bar]	1,01325
Specified temperature [C]	600
Specified heat duty [Watt]	-548000
Outlet temperature [C]	600
Outlet pressure [bar]	1,01325
Calculated heat duty [Watt]	-155472
Net heat duty [Watt]	-155472
Calculated vapor fraction	1
Total feed stream CO2e flow [kg/hr]	0
Total product stream CO2e flow [kg/hr]	61,4086706
Net stream CO2e production [kg/hr]	61,4086706
Utility CO2e production [kg/hr]	0
Total CO2e production [kg/hr]	61,4086706

Table B.30: Aspen data for the mixers in the simpler PS process.

Name	B1	MAKEUP	MIXER1
Property method	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3
Specified pressure [bar]	0	0	0
Outlet temperature [C]	111,884186	32,5096294	599,846775
Calculated outlet pressure [bar]	1,1	1,1	1
Vapor fraction	0,923970032	1	0,995952475
First liquid /Total liquid	1	1	1
Total feed stream CO2e flow [kg/hr]	0	0	0
Total product stream CO2e flow [kg/hr]	0	0	0
Net stream CO2e production [kg/hr]	0	0	0

Table B.31: Aspen data for the splitter used in the simpler PS process.

Name	B4	SPLITTER
Property method	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA
Water solubility method	3	3
First calculated split fraction	0,916935353	0,02424
Second outlet stream	0,083306223	0,97576
Second specified split fraction	0,083306223	0,97576
Second calculated split fraction	0,0830646467	0,97576
Total feed stream CO2e flow [kg/hr]	0	0
Total product stream CO2e flow [kg/hr]	0	0
Net stream CO2e production [kg/hr]	0	0

Table B.32: Aspen data for design specifications in the simpler PS process.

Name	B2	B3	DS-1
Specification	FO2IN/FO2OUT	QREAC	STYRENE
Specification target	6	-155.472	0.005
Specification tolerance	0.1	0.001	0.001
Lower bound	0.011	0.01	25
Upper bound	100000	1	200
Comment	Air to fuel ratio of 1.2. Satisfied by varying the inlet air mole flow.	Split fuel so heat in reactor is satisfied. Varying the oil split ratio so enough fuel is fed to the furnace.	A maximum of 0.5 mol% of styrene in gas from condenser. This is achieved by varying the flash temperature.

Table B.33: Aspen data for utilities in the simpler PS process.

Name	CW	HPSGEN	HPSTEAM	LPSGEN	LPSTEAM	MPSGEN	MPSTEAM
Utility type	WATER	STEAM	STEAM	STEAM	STEAM	STEAM	STEAM
Specified price [$/kg]	6	-155.472	0.005				
Specified cooling value [J/kg]	0.1	0.001	0.001				
Specified inlet degrees subcooled [C]	0.011	0.01	25				
Specified outlet degrees subcooled [C]	100000	1	200				
Specified energy price [$/J]	2,12E-10	-1,48867E-05	1,48867E-05	-7,73841E-06	7,73841E-06	-1,13126E-05	1,13126E-05
Specified inlet pressure [bar]	1,01325						
Specified outlet pressure [bar]	1,01325						
Specified inlet temperature [C]	20	249	250	124	125	174	175
Specified outlet temperature [C]	25	250	249	125	124	175	174
Specified inlet vapor fraction	0	1	0	1	0	1	
Specified outlet vapor fraction	1	0	1	0	1	0	
Specified CO2 emission factor [kg/J]	5,589E-08	5,589E-08	5,589E-08	5,589E-08	5,589E-08	5,589E-08	
Specified CO2 energy source efficiency factor	1	-0,85	0,85	-0,85	0,85	-0,85	0,85
Calculated heating/cooling value [J/kg]	-20875,7611	-1719323,71	1719323,71	-2191878,97	2191878,97	-2034751,64	2034751,64
Calculated inlet enthalpy [J/kg]	-15886670,9	-14890752,4	-13171428,7	-15450574,8	-13258695,8	-15234876,7	-13200125,1
Calculated outlet enthalpy [J/kg]	-15865795,1	-13171428,7	-14890752,4	-13258695,8	-15450574,8	-13200125,1	-15234876,7
Calculated inlet pressure [bar]	1,01325	39,0866691	39,7537159	2,25120518	2,32178779	8,7169648	8,92539509
Calculated outlet pressure [bar]	1,01325	39,7537159	39,0866691	2,32178779	2,25120518	8,92539509	8,7169648
Calculated inlet temperature [C]	20	249	250	124	125	174	175
Calculated outlet temperature [C]	25	250	249	125	124	175	174
Calculated inlet vapor fraction	0	0	1	0	1	0	1
Calculated outlet vapor fraction	0	1	0	1	0	1	0
Calculated purchase price [$/J]	2,12E-10	1,48867E-08	-7,73841E-09	7,73841E-09	-1,13126E-08		
Calculated total cost [$/sec]	3,86233648E-05	0	0,00137592357	-0,00052530686	0,000822349437	-0,000938714738	0
Calculated total usage rate [kg/hr]	31417,7028	0	193,526625	111,492914	174,53824	146,812251	0
Calculated CO2 emission factor [kg/J]	5,589E-08	5,589E-08	5,589E-08	5,589E-08	5,589E-08	5,589E-08	
Calculated CO2 emission rate [kg/hr]	21,8782993	-16,0686363	25,1548857	-19,642144			

Figure B.2 show the full model flowsheet of the simpler PS process.

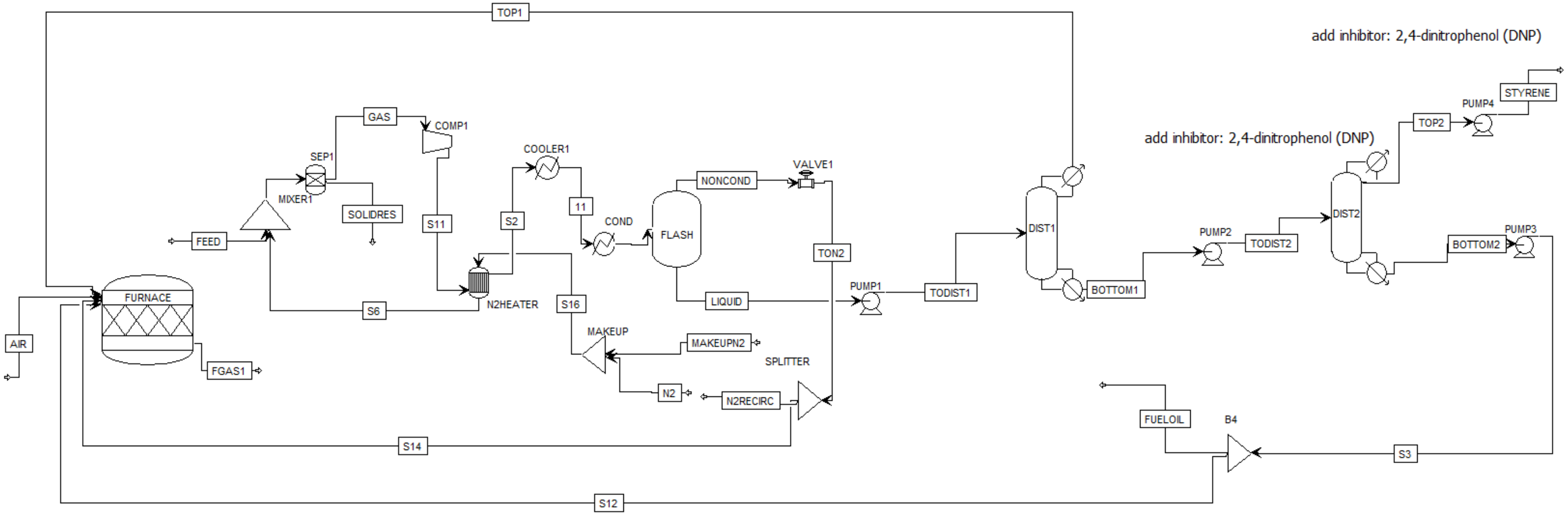


Figure B.2: Aspen flowsheet of the simpler PS process.

C

PVC process data

C.1 Product composition

The PVC process is focused around a pyrolysis study executed in a batch reactor at a pressure of 2 kPa and a temperature of 520°C [18]. The production distribution from these experiments is complex, and a simpler one showing the liquid, solid, gas and HCl yield is shown in Table C.1. To be able to input the products in Aspen, the sum has to be 100 %, therefore the fractions are adjusted by a weighted fraction so that the sum adds up to 100, according to Equation C.1 where the example of HCl is used. These values are also given in Table C.1.

$$\text{New HCl frac} = 58.19 + \frac{58.19}{99.45} \cdot (100 - 99.45) \approx 58.512 \tag{C.1}$$

In Table C.2-C.3 the complex product distribution in the liquid is shown [18]. This product distribution is used in the Aspen model after some simplifications.

To make the modelling easier, the first simplification of the liquid distribution is to remove the components which has a lower mass fraction than 0.5 *wt*% in Table C.2-C.3 except for the category chlorinated hydrocarbons found in the end on Table C.3. This is to make the modelling of these compounds as accurate as possible. With a few compounds removed, their mass fractions are split up between the remaining ones by a weighted fraction with the same methodology as in Equation C.1. To further make the sum of liquids add up to the value given in the third column in C.1, they are adjusted slightly by a weighted fraction by using Equation C.1. Further simplifications are also done by representing certain compounds by others, according to Table C.4 where the final liquid distribution is also given.

Table C.1: A rough distribution of the products from the experiment at 520°C by Miranda et al (1999).

Group	Mass fraction [wt% PVC basis]	New mass fraction [wt%]
HCl	58.19	58.512
Liquid	32.39	32.569
Other gases (not HCl)	0.34	0.342
Solid residue	8.53	8.577
Total products	99.45	100

Table C.2: Product composition in the liquid from the experiment by Miranda et al (1999) at 520°C and vacuum.

Number	Compound	Mass fraction [wt% liquid basis]
1	Hexatriene	0.01
2	Hexadiene	0.03
3	Benzene	17.91
4	Heptene	0.36
5	Heptane	0.24
6	Methylhexene	0.08
7	1-ethyl-3-methylenecyclobutane	0.11
8	3-methyl-1,3,5-hexatriene	0.01
9	Ethylcyclopentene	0.07
10	1-methylcyclohexene	0.07
11	Dimethylcyclopentene	0.11
12	3-methylcyclohexene	0.03
13	Toluene	5.28
14	1,6-heptadiene	0.01
15	Methylhexadiene	0.08
16	Octene	0.25
17	Octane	0.22
18	Methylheptadiene	0.31
19	Propylcyclopentane	0.31
20	Ethylcyclohexene	0.03
21	Cyclooctadiene	0.07
22	Ethylbenzene	0.84
23	1,3-dimethylbenzene	1.21
24	Styrene	0.98
25	p-xylene	1.09
26	Nonane	0.37
27	Propylcyclohexane	0.24
28	2-propenylbenzene	0.24
29	Propylbenzene	0.25
30	Ethylmethylbenzene	1.01
31	1,2,3-trimethylbenzene	0.24
32	Propenylbenzene	0.18
33	Decane	0.18
34	Cyclopropylbenzene	0.39
35	Indane	0.6

Table C.3: Product composition in the liquid from the experiment by Miranda et al (1999) at 520°C and vacuum, cont.

Number	Compound	Mass fraction [wt% liquid basis]
36	Indene	0.65
37	Butylbenzene	0.38
38	Methylpropylbenzene	0.36
39	Methylpropenylbenzene	0.75
40	Butanedienylbenzene	0.39
41	Dihydromethyl-(1H)-indene	0.35
42	Methyl-(1H)-indene	0.93
43	(1-methylene-2-propenyl)benzene	0.23
44	(1-methyl-2-cyclopropen-1-yl)benzene	0.26
45	Pentylbenzene	0.23
46	1,2,3,4-tetrahydronaphthalene	0.31
47	1,2-dihydronapthalene	1.2
48	Naphthalene	2.73
49	2,3-dihydro-1,6-dimethyl-1-(H)-indene	0.15
50	1,2,3,4-Tetrahydro-1-methylnapthtalene	0.5
51	1,2-Dihydro-6-methylnaphthalene	0.96
52	Methylnaphthalene	2.93
53	Biphenyl	0.41
54	1-Ethylnaphthalene	0.53
55	4-methyl-1,1-biphenyl	0.28
56	Dimethylnaphthalene	2.36
57	Acenaphthene	0.29
58	2-methyl-1,1-biphenyl	0.24
59	Trimethylnaphthalene	1.38
60	1,2,3,4-tetrahydrofluorene	0.54
61	Fluorene	0.31
62	2,4a-dihydrofluorene	1.23
63	1-(2-propethyl)naphthalene	1.7
64	1,2,3,4-tetrahydrophenanthrene	0.99
65	Phenanthrene	0.79
66	Anthracene	1
67	Methylphenanthrene	2.8
68	9-Ethylphenanthrene	0.85
69	Pyrene	0.92
70	11(H)-benzo-(b)fluorene	2.23
-	Others	34.14
-	Chlorinated hydrocarbons	0.3
-	Total	100.01

Table C.4: Final distribution of components in the liquid after numerous simplifications which is input in Aspen.

Number	Compound	Mass fraction [wt% PVC basis]	Comments
3	Benzene	6.39	
13	Toluene	1.88	
22	Ethylbenzene	0.3	
23	1,3-dimethylbenzene	0.43	
24	Styrene	0.35	
25	p-xylene	0.39	
30	Ethylmethylbenzene	0.36	
35	Indane	0.21	
36	Indene	0.23	
39	Methylpropenylbenzene	0.27	
42	Methyl-(1H)-indene	0.33	
47	1,2-dihydronapthalene	0.43	
48	Naphthalene	0.97	
52	Methylnaphthalene	1.57	Assumed to represent 50 and 51
54	1-Ethylnaphthalene	0.19	
56	Dimethylnaphthalene	0.84	
59	Trimethylnaphthalene	1.1	Assumed to represent 63
60	1,2,3,4-tetrahydrofluorene	0.63	Assumed to represent 62
64	1,2,3,4-tetrahydrophenanthrene	0.35	
65	Phenanthrene	0.28	
66	Anthracene	0.36	
67	Methylphenanthrene	6.01	
68	9-Ethylphenanthrene	1.83	
69	Pyrene	1.98	
70	11(H)-benzo-(b)fluorene	4.79	
-	Others	0	Split between 67-70
-	Chlorinated HCs	0.098	
-	Total	32.57	

Due to the lack of data from experiments at 520°C, the composition in the remaining gas (excluding HCl) is taken to be the same as the gas from experiments carried out at 500°C. The values are given in Table C.5. The original values are given in vol% and to recalculate them in terms of weight, it is assumed that the ideal gas law applies. Also, it is assumed that the group others are heavier than pentane and can be represented by the same. The gas mass fractions adjusted according to the new fractions in Table C.1 are found in Table C.5.

Table C.5: Composition in the gas (excluding HCl) from experiments run at 500°C.

Component	Concentration [vol%] at 500°C	Mass fraction [wt% on PVC basis]
Hydrogen	33.22	0.01143
Methane	24.12	0.0664
Carbon monoxide	0.32	0.00154
Carbon dioxide	2.4	0.01816
Ethylene	16.6	0.07995
Ethane	11.27	0.05815
Propylene	3.85	0.027814
Propane	3.65	0.027625
Butene	0.8	0.007706
Butane	1.49	0.014866
Pentane	0.55	0.0282
Others	1.73	Represented by pentane
Total	100	0.342

Finally, a number of chlorinated HCs was present in the products according to Table C.6. These are simplified so that every compound is represented by either chlorobenzene or benzylchloride according to a weighted fraction. These values are found in the third column in Table C.6.

Table C.6: Distribution of chlorinated compounds in the products, both from experiments and the assumed distribution used in Aspen.

Compound	Mass fraction [wt% pyrolysis oil basis]	Mass fraction [wt% PVC basis]
3-chloro-2-methyl-1-butene	0	0
1-chlorocyclopentene	0	0
1-chloro-3-methyl-1-butane	<0.001	0
Chlorobenzene	0.05	0.02
3-chlorocyclohexene	<0.001	0
1-chloro-2-ethyl-benzene	0.01	0
3-chloro-3-methylheptane	0.01	0
Benzylchloride	0.2	0.08
(2-chloro-ethyl)benzene	<0.001	0
Ethylchloromethylbenzene	0.01	0
(3-chloro-1-propenyl)benzene	0.02	0
3-chloroallyl benzene	0	0
3-chloro-1-phenyl-2-butene	<0.001	0
(2-chloro-2-butenyl)benzene	0.01	0
Total (pyrolysis oil basis)	0.31	0.31
Total (PVC basis)	0.10	0.10

When using the input in Aspen, the products from pyrolysis are split up to represent the release of compounds in the first reactor and the feed to the second reactor. In the experiments, the liquid consists of a light and a heavy fraction [18]. In the study, they show gas chromatograms from the experiments at 520 °C and in the chromatogram for the heavy liquid, the compounds 67-70 in Table C.4 are included but not in the light liquids chromatogram. Therefore it is assumed that the compounds 67-70 which also represents others in Table C.4 are included in the heavier liquid fraction. The experiments run at 320°C are also given in the study. At those experiments, a product distribution is found which is different than the one at 520°C. To model the two pyrolysis reactors, the products leaving the first reactor are assumed to be the same amounts as in the experiment run at 320°C while the remaining compounds are just separated off and fed to the second pyrolysis reactor. The split is done so that 21.1% of the lighter and 5.1% of the heavier liquid compounds leave in the first reactor alongside 98.8% of the HCl and 11.76% of the gaseous compounds, in accordance with Table C.7. The rest including the solid residue, represented as pure carbon, is modelled as to be released in the second reactor at 520°C.

Table C.7: A rough distribution of the products from the experiments at 320°C and 520°C [18]. X(T) is the mass fraction in *wt*% of HCl, other gases, light liquid and heavy liquid respectively, at temperature T.

Final pyrolysis temperature [°C]	HCl [wt% PVC basis]	Other gases [wt% PVC basis]	Light liquid [wt% PVC basis]	Heavy liquid [wt% PVC basis]
320	57.5	0.04	2.7	1
520	58.19	0.34	12.79	19.6
Fraction (X(320°C) / X(520°C))	0.988	0.1176	0.211	0.051

C.2 Revenues and costs

The produced products and their generated revenues is presented in Table C.8. The chlorinated hydrocarbons (CHCl) are found in one of the streams sent to combustion and subsequent flue gas treatment.

Table C.8: Annual production capacity and potential income from the PVC process.

Product	Amount [t/yr]	Price [SEK/kg]	Revenue [MSEK/yr]
HCl	1929.6	0.47	0.90
Benzene	187.5	7.44	1.40
Fuel oil	679.86	1.71	1.16
C_1-C_5 fraction	10.22	Combusted	
HCL & C_1-C_7 fraction	19.78	Combusted	
CHCl & C_6-C_{13} fraction	180.72	Combusted	
Total revenue			3.46

The running costs for the PVC process are given in Table C.9.

Table C.9: Running costs for the PVC process.

Category	Cost [MSEK/yr]
Running costs excluding utilities, Aspen	15.04
PVC waste	0
Energy utilities	0.95
$CaCO_3$	0.02
Flue gas treatment	0.23
Total running costs	16.24

Below is the investment cost from Aspen and for the reactor, see Table C.10.

Table C.10: Investment cost for the PVC process.

Category	Cost [MSEK]
Investment cost, Aspen	271.66
Reactors and flue gas train	57.71
Total ISBL investment cost	329.37
Total ISBL & OSBL investment cost	461.12

Reactor vessels and furnace are cost estimated by the Taylor method. The reactors are operating under vacuum and are not of the type fluidized bed. Thus, the cost estimations from [68] for fluidized beds are not truly valid. However, the cost of flue gas treatment and fuel feeding is assumed to be roughly the same and is taken from that study. The investment cost for fuel feeding and flue gas cleaning is calculated for both the reactors with the method described in Appendix D.1. The highest values of the two are taken as the investment cost for those categories.

The operating conditions are summarized for reactors and furnace, as described in Section 4.7.3. The values are presented in Table C.11. Redidence time of the reactors are assumed to be 40 min to mimic the study by Miranda et al (1999). The furnace is assumed to operate with a maximum temperature of 1400°C to make an overestimation of the cost. Platinum is used as material because it has a maximum furnace operating temperature of 1500°C [89]. This will most likely fall under the precious metals category in the Taylor method. Hence, the high score for material of the furnace, together with the other scores given in Table C.12. Finally, the total scores are given in Table C.13 and are used to find the investment cost of the reactor system.

Table C.11: Operating conditions to use in the Taylor method for reactors and combustor.

Equipment	Relative throughput [t/t product]	Reaction time [h]	Temp. [°C]	Pres. [atm]	Materials of construction
Reactor 1	1.18	0.66	320	0.02	SS 304
Reactor 2	0.44	0.66	520	0.02	SS 304
Furnace	0.078	-	1400	1	Precious metals

Table C.12: Scoring table for the Taylor method.

Equipment	Relative throughput [t/t product]	Reaction time [h]	Temp. [°C]	Pres. [atm]	Materials of construction
Reactor 1	0.26	0	0	1.89	1
Reactor 2	-1.62	0	1.03	1.89	1
Furnace	-3	0	1.5	0	4

Table C.13: Total scores and costliness indices for the equipment.

Equipment	Total score (S)	Costliness index (I)
Reactor 1	3.146	2.283
Reactor 2	2.299	1.828
Furnace	2.500	1.927
Total	-	6.038

C.3 Aspen data

The extracted Aspen data for components can be found in Table C.14-C.25.

Table C.14: Heat exchanger data from Aspen for the PVC process.

Name	COND1	COND2	COOLER1	COOLER2	COOLER3	COOLER4	COOLER5	COOLER6	SUPH
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES	YES	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3	3	3	3	3	3
Specified pressure [bar]	-0,1	-0,1	-0,001	-0,01	-0,05	-0,1	-0,001	-0,1	0
Specified temperature [C]	30	30	150	150	150	200	300		
Specified vapor fraction	0	1	1						
Calculated pressure [bar]	2,82099853	3,93489119	0,019	0,134585448	0,723615712	2,92099853	0,019	4,03489119	0,353559114
Calculated temperature [C]	30	30	102,230663	133,158266	165,294569	186,591693	209,994318	378,74723	327,097345
Calculated vapor fraction	0,985235877	0,0688604369	1	1	1	1	1	1	1
Calculated heat duty [Watt]	-10977,78	-32370,1552	-13574,864	-16254,9159	-14302,2322	-12474,7368	-21327,3786	-723,801414	3241,43079
Degrees of superheating [C]	10	10	10	30	30	5	60		
Net duty [Watt]	-10977,78	-32370,1552	-13574,864	-16254,9159	-14302,2322	-12474,7368	-21327,3786	-723,801414	3241,43079
First liquid / total liquid	1	1							
Total feed stream CO2e flow [kg/hr]	0,81278495	7,84652049	0,81278495	0,81278495	0,81278495	0,81278495	7,84652049	7,84652049	7,84652049
Total product stream CO2e flow [kg/hr]	0,81278495	7,84652049	0,81278495	0,81278495	0,81278495	0,81278495	7,84652049	7,84652049	7,84652049
Net stream CO2e production [kg/hr]	0	0	0	0	0	0	0	0	0
Utility CO2e production [kg/hr]	0	0	0	0	-3,38548979	-2,9529023	-5,04841634	-0,171331459	0
Total CO2e production [kg/hr]	0	0	0	0	-3,38548979	-2,9529023	-5,04841634	-0,171331459	0
Utility usage [kg/hr]	1893,10502	5582,1945	2340,96903	2803,14078	23,4903644	22,0710242	37,7336288	1,51552909	
Utility cost [$/sec]	2,32728937E-06	6,8624729E-06	2,87787116E-06	3,44604217E-06	-0,000110676536	-0,000141121708	-0,000241268104	-1,07750145E-05	
Utility ID	CW	CW	CW	CW	LPSGEN	MPSGEN	MPSGEN	HPSGEN	

Table C.15: Aspen flash data for PVC process.

Name	FLASH	FLASH2
Property method	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA
Water solubility method	3	3
Temperature [C]	5	10
Pressure [bar]	1	1
Specified vapor fraction		
Specified heat duty [Watt]	0	
EO Model components		
Outlet temperature [C]	5	10
Outlet pressure [bar]	2,72099853	3,83489119
Vapor fraction	0,979101721	0,0597480119
Heat duty [Watt]	-1868,40066	-995,75983
Net duty [Watt]	-1868,40066	-995,75983
First liquid / total liquid	1	1
Total feed stream CO2e flow [kg/hr]	0,81278495	7,84652049
Total product stream CO2e flow [kg/hr]	0,81278495	7,84652049
Net stream CO2e production [kg/hr]	0	0
Utility CO2e production [kg/hr]	0,375929687	0,200350861
Total CO2e production [kg/hr]	0,375929687	0,200350861
Utility usage [kg/hr]	1681,56059	896,183847
Utility cost [$/sec]	5,11941781E-06	2,72838193E-06
Utility ID	REFRIGER	REFRIGER

Table C.16: Aspen data for separators in the PVC process.

Name	ADSORBER	SEP1	SOLIDSEP
Property method	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3
Inlet flash pressure [bar]	0	0	0
Heat duty [Watt]	-188,528928	-0,687438371	-0,515605756
Total feed stream CO2e flow [kg/hr]	2,06747741	6,91143665	7,84652049
Total product stream CO2e flow [kg/hr]	2,06747741	6,91143665	7,84652049
Net stream CO2e production [kg/hr]	0	0	0
Utility CO2e production [kg/hr]	0	0	0
Total CO2e production [kg/hr]	0	0	0

Table C.17: Aspen data for pumps in the PVC process.

Name	PUMP2	PUMPX	PUMPX1	PUMPX2
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3
Specified discharge pressure [bar]	4	5,2	5,11	1,15
Pump efficiencies	0,7	0,7	0,7	0,7
Fluid power [Watt]	0,510558967	5,18967275	2,54076257E-15	0,0333661194
Calculated brake power [Watt]	0,729369952	7,41381821	3,62966081E-15	0,0476658849
Electricity [Watt]	0,729369952	7,41381821	3,62966081E-15	0,0476658849
Volumetric flow rate [cum/hr]	0,0165008026	0,13685958	0,157139887	0,12011803
Calculated discharge pressure [bar]	3,83489119	5,2	5,11	1,15
Calculated pressure change [bar]	1,11389265	1,36510881	5,82076609E-16	0,01
NPSH available [J/kg]	0	7,26025371	0	0
Head developed [J/kg]	115,007945	139,963662	6,98164731E-14	1,11661504
Pump efficiency used	0,7	0,7	0,7	0,7
Net work required [Watt]	0,729369952	7,41381821	3,62966081E-15	0,0476658849
Total feed stream CO2e flow [kg/hr]	0,00017102772	2,06764844	4,80235347E-11	0
Total product stream CO2e flow [kg/hr]	0,00017102772	2,06764844	4,80235347E-11	0

Table C.18: Aspen data for compressors in the PVC process.

Name	COMP1	COMP2	COMP3	COMP4	COMP5
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3	3
Model Type	ISENTROPIC	ISENTROPIC	ISENTROPIC	ISENTROPIC	ISENTROPIC
Specified discharge pressure [bar]	0,02	1	3	0,3535591144	2
Specified pressure ratio	3,2	3	100	4	
Specified power required [Watt]	10000	1000	10000	5000	
Isentropic efficiency	0,85	0,85	0,85	0,85	0,85
Indicated horsepower [Watt]	18121,9618	16241,1436	13694,5861	3996,66044	4036,382
Calculated brake horsepower [Watt]	18121,9618	16241,1436	13694,5861	3996,66044	4036,382
Net work required [Watt]	18121,9618	16241,1436	13694,5861	3996,66044	4036,382
Power loss [Watt]	0	0	0	0	0
Efficiency (polytropic / isentropic) used	0,85	0,85	0,85	0,85	0,85
Calculated discharge pressure [bar]	0,144585448	0,773615712	3,02099853	0,353559114	4,13489119
Calculated pressure change [bar]	0,125585448	0,639030263	2,29738282	0,334559114	3,78133207
Calculated pressure ratio	7,60976043	5,74813787	4,17486586	18,6083744	11,6950491
Outlet temperature [C]	390,000066	390,002181	381,518812	277,108008	388,989542
Isentropic outlet temperature [C]	348,352114	352,726748	350,121927	267,514567	380,504229
Vapor fraction	1	1	1	1	1
Head developed [J/kg]	215617,005	193238,832	162939,623	102349,018	103366,233
Isentropic power requirement [Watt]	15403,6675	13804,972	11640,3982	3397,16137	3430,9247
Inlet heat capacity ratio	1,34692524	1,34268921	1,33983196	1,04180051	1,03623905
Inlet volumetric flow rate [cum/hr]	11025,3389	1684,23542	337,6378	2083,49673	138,369416
Outlet volumetric flow rate [cum/hr]	2559,56421	478,262556	120,79714	126,625401	12,4459197
Inlet compressibility factor	0,999934848	0,999639338	0,998487083	0,999412868	0,994139395
Outlet compressibility factor	0,999946794	0,999715798	0,998811677	0,992411706	0,948018761
Total feed stream CO2e flow [kg/hr]	0,81278495	0,81278495	0,81278495	7,84652049	7,84652049
Total product stream CO2e flow [kg/hr]	0,81278495	0,81278495	0,81278495	7,84652049	7,84652049

Table C.19: Aspen data for RadFrac units (distillation towers) in the PVC process.

Name	DIST1	DIST2	DIST3
Property method	PENG-ROB	PENG-ROB	PENG-ROB
Henry's component list ID	YES	YES	YES
Electrolyte chemistry ID	STEAM-TA	STEAM-TA	STEAM-TA
Use true species approach for electrolytes	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3
Number of stages	12	15	10
Condenser	PARTIAL-V	TOTAL	TOTAL
Reboiler	KETTLE	KETTLE	KETTLE
Number of phases	2	2	2
Free-water	NO	NO	NO
Top stage pressure [bar]	5	1	1
Specified reflux ratio	1	1,44	0,8
Specified bottoms rate [kmol/hr]	0,85	0,85	0,85
Specified boilup rate [kmol/hr]	0,144585448	0,773615712	3,02099853
Specified distillate rate [kmol/hr]	0,125585448	0,639030263	2,29738282
EO Model components	7,60976043	5,74813787	4,17486586
Calculated molar reflux ratio	0,548069505	3,74933021	4,12551934
Calculated bottoms rate [kmol/hr]	0,966784716	0,667003968	0,456285378
Calculated boilup rate [kmol/hr]	1,14899234	0,619003261	0,922566609
Calculated distillate rate [kmol/hr]	0,0611332843	0,299780748	0,21071859
Condenser / top stage temperature [C]	32,426774	79,8133277	133,202444
Condenser / top stage pressure [bar]	5	1	1
Condenser / top stage heat duty [Watt]	-374,532276	-12070,9658	-12848,491
Condenser / top stage subcooled duty	2559,56421	478,262556	120,79714
Condenser / top stage reflux rate [kmol/hr]	0,0335052888	1,12397702	0,869323619
Condenser / top stage free water reflux ratio	0,999946794	0,999715798	0,998811677
Reboiler pressure [bar]	5,11	1,14	1,09
Reboiler temperature [C]	201,839775	188,870219	306,193551
Reboiler heat duty [Watt]	12782,2275	9700,69011	17971,4306
Total feed stream CO2e flow [kg/hr]	2,06764844	4,80235347E-11	0
Total product stream CO2e flow [kg/hr]	2,0676415	4,80235348E-11	0
Net stream CO2e production [kg/hr]	-6,94092474E-06	8,29188529E-20	0
Utility CO2e production [kg/hr]	0	2,29625606	0
Total CO2e production [kg/hr]	-6,94092474E-06	2,29625606	0
Condenser utility usage [kg/hr]	2081,62359		
Condenser utility cost [$/sec]	2,55904475E-06		
Condenser utility ID		CW	
Reboiler utility usage [kg/hr]	20,3117564		
Reboiler utility cost [$/sec]	0,000144411263		
Reboiler utility ID		HPSTEAM	
Basis for specified distillate to feed ratio	MASS	MASS	MASS
Specified distillate to feed ratio	0,01852	0,1789	0,21

Continued on next page

Table C.19 – continued from previous page

Basis for specified bottoms to feed ratio	MOLE	MOLE	MOLE
Basis for specified boilup ratio	MOLE	MOLE	MOLE
Calculated molar boilup ratio	1,18846763	0,92803535	2,02190702
Calculated mass boilup ratio	0,730351728	0,582170959	1,7119078

Table C.20: Aspen data for reactors (RStoich) in the PVC process.

Name	PYRO2	PYRREAC1	PYRREAC2
Property method	PENG-ROB	PENG-ROB	PENG-ROB
Use true species approach for electrolytes	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3
Specified pressure [bar]	0,02	1,1	1,2
Specified temperature [C]	520	320	520
Specified heat duty [Watt]	-308000	-308000	
Outlet temperature [C]	520	320	520
Outlet pressure [bar]	0,02	1,1	1,2
Calculated heat duty [Watt]	22047,8243	-178887,336	-50365,1343
Net heat duty [Watt]	22047,8243	-178887,336	-50365,1343
Calculated vapor fraction	0,258219901	1	1
First liquid / total liquid	1		
Total feed stream CO2e flow [kg/hr]	6,0986517	0	7,84668458
Total product stream CO2e flow [kg/hr]	7,84652049	61,2574085	19,9157975
Net stream CO2e production [kg/hr]	1,7478688	61,2574085	12,0691129
Total CO2e production [kg/hr]	1,7478688	61,2574085	12,0691129

Table C.21: Aspen data for mixers in PVC process.

Name	B3	B8	B9	MIXER3
Property method	PENG-ROB	PENG-ROB	PENG-ROB	PENG-ROB
Henry's component list ID				
Electrolyte chemistry ID				
Use true species approach for electrolytes	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3
Specified pressure [bar]	0	0	0	0
Temperature estimate [C]				
EO Model components				
Outlet temperature [C]	520,000036	61,3398573	91,2190693	9,39496964
Calculated outlet pressure [bar]	1,2	1	1	3,83489119
Vapor fraction	1	0,809945032	0,480820179	0
First liquid /Total liquid	1	1	1	1
Total feed stream CO2e flow [kg/hr]	19,9157975	7,84668458	7,84669152	2,06764844
Total product stream CO2e flow [kg/hr]	19,9157975	7,84668458	7,84669152	2,06764844
Net stream CO2e production [kg/hr]	0	0	0	0

Table C.22: Aspen data for splitter in the PVC process.

Name	B13
Property method	PENG-ROB
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
First outlet stream	0,81336
First specified split fraction	0,81336
First calculated split fraction	0,81336
Second calculated split fraction	0,18664

Table C.23: Design specifications (part 1) on certain equipment in the PVC process.

Name	B2	DSCOMP1	DSCOMP2	DSCOMP3	DSCOMP5
Specification	CACO3	TCOMP	TCOMP	PCOMP	PCOMP
Specification target	0.5*HCL	390	390	PFLASH + 0.3	PFLASH + 0.3
Specification tolerance	0.01	0.1	0.1	0.01	0.1
Lower bound	0.01	0.1	0.1	0.1	1.2
Upper bound	1000	1000	1000	10	5
Comment	Stoichiometric inflow of limestone to reactor.	Vary compressor work so that maximum temperature out is 390 °C.	Vary compressor work so that maximum temperature out is 390 °C.	Vary compressor work so that the outlet pressure is compensating the subsequent pressure drop.	Vary compressor work so that the outlet pressure is compensating the subsequent pressure drop.

Table C.24: Design specifications (part 2) on certain equipment in the PVC process.

Name	DSFLASH	DSFLASH2	DSPUMP2	SPLITB13	VARYO2	VARYO25
Specification	(BENZYL+CHLOROB)*1e6	(BENZYL+ CHLOROBE)*1e6	PPUMP	QR2	FO2IN/FO2OUT	FO2IN/FO2OUT
Specification target	10	10	PFLASH2	-178.9	6	6
Specification tolerance	0.1	0.01	0.01	0.01	0.1	0.1
Lower bound	1	0.1	1	0.5	0.001	0.001
Upper bound	5	5	10	1	100000	1000000
Comment	< 10 ppm chlorinated HCs. Vary flash operating pressure so that the target is achieved.	< 10 ppm chlorinated HCs. Vary flash operating pressure so that the target is achieved.	Vary pump2 outlet pressure so that it equals flash2 outlet pressure.	Vary splitter ratio so that the furnace heat demand is satisfied.	Gives an air flow to combustors so that 1.2 in air to fuel ratio is achieved. Accomplished by varying the inlet air molar flow rate.	Gives an air flow to combustors so that 1.2 in air to fuel ratio is achieved. Accomplished by varying the inlet air molar flow rate.

Table C.25: Aspen data for utilities in the PVC process.

Name	CW	FIREHEAT	HPSGEN	HPSTEAM	LPSGEN	LPSTEAM	MPSGEN	MPSTEAM	REFRIGER
Utility type	WATER	GENERAL	STEAM	STEAM	STEAM	STEAM	STEAM	STEAM	REFRIGERATIO
Specified cooling value [J/kg]		600000							-4000
Specified energy price [$/J]	2,12E-10	4,25E-09	-1,48867E-08	1,48867E-08	-7,73841E-09	7,73841E-09	-1,13126E-08	1,13126E-08	2,74E-09
Specified inlet pressure [bar]	1,01325								
Specified outlet pressure [bar]	1,01325								
Specified inlet temperature [C]	20	1000	249	250	124	125	174	175	-25
Specified outlet temperature [C]	25	400	250	249	125	124	175	174	-24
Specified inlet vapor fraction	0	1	0	1	0	1			
Specified outlet vapor fraction	1	0	1	0	1	0			
Specified CO2 emission factor [kg/J]	5,589E-08	5,589E-08	5,589E-08	5,589E-08	5,589E-08	5,589E-08	5,589E-08	5,589E-08	
Specified CO2 energy source efficiency factor	1	0,85	-0,85	0,85	-0,85	0,85	-0,85	0,85	1
Calculated heating/cooling value [J/kg]	-20875,7611	600000	-1719323,71	1719323,71	-2191878,97	2191878,97	-2034751,64	2034751,64	-4000
Calculated inlet enthalpy [J/kg]	-15886670,9	-14890752,4	-13171428,7	-15450574,8	-13258695,8	-15234876,7	-13200125,1		
Calculated outlet enthalpy [J/kg]	-15865795,1	-13171428,7	-14890752,4	-13258695,8	-15450574,8	-13200125,1	-15234876,7		
Calculated inlet pressure [bar]	1,01325	39,0866691	39,7537159	2,25120518	2,32178779	8,7169648	8,92539509		
Calculated outlet pressure [bar]	1,01325	39,7537159	39,0866691	2,32178779	2,25120518	8,92539509	8,7169648		
Calculated inlet temperature [C]	20	1000	249	250	124	125	174	175	-25
Calculated outlet temperature [C]	25	400	250	249	125	124	175	174	-24
Calculated inlet vapor fraction	0	0	1	0	1	0	1		
Calculated outlet vapor fraction	0	1	0	1	0	1	0		
Calculated purchase price [$/J]	2,12E-10	-1,48867E-08	1,48867E-08	-7,73841E-09	-1,13126E-08	2,74E-09			
Calculated total cost [$/sec]	1,80727204E-05	0	-1,07750145E-05	0,000144411263	-0,000110676536	0	-0,000382389812	0	7,84779974E-06
Calculated total usage rate [kg/hr]	14701,0329	0	1,51552909	20,3117564	23,4903644	0	59,804653	0	2577,74444
Calculated CO2 emission factor [kg/J]	5,589E-08	5,589E-08	5,589E-08	5,589E-08	5,589E-08	5,589E-08	5,589E-08	5,589E-08	
Calculated CO2 emission rate [kg/hr]	-0,171331459	2,29625606	-3,38548979	-8,00131864	0,576280547				

Figure C.1 show the full model flowsheet of the PVC process.

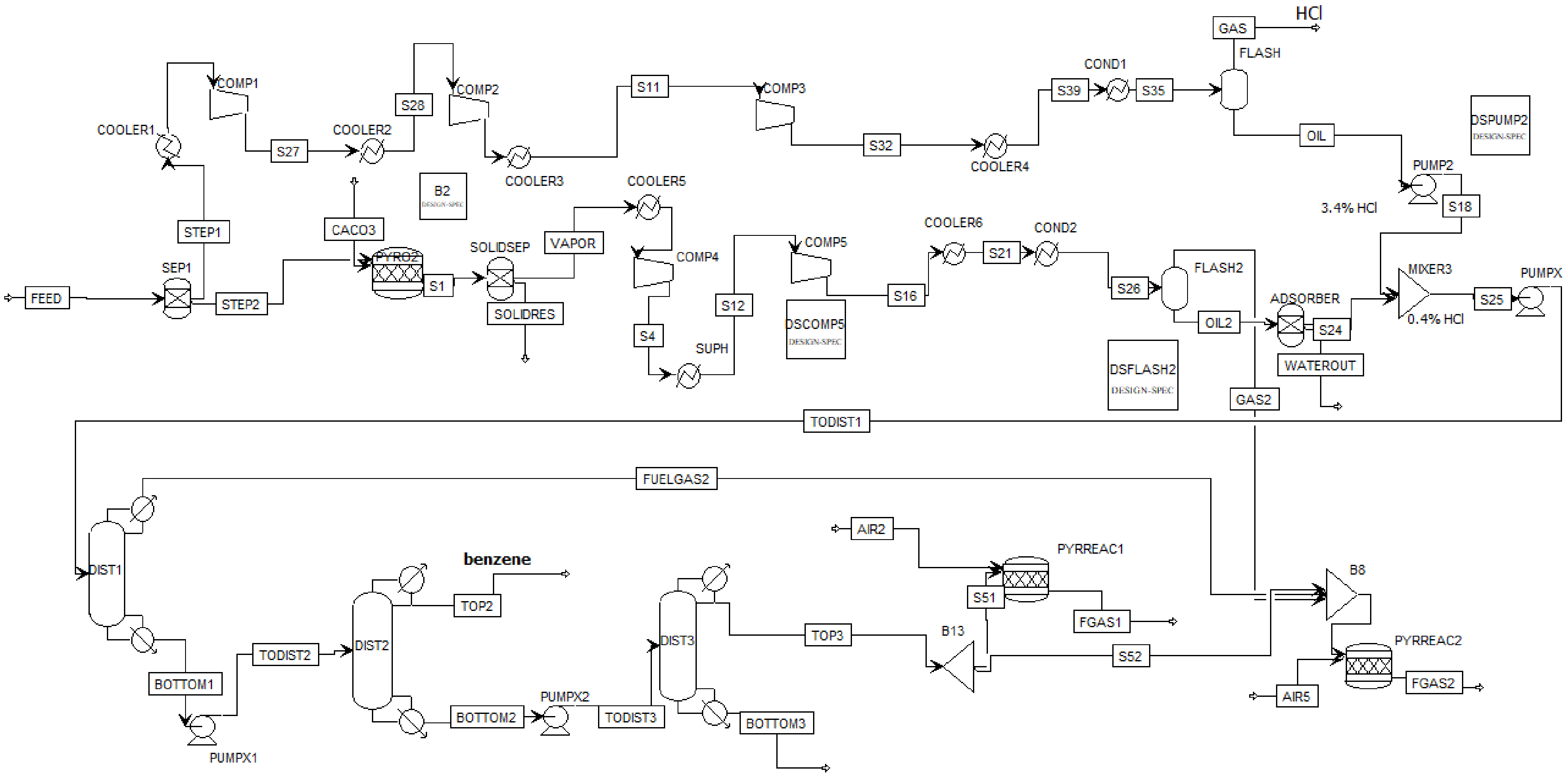


Figure C.1: Aspen flowsheet of the PVC process.

D

Pyrolysis reactor calculations

D.1 DFB costs

Where a fluidized bed reactor is used, the investment costs for the pyrolysis reactor, the feeding system, the combustor and the flue gas train are calculated using economic parameters from Alamia et al. [68]. The costs are calculated with the formula $C = C_{ref}(\frac{P}{P_{ref}})^{SF}$. The reference power P_{ref} is 20 MW, and the other parameters are given in Table D.1. The study by Alamia et al. considers a gasifier, converting biomass into syngas (carbon monoxide and hydrogen) which is subsequently methanized, and the power refers to the output of methane. Here, the output of pyrolysis products are used as the power.

Table D.1: Parameters for DFB investment cost calculations [68].

Part of process	C_{ref} [M€]	SF
Fuel feeding	8.25	0.62
Gasifier	11	0.8
Flue gas cleaning	8.25	0.55

D.2 Heat requirements

To calculate the heat demand for pyrolysis, assuming that the fluidization medium does not partake in the reactions, the pyrolysis process can be divided into the following steps:

$$\text{Polymer (25 °C)} \rightarrow \text{Monomer (25 °C)} \rightarrow \text{Pyrolysis products } (\text{T}_{\text{reactor}}) \tag{D.1}$$

The first step is the depolymerization, for which the heat is the negative of the heat of polymerization, readily available in literature [38]. For the second step, the total heat can be found by subtracting the enthalpy for the entire product stream by the enthalpy of the corresponding amount of monomer. Aspen automatically calculates these values for any stream that is put into the model. To these heats, the heat required for the fluidization gas is added, depending on the extent to which it can be preheated by heat integration. The total heat that must be supplied by the combustor can thus be calculated:

$$\begin{aligned}\dot{Q}_{comb} &= \dot{Q}_{out} - \dot{Q}_{in} \\ &= \dot{m}_{out}h_{out}(T_{reactor}) - \Big(\sum_{polymers} \dot{m}_{polymer}h_{polymer}(25\ °\text{C}) + \dot{m}_{gas}h_{gas,in}\Big)\end{aligned} \tag{D.2}$$

with $h_{polymer} = h_{monomer} + h_{polymerization}$, and index "out" referring to pyrolysis products and fluidization gas together.

E

Dimensions of adsorber

Both the mixed and the PVC process uses adsorbers where the dimensions are calculated outside Aspen. The procedure is described below. Water is adsorbed by a zeolite with data given below in Table E.1.

Table E.1: Used data for the zeolite to capture water.

Zeolite bulk density [kg/m^3]	Equilibrium water capacity [wt%]
700	21

The adsorbers are used in pairs where one operates at a time, for 24 hours straight. Meanwhile, the other adsorber is regenerated for a new operation cycle. The zeolite is assumed to be 70 % saturated at the end of the cycle. The water mass flow is extracted from Aspen and combined with the equilibrium water capacity, the uninterrupted run time and the saturation efficiency to calculate the required adsorber mass in kg, Equation E.1:

$$\text{Adsorber mass} = \frac{\text{Water mass flow } [kgw/day] \cdot \text{Uninterrupted runtime [days]}}{\text{Equilibrium water capacity } [kgw/kgzeolite] \cdot \text{Efficiency}} \tag{E.1}$$

The adsorber volume (V_{ads}) is calculated from the adsorber mass and the zeolite density:

$$V_{ads} = \frac{\text{Adsorber mass } [kg]}{\text{Zeolite density } [kg/m^3]} \tag{E.2}$$

The velocity (v) of gas through the column is assumed to be 0.1 m/s and for liquid 0.01 m/s. The cross-sectional area of the column is calculated based on the volumetric flow rate of the stream in, the assumed void fraction of the column of 0.4 and the velocity of the stream:

$$A_{cs} = \frac{\text{Volumetric flow rate } [m^3/s]}{\text{Void frac} \cdot \text{v } [m/s]} \tag{E.3}$$

The column height (H) is now easily derived from the adsorber volume and the cross-sectional area:

$$H = \frac{V_{ads}}{A_{cs}} \tag{E.4}$$

Finally, the diameter (D) is calculated assuming the columns are cylindrical:

$$D = \sqrt{\frac{4A_{cs}}{\pi}} = 2\sqrt{\frac{A_{cs}}{\pi}} \tag{E.5}$$

In those cases where the height to diameter ratio (H/D) exceeds 20, the dimensions are adjusted so a ratio of 20 is achieved.

F

Vacuum pump calculations

The vacuum system in the PS processes is modelled as a vacuum pump in Aspen. The type is chosen to be oil-sealed vacuum pump because it will handle the low pressure of 6.89 kPa [90], and it can be cost estimated in Aspen. The dimension is calculated and input in Aspen, allowing the software to estimate the cost. The distillation column Dist4 shown in Figure 4.4 has dimensions presented below for each of the plant sizes:

Table F.1: Dimensions of the distillation tower separating styrene under vacuum. Applicable for both the PS processes.

Plant size [t/yr]	Diameter [m]	Vessel height [m]	Vessel volume [m^3]
2100	0.9144	19.51	12.8
21000	2.90	19.51	128.9

Assuming that only air is leaking in to the system and needs to be pumped away, the amount of air leakage is taken as the highest value from Figure 4 in [90], at the distillation vessel volume. The air leakage is calculated in volumetric rate which is input in Aspen to estimate the cost. The density of air at 6.89 kPa and 65°C was taken as 0.0707 kg/m^3. The values are presented below:

Table F.2: Calculated data for the vacuum pumps at each plant size.

Plant size [t/yr]	Air leakage [kg/h]	Air leakage [m^3/h]	Size factor	Break power (kW)
2100	4.5	63.65	0.191	1.67
21000	11.2	158.42	0.476	3.87

The size factor (SF) is calculated with the expression

$$\mathrm{SF} = \frac{2.2 \cdot \text{Air leakage [kg/h]}}{\text{Operating pressure } [mmHg]} \tag{F.1}$$

and the break power (P) in kW is found as:

$$P = 7.68 \cdot \mathrm{SF}^{0.924} \tag{F.2}$$

For liquid ring-sealed pumps the valid range of SF is $0.05 - 35$. The calculated size factors and power are found in Table F.2. The power of the vacuum pumps is added to the rest of the power consumption that Aspen gives.

G

Calculations for packed column

The vacuum distillation column used for styrene separation in the PS processes is of the type packed column because the pressure drop is lower than for a column with trays. The cost of the packing material was calculated outside Aspen using cost equations in [62]. Aspen estimates the dimensions for each of the vacuum columns in the respective plant sizes. The values are presented in Table G.1. In the study by Bassil et al (2018) they used a metal pall ring (FlexiRing) [40]. The data from this study is used to calculate the amount of necessary packing material here. The height equivalent of a theoretical stage (HETP) is the height of a theoretical stage if the column used trays. The calculations to find HETP are cumbersome so simplifications are made. In Bassil et al (2018), they used a HETP value of 0.381 m (1.25 ft) and a packing void fraction of 0.93. The values are also used in this study.

Table G.1: Column data for the PS processes at the different plants sizes.

Plant size [t/yr]	Diameter, D_c [m]	Equilibrium stages
2100	0.9144	20
21000	2.90	20

The number of equilibrium stages from Aspen is combined with the HETP from the study by Bassil et al (2018) to find the height (h) of the packed section, according to:

$$h = \text{Equilibrium stages} \cdot \text{HETP} \tag{G.1}$$

The height is used together with the column diameter (D_C) and the void fraction to derive the packed section volume (V_{pack}):

$$V_{pack} = \pi \left(\frac{D_c}{2} \right)^2 \cdot \text{HETP} \tag{G.2}$$

The volume is used in the cost equation below [62]:

$$\text{Cost (US\$ 2010)} = a + b \cdot V_{pack}^{c} \tag{G.3}$$

where a, b and c are constants. The constants are taken for SS304 pall rings and are presented in Table G.2 [62].

Table G.2: Constants for SS304 pall rings, taken from [62].

a	b	c
0	8500	1

The estimated cost is in $US\$$ of 2010 with a Chemical Engineering Plant Cost Index (CEPCI) of 532.9 [62]. This is recalculated by the average 2018 CEPCI of 603.1 [91] by:

$$\text{Cost (US\$ 2018)} = \frac{\text{CEPCI 2018}}{\text{CEPCI 2010}} \cdot \text{Cost (US\$ 2010)} \tag{G.4}$$

H

Calculation of steam prices

The procedure for calculating steam prices is taken from [92]. It is briefly described in this section.
Expression for calculating the cost of generating steam (C_G) is given in Equation H.1:

$$C_G = C_F + C_W + C_{BFW} + C_P + C_A + C_B + C_D + C_M \tag{H.1}$$

where the different variables are given in the list below:

1. Total fuel cost (C_F)
2. Raw water supply (C_W)
3. Boiler feed water treatment - including clarification, softening and demineralization (C$_{BFW}$)
4. Feedwater pumping power (C$_p$)
5. Combustion air fan power (C_A)
6. Sewer charges for boiler blowdown (C_B)
7. Ash disposal (C_D)
8. Environmental emission control (C_E)
9. Maintenance, materials and labor (C_M)

The fuel cost (C_F) is the main contributor to the cost, roughly 90 % of the total. The total fuel cost is given by the expression:

$$C_F = a_F \cdot \frac{(H_S - h_W)}{\eta_B} \tag{H.2}$$

where a_F is the cost of fuel, η_B is the boiler efficiency and H_S and h_w is the enthalpy of HP steam and boiler feedwater, respectively. Considering the total fuel cost being predominant, an approximation of Equation H.1 is usually enough:

$$C_G = C_F \cdot (1 + 0.3) \tag{H.3}$$

where 0.3 is a typical number for category 2-9 in oil- and gas-fired facilities. In Sweden, biomass is a common fuel and this approximation might not be truly valid, still the assumption is made for simplification.

For a plant producing the steam on-site, the cost of steam generation (C_G) is the only factor to consider. If the cost of HP steam (C_{HP}) is assumed to be equal to C_G, the cost of generating LP steam by a back-pressure turbine can be estimated by the expression:

$$C_{LP} = C_{HP} - a_E \cdot \frac{(H_S - H_{SL})}{\eta_T \cdot \eta_G} \tag{H.4}$$

where a_E is the electricity cost, H_{SL} is the enthalpy of low-pressure steam from isentropic expansion of HP steam and η_T and η_G are the isentropic turbine efficiency and the generator electrical efficiency, respectively. Values used in these calculations are presented in Table H.1.

Table H.1: Values of different parameters to estimate the cost of steam

Parameter	Value	Unit	Comment	Reference
a$_F$	195	SEK/MWh	Skogsflis	[93]
H$_S$	2800	kJ/kg	Saturated steam ≈ 250°C	Read from Mollier chart
h$_w$	105.6	kJ/kg	Saturated liquid ≈ 25 °C	Read from Mollier chart
η_b	0.8	-	-	[92]
H$_{SL}$	2300	kJ/kg	-	Read from Mollier chart
η_T	0.85		-	
η_g	0.99		-	
$\Delta H_{vap,250}$	1713	kJ/kg	-	Read from Mollier chart
$\Delta H_{vap,125}$	2245	kJ/kg	-	Read from Mollier chart

The cost of MP steam is taken as the average of the HP and LP steam cost. With the presented procedure, the costs are calculated and the result is presented in Table H.2.

Table H.2: Calculated costs of steam at different levels.

	LP steam	MP steam	HP steam
Cost (SEK/kWh)	0.259	0.379	0.498

I

Validation of thermodynamic properties

For the PS processes, two modelled compounds are not found in the Aspen compound data base. These are 2,4-diphenyl-1-pentene ($\mathrm{C_{17}H_{18}}$) and 2,4,6-triphenyl-1-hexene ($\mathrm{C_{24}H_{24}}$), respectively. The compounds are added manually by drawing the molecular structure in Aspen, by the built in "User defined" tab in the component section. The molecular structures are found in Figure I.1. Due to the lack of data on these compounds, Aspen is allowed to manually estimate the thermodynamic properties. These estimates are verified by comparing liquid density (ρ_L), ideal gas heat capacity ($C_{p,g}$) and boiling point (T_b) with experimental data from similar compounds. 2,4-diphenyl-1-pentene is compared with the isomer 1,1-diphenyl-1-pentene and 2,4,6-triphenyl-1-hexene is compared with the isomers 5-n-hexyl-1,2-benzanthracene and 2-hexyltetracene. For 2,4,6-triphenyl-1-hexene, ρ_L and T_b are compared with data for 5-n-hexyl-1,2-benzanthracene and $C_{p,g}$ is compared with 2-hexyltetracene.

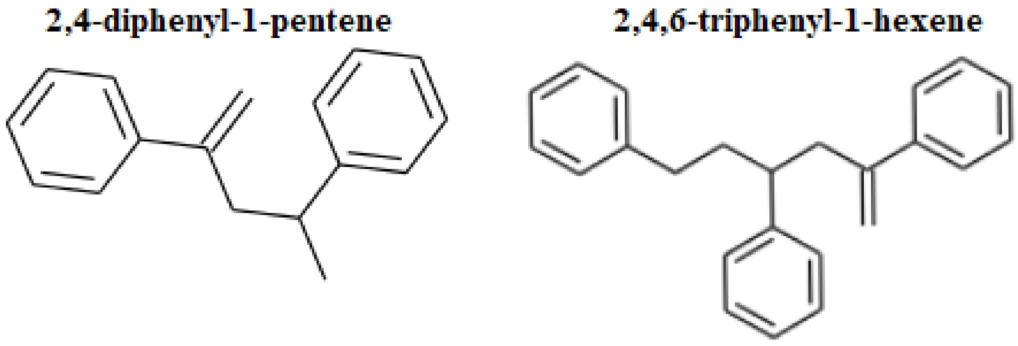


Figure I.1: The molecular structures of 2,4-diphenyl-1-pentene and 2,4,6-triphenyl-1-hexene.

The boiling points estimated by Aspen are compared with data found in literature [94]. The comparison is presented in Table I.1. The deviation is high for $C_{24}H_{24}$, close to 20%. One explanation is the difference in molecular structure between the two isomers, making it reasonable that the actual boiling points for 2,4,6-triphenyl-1-hexene and 5-n-hexyl-1,2-benzanthracene should differ. There is a possibility that boiling points for mixtures are estimated by Aspen to be slightly lower than the actual boiling point. However, since there is such small amount of $C_{24}H_{24}$ in the system, this should not pose a major problem. The only thing that can actually be verified is that the boiling point should be higher than 350°C, as seen in Table 4.4, and this is correctly estimated by Aspen.

Table I.1: Boiling points estimated by Aspen and taken from literature for comparison.

Compound	$T_{b,Aspen}$ $[°C]$	$T_{b,Literature}$ $[°C]$	Deviation [%]
$C_{17}H_{18}$	313.30	308.76	1.45
$C_{24}H_{24}$	435.69	519.36	19.2

Liquid densities as a function of temperature are taken in Aspen from analysis of pure compounds. The points are compared with densities found in literature for similar compounds [95]. The values are presented in Table I.2-I.3. The highest deviation is roughly 6.6 % which is low, concluding that the estimated densities are verified.

Table I.2: Comparison between densities from Aspen and those found in literature for $C_{17}H_{18}$.

T [°C]	$\rho_{L,Aspen}$ [kg/m^3]	$\rho_{L,Literature}$ [kg/m^3]	Deviation [%]
25	1011.12	977.58	3.32
50	990.10	961.53	2.89
80	970.87	941.89	2.99
102	952.38	927.19	2.65
135	925.93	904.62	2.30
168	900.90	881.37	2.17
201	869.57	857.34	1.41
245	833.33	823.87	1.14
278	806.45	797.49	1.11
300	787.40	779.18	1.04

Table I.3: Comparison between densities from Aspen and those found in literature for $C_{24}H_{24}$.

T [°C]	$\rho_{L,Aspen}$ [kg/m^3]	$\rho_{L,Literature}$ [kg/m^3]	Deviation [%]
25	1002.00	1034.16	3.21
50	990.10	1023.77	3.40
80	970.87	1008.00	3.82
102	961.54	997.36	3.72
135	943.4	981.18	4.00
168	917.43	964.73	5.16
201	900.90	947.99	5.23
245	877.19	925.17	5.47
278	854.70	907.65	6.19
300	840.34	895.75	6.59

The ideal gas heat capacities are also taken from analysis of pure compounds in Aspen. For $C_{17}H_{18}$, experimental values for comparison are taken from [96] and for $C_{24}H_{24}$ calculated values from predictive C_p model are taken from [97]. The results and comparison for $C_{17}H_{18}$ can be found in Table I.4 and for $C_{24}H_{24}$ in Table I.5. Similar to the liquid densities the deviation is small, 5.9 % in the worst case. It can be concluded that the estimation by Aspen is reasonable and that the heat capacities are verified.

Table I.4: Comparison between ideal gas heat capacities from Aspen and those found in literature for $C_{17}H_{18}$.

T [°C]	$C_{p,g,Aspen}$ [kJ/(kmol·K)]	$C_{p,g,Literature}$[kJ/(kmol·K)]	Deviation [%]
303	481.39	466.91	3.00
327	494.68	480.63	2.84
367	515.45	502.21	2.57
431	545.25	533.41	2.17
479	565.05	554.11	1.94
527	582.86	572.50	1.78
583	601.38	591.04	1.72
631	615.53	604.43	1.80
679	628.26	615.51	2.03
711	636.04	621.62	2.27

Table I.5: Comparison between ideal gas heat capacities from Aspen and those found in literature for $C_{24}H_{24}$.

T [°C]	$C_{p,g,Aspen}$ [kJ/(kmol·K)]	$C_{p,g,Literature}$[kJ/(kmol·K)]	Deviation [%]
303	667.63	628.28	5.89
327	686.04	648.27	5.5
367	714.74	679.90	4.87
431	755.78	726.13	3.92
479	782.94	757.27	3.28
527	807.32	785.38	2.7
583	832.61	814.36	2.2
631	851.88	835.92	1.87
679	869.20	854.45	1.70
711	879.76	865.12	1.66