Techno-economic evaluation for FDPA, a novel biobased monomer

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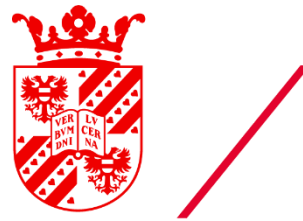
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Summary

Traditional polymer production is under constant scrutiny due to plastic production being one of the main polluters on the planet with their petrochemical feedstocks. Biobased polymers on the other hand, are defined as polymers which can be produced from biomass feedstocks therefore, severing the reliance on petrochemical feedstocks and their destructive effect on our plant. In order to produce these polymers, biobased monomers are required on a large scale. However, research into these biobased molecules is limited and their potential for commercial applications is not yet fully realized. Furan-2,5-dipropionic acid (FDPA) is one such biobased monomer which may have potential to be produced on a large scale to feed the biobased polymer industry in the future.

This research aims to discover this potential by calculating an estimate for the production cost, desired profit margin and therefore the selling price of FDPA. To calculate this selling price a synthetic route of FDPA utilizing furfural and levulinic acid feedstocks and sodium carbonate catalyst is selected and a commercial scale process design is produced. From this design an economic evaluation of FDPA is made, calculating the production costs and desired profit of the process to be €5105 and €942 per tonne of FDPA respectively. These values determine a selling price of €6047 per tonne of FDPA produced from the proposed process. From these values, the economic feasibility of FDPA is concluded by comparing the production cost of FDPA with that of biobased market competitor FDCA which has a production cost of €3700.

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1. Introduction

Biobased polymers are of high interest due to the large quantities of petrochemicals required to produce conventional plastics, which are used in everyday life, and the corresponding negative impact that this has on the planet. As the name suggests, biobased materials are materials which can be produced from biomass feedstocks and therefore, sever the reliance on alternate feedstocks such as petrochemicals. In order to produce these polymers, biobased monomers are required on a large scale. However, research into these biobased molecules is limited and their potential for commercial applications is not yet fully understood.

FDPA is one such biobased monomer which may have potential to be produced on a large scale to feed the biobased polymer industry in the future. The economic potential of identifying a novel biobased monomer such as FDPA would be great if the production process were determined to be feasible as, the biobased monomer market is largely untapped with room for expansion within the market. With no information on whether FDPA can be produced commercially, this research identifies the most promising synthetic route to produce FDPA and determines a preliminary process design for commercial production. A techno-economic evaluation of the process design is conducted in order to obtain a first estimate for the potential selling price of FDPA which will offer insight into whether FDPA can compete in the future in the biobased monomer market. The objective of this study is to obtain an initial estimate for the selling price of FDPA.

The structure of this research is as follows. Firstly, a problem context provides background information on biobased monomers and details of FDPA and its synthesis. Included in the problem context are the research statement, objective and questions to provide the direction in which the study is aiming for. Next, a literature review is presented which contains more detailed information on the synthesis of FDPA as stated in previous studies. In addition to synthetic route information, the literature review includes an overview of the Principles of Green Chemistry which will be used for the evaluation of the various synthetic routes found. Using data from the literature review, a detailed analysis of the possible synthetic routes of FDPA is made and a selection process is conducted to attain the most promising synthetic route for adaptation for a continuous process. A preliminary process design is generated for the chosen route and flows are calculated to form a basis for the economic analysis to be conducted. The result of the economic analysis will yield a selling price for FDPA based on the process design and economic metrics will be used to discuss the feasibility of FDPA production. Finally, a sensitivity analysis will be performed for the process with the intention of identifying process parameters which can be changed to improve the feasibility of the process. After the conclusion of this study, the intention is to provide an insight into the economic feasibility of the process and, as a result, the future of FDPA production.

2. Problem context

In this section of the report, general background information regarding the production of FDPA is provided in order to provide insight and direction into the proceeding research.

2.1. Biobased monomers

As the name suggests, a biobased monomer is a molecule which can be synthesised from renewable sources such as biomass instead of conventional petroleum sources (Masutani, and Kimura, 2015). While biomass has been used commonly as a fuel throughout human history, the use of biomass, specifically biobased monomers, as the chemical building blocks for industry is reasonably uncommon, as stated by (Nakajima, 2017). However, as public concern regarding fossil fuel usage has grown in previous years, the search for alternative, renewable methods has escalated. This has culminated in research being conducted into biobased polymer production as, conventional polymer production requires petrochemical feedstock. The already high and growing interest in biobased polymers makes the biobased monomers from which they are derived, highly desirable. While interest is high in biobased monomers, the industrial potential and economic feasibility is still yet to be determined as, limited research has been conducted in the industrial setting for many of these molecules.

2.2. FDPA

FDPA is a novel biobased monomer for which little research has been conducted into. However, the structure of the molecule is very similar to that of Furan 2,5-dicarboxylic acid (FDCA), with the main distinction between the two being that FDPA has two additional carbons linking each carboxylic acid group to the furan ring, illustrated in figures 1 and 2.
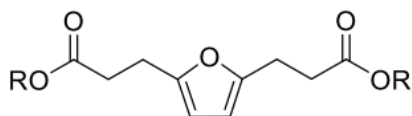
Figure 1- Molecular structure of FDPA (Lewkowski J, 2001)

Figure 2- Molecular structure of FDCA (Gruter & de Jong, 2009)

Due to the lack of information with regards to FDPA and the similarity between FDPA and FDCA, FDCA will be used to provide context to gain further insight into the technical and economic feasibility of industrial FDPA production. Both molecules can be considered Furnanics due to the aromatic furan ring in the molecule's structures (Gruter & de Jong, 2009). FDCA, like FDPA, is considered a biobased monomer as, it can be derived from 5-hydroxymethylfurfural (HMF) which is produced using hexose feedstock sources such as fructose, glucose, mannose, polyfructosane (inulin), LCF, cellulose and wood (Gruter & de Jong, 2009). Commercial plants have been planned for FDCA production by the company Avantium for 2023 (Avantium.com). This is promising for research conducted into FDPA as, it suggests that there is a demand and potential market for biobased monomers such as FDPA. However, this does not provide any certainty that FDPA production will be technically or economically feasible on commercial scale as, the synthetic routes and starting materials required to produce FDPA differ to that of FDCA. With respect to FDPA, it is stated that furfural and levulinic acid, and 2,5-diformylfuran (DFF) can be used as feedstocks for production by two separate synthetic routes on a lab scale (Hachihama & Hayashi,

1954) (Serum, 2018). These feedstocks can all be sourced from the degradation of biomass and therefore sever the ties to the reliance on petroleum-based and natural gas feedstocks (Hachihama & Hayashi, 1954) (Dai, 2021).

2.3. Synthetic routes

As FDPA is a novel chemical, a limited variety of information on preparation techniques and methods is available. Despite this, (Hachihama & Hayashi, 1954) and (Serum, 2018) provide detailed synthetic routes to obtain FDPA from furfural and levulinic acid, and DFF. It is stated that furfural and levulinic acid are of high interest as they can be obtained from degrading carbohydrates with acid at a low cost and in abundancy from agricultural and industrial waste/by-products. Similarly, it is stated by (Dai, 2021) that DFF can be produced from carbohydrate derived HMF through oxidation, or from fructose by dehydration and oxidation and is therefore of high interest for the same reasons as stated above. Synthetic routes 1 and 2 are obtained from (Hachihama & Hayashi, 1954) and (Serum, 2018) respectively.

Synthetic route 1:

From furfural and levulinic acid, δ-furfurylidenelevulinic acid can be produced through either being heated with a strong alkali, such as sodium hydroxide, in a condensation reaction or by being heated with a weak alkali, such as sodium carbonate, in a condensation reaction. While the reaction with a weak alkali had a lower reaction rate, the yield was greater than that of the reaction with a strong alkali. Furthermore, the reaction in the presence of a strong alkali produced β-furfurylidenelevulinic acid as a major product and β,δ-difurfurylidenelevulinic acid and resinous by-products were produced despite careful control of the reaction conditions. Therefore, the reaction route in the presence of weak alkali is preferred.

Alternative pathways for the aldol condensation reaction to obtain δ-furfurylidenelevulinic acid from furfural and levulinic acid are also available. These are characterised by heterogenous catalysts taking the place of sodium carbonate in the reaction. The most promising catalysts found, by looking at selectivity and yield of δ-furfurylidenelevulinic acid, were found to be magnesium oxide, as stated by (Su, 2019) and (Liang et al, 2016), and potassium modified, hierarchical MFI zeolite, as stated by (Su, 2019).

Then, from δ-furfurylidenelevulinic acid, dilevulinic acid could be formed through heating it with alcoholic hydrochloric acid. Finally, it is stated that FDPA can be obtained by heating dilevulinic acid at 180°C for 5 hours in a stream of Nitrogen under reduced pressure conditions. Further details regarding the specific conditions of each reaction step and their corresponding yields is provided in (Hachihama & Hayashi, 1954). An overview of the first two reaction steps is illustrated in figure 3 (Li et al 2018).
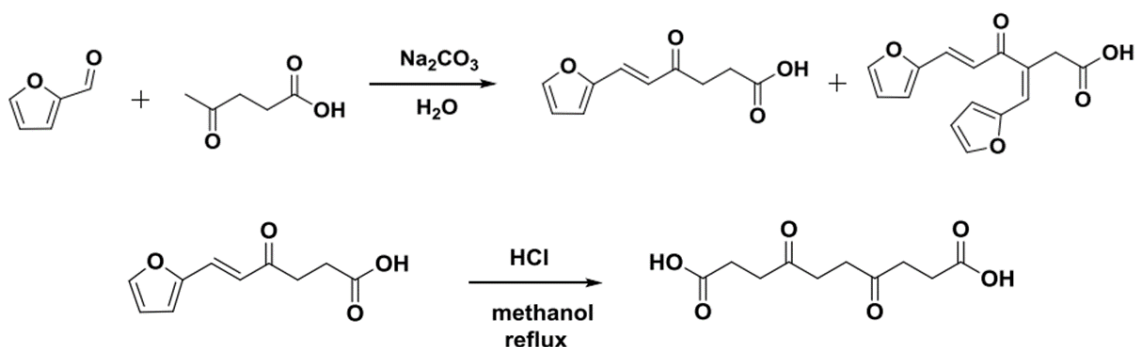
Figure 3-An overview of the first two reaction steps and intermediate products (δ-furfurylidenelevulinic acid and dilevulinic acid) to produce FDPA from furfural and levulinic acid. (Li et al, 2018)

Synthetic route 2:

 From DFF, furan-2,5-diacrylic acid can be produced by mixing with malonic acid, piperidine and pyridine. (Serum, 2018). Next, dimethyl 3,3'-diacrylate is formed by reacting sodium chloride, methanol and sulfuric acid with the product from the previous step. The final reaction step produces FDPA from mixing the dimethyl 3,3'-diacrylate with tetrahydrofuran (diluted with methanol), copper (I) chloride and sodium borohydride. These three steps are illustrated in figure 4 and further detail of the synthetic route is provided by (Serum, 2018).
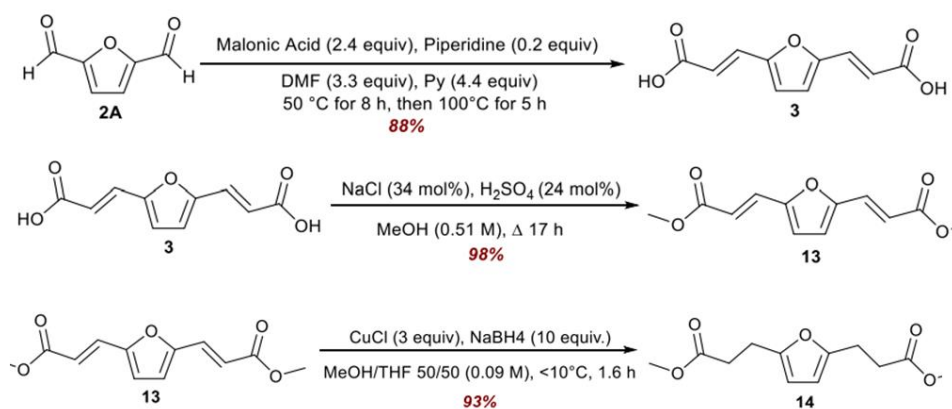
Figure 4-An overview of the reaction steps and intermediate products to produce FDPA from DFF (Serum, 2018)

2.4. Market competition

Currently there is a lack of public information on FDPA being produced on a small scale, let alone commercially. Additionally, as stated by (Motagamwala et al, 2018), there is a limited production of FDCA commercially. It is provided that there are two large scale producers of FDCA, Avantium and a pilot plant from AVA Biochem. As both molecules are similar in structure and can be polymerised, they can be considered potential market competitors.

In order to determine a basic reference for the level of the market competition, the minimum selling price (cost per tonne) of FDCA has been obtained at €3700 per tonne

(Triebl, 2013). This value will provide an aspect of comparison for the price of FDPA determined later in this study due to data corresponding to the minimum selling price of FDPA not being available for commercial production.

2.5. Stakeholder analysis

This research project involves multiple parties with not only a stake in the outcome of the research with respect to the commercial production of FDPA but also the commercial downstream implications such as polymer production. A list of the relevant stakeholders is presented below in table 1 with their relevant interest and power in the research project.

Stakeholders	Description/relevance
Hanzehogeschool Groningen	Hanze is working on synthesising FDPA and developing the process for large scale production with the intention to form a start up company with NHL Stenden for polymer production from FDPA. Therefore, there is high interest in this research present from Hanze. The influence which Hanze holds in this research is of a moderate level as information may be shared between Hanze and the researcher(s).
NHL Stenden	As stated previously, NHL Stenden wishes to start up a company for polymerisation from FDPA if the process is viable on a large scale. Therefore, the interest in the research is high while the influence on the research is low.
Biofuran	Biofuran is a company specialising in organic chemistry, applications of furans derived from biomass (carbohydrates) marketing and techno-economic evaluations. Therefore, they have a high interest marketing capabilities of FDPA for commercial applications and, as a result, the outcome of this research also. However, the power held in this research is low.
CuRe Technology	CuRe Technology is a company specialising in polymer chemistry, chemical recycling polyesters specialties and pilot plant facilities. Therefore, they have a moderate to high level of interest in this research as PEF derived from FDPA is biodegradable. The level of influence held in this research, like Biofuran, is low.

Table 1-presenting the stakeholders of this research project and their relevant interest and power in the research project

Below, in figure 5, a diagram depicting the stakeholders and their respective levels of interest and power is presented.
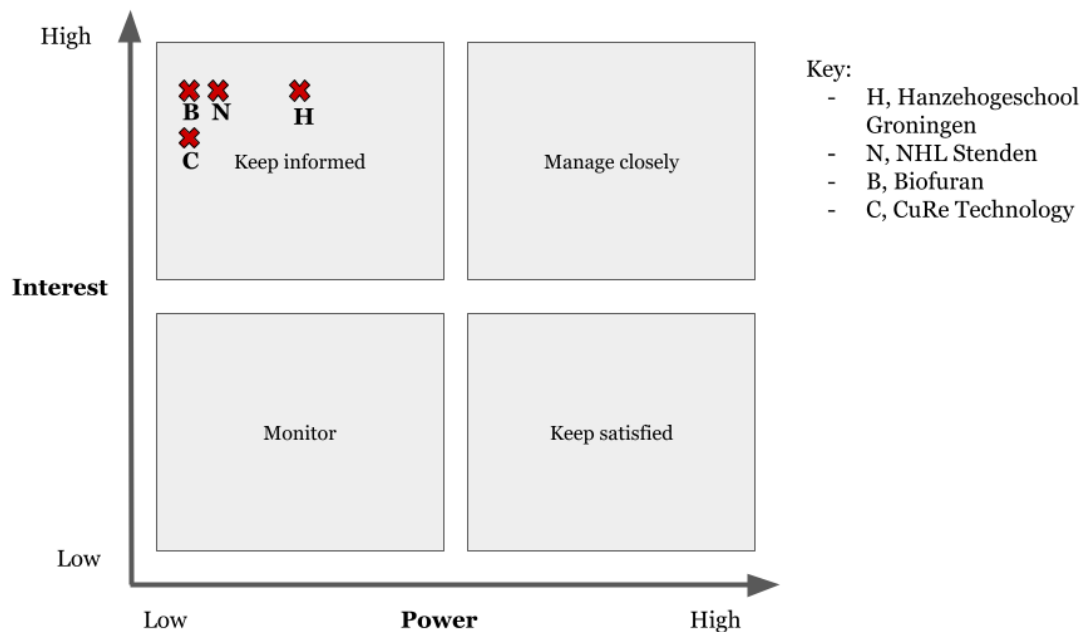
Figure 5- A Mendelow diagram illustrating the relative power and interest of the stakeholders in the outcome of the research project. A key is presented to represent each of the stakeholders.

2.6. System analysis

To further understand the process of determining the commercial potential of FDPA for polymer production, figure 6 presents a system diagram of the FDPA synthetic pathways. The two main chains in the centre of the diagram illustrate the two separate synthetic routes and the reaction conditions for each step in the procedure.

The first route begins with furfural and levulinic acid feedstock which will be used as input for the selected aldol condensation pathways. There are three aldol condensation pathways selected with each route using a different catalyst, as shown in the diagram. The reaction conditions, as obtained from literature, are also presented in the diagram. Leading on from the aldol condensation, the synthetic route to produce FDPA follows the same experimental procedure as stated by (Hachihama & Hayashi, 1954) with the reaction conditions also included for these steps.

The second route begins with DFF which is used as input for the pathway. The reaction conditions, as obtained from literature, are also presented for the following reaction steps (Serum, 2018).

The system boundary for this research is indicated by the solid box outline labelled 'System boundary' and this illustrates that the preparation of the feedstock chemicals and the production of polymers from FDPA will not be included in the scope of this research.
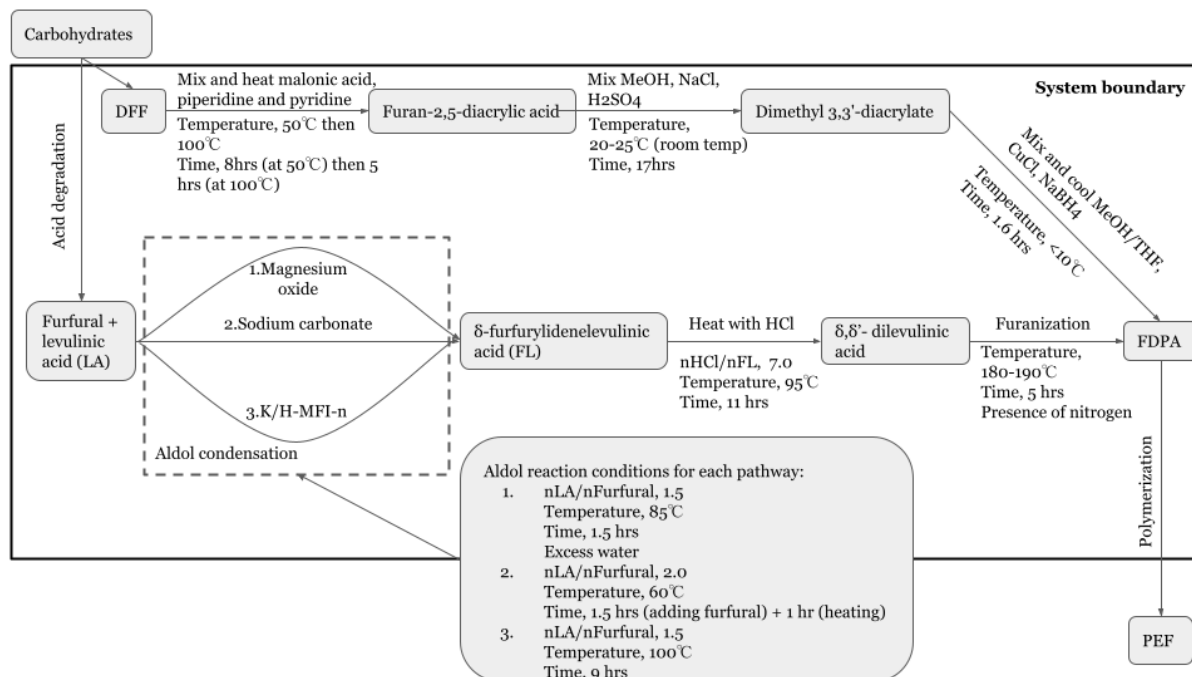
Figure 6- Illustration of the FDPA problem system and the alternate synthetic routes

2.7. Problem statement and objective

From the background information gathered, a problem statement and objective can be produced to convey the direction and purpose of this research paper.

2.7.1. Problem statement

Biobased polymers are becoming of greater interest as the Netherlands and Europe attempt to reduce their reliance on petrochemicals and natural gas. FDPA has been identified as a biobased monomer which has a high potential to be used to produce these polymers of interest. However, commercial production of FDPA and the associated economics of this process have not been established yet. Therefore, the most promising synthetic routes to produce FDPA will need to be determined and from this a preliminary process design, techno-economic evaluation, sensitivity analysis and market analysis needs to be produced in order to make a comparison with the economics of FDCA production so it can be identified whether FDPA production is commercially feasible.

2.7.2. Research objective

As stated in the system description, the scope of this research is to determine the most promising synthetic routes of FDPA production so that a preliminary process design, techno-economic evaluation, sensitivity analysis and market analysis can be produced to identify whether the production FDPA is commercially feasible. The preliminary process design should provide data regarding the amount of raw materials required per tonne of FDPA and provide yield data while the economic analysis should determine the selling price from this data and additional sources. Finally, the feasibility of FDPA production will be determined by comparing the selling price of FDPA with its market competitor, FDCA.

3. Research questions

To ensure that the research project follows the correct path, a set of research questions are formulated. The central research question provides the main aim of the research in its entirety while the sub questions are presented to assist in answering the central question and achieving the research objective.

Central question:

Is large scale production of FDPA technically and economically feasible for commercial biobased polymer production?

Sub questions:

a) What are the relevant factors to evaluate FDPA synthetic routes for commercial production?
b) Which synthetic route is most promising with respect to the factors found?
c) What possible process design can be configured for the most promising FDPA synthetic route found from literature?
d) What value of production cost (€/tonne) can be calculated from the process design of FDPA?
e) For which cost variable is the production cost of FDPA most sensitive?
f) How does the theoretical production cost of FDPA compare to the existing production cost of FDCA?

4. Literature review

The following section will discuss in more detail the synthetic routes which can be used to produce FDPA and the Principles of Green Chemistry using existing literature. Information on the synthetic routes will include reaction steps and conditions, catalyst options, and differences in process starting materials. With respect to the Principles of Green Chemistry, the principles themselves will be stated along with an explanation of each principle. The information presented in this section will be used to provide a basis for the selection of a synthetic route for the process design.

4.1. Synthesis of FDPA

As stated in section 2.3 of the problem context, there are two different primary synthetic pathways for producing FDPA that can be obtained from literature. The first primary route is a three-step batch process presented by (Hachihama & Hayashi, 1954) whereby furfural and levulinic acid undergo an aldol condensation reaction to produce δ-furfurylidenelevulinic acid in the first step. In the second step, δ-furfurylidenelevulinic acid is refluxed under acidic conditions to produce dilevulinic acid. The third and final step states how FDPA is produced from dilevulinic acid heated in a stream of nitrogen. In this study, the reaction conditions are varied for each step of the batch process and the yield of product at each step is calculated after being purified. The reaction conditions which are varied are that of temperature, reaction time, amount of reactant, and amount of solvent involved in each step of FDPA production. Furthermore, the study conducts step one of the reaction with two

different condensing agents, sodium hydroxide and sodium carbonate, the latter of which was determined to be favourable due to the higher yield of δ-furfurylidenelevulinic acid and greater control of reaction conditions. The results of the research provide insight into the reaction conditions required to produce the highest yields of intermediate products and FDPA while providing a detailed experimental setup which can form a basis for producing a preliminary process design. The specific reaction conditions which are required to achieve the highest yields found in the research will be presented in the subsequent sections, 4.1.1, 4.1.2 and 4.1.3.

The second primary synthetic route is a three-step batch process described by (Serum, 2018). The first step of the reaction consists of heating a mixture of DFF, malonic acid, piperidine and pyridine to produce furan-2,5-diacrylic acid. In the second step, a mixture of furan-2,5-diacrylic acid, sodium chloride, methanol and sulfuric acid is refluxed to produce dimethyl 3,3'-diacrylate. In the final step, FDPA is produced by reacting dimethyl 3,3'-diacrylate with tetrahydrofuran (diluted with methanol), copper (I) chloride and sodium borohydride. This research focuses on the valorisation of FDCA by utilizing Diels-Alder reactions with benzene. The overall process which is derived from this research provides a detailed experimental setup, reaction conditions and crude yields, that is the yield before purification, for producing FDCA. However, the product of the third step is FDPA therefore, the first three reaction steps could be used to describe a route of synthesis for FDPA. The details of these three steps from the study are suitable for forming a basis to produce a preliminary process design for FDPA production. The specific reaction conditions which are presented in the research will be discussed in the following sections, 4.1.1, 4.1.2 and 4.1.3.

4.1.1. Starting materials

As discussed briefly in the research context and synthetic routes section, the starting materials of both synthetic routes, although derived from biomass, are different. A difference in starting materials can affect factors such as cost and sustainability. As a result, these differences should be identified and explored.

It is stated by (Hachihama & Hayashi, 1954) and (Li et al, 2018) that the starting materials for primary synthetic route one are furfural and levulinic acid. These are presented as low-cost substances which are in high abundance as, they can be obtained from acid degraded carbohydrates found in agricultural and industrial process waste. The price of furfural and levulinic acid is found to be €700 and €750 per tonne respectively (Alibaba.com) and with developments in biobased monomer production, there is a high possibility that these prices could decrease in the future. The result of sourcing furfural and levulinic acid from waste, in addition to low cost and high availability, is that the sustainability of the process is improved. The notion of sustainable process design is an important aspect in green chemistry and new process designs should work towards producing greener processes. This will be discussed in more detail in section 4.2.

In addition to furfural and levulinic acid, synthetic route one requires ethanol, 37% diluted hydrocholoric acid and a condensing agent as inputs for the process (Hachihama & Hayashi, 1954) (Li et al, 2018). Excluding the condensing agent, the additional substances required for synthetic route one are commonly used in industrial processes and therefore are readily available and relatively low cost at €250

per tonne for hydrochloric acid and €500 per tonne for ethanol (Alibaba.com). Assessing the starting materials and input chemicals as a whole over the first synthetic route suggests that this process may scale up well for commercial production of FDPA as, the substances discussed are low cost and highly abundant while also contributing to issues regarding sustainability which will be discussed further in section 4.2.

The starting materials, as stated by (Serum, 2018), for synthetic route two are DFF and malonic acid. As discussed briefly in the research context, DFF can be derived from biomass. It is presented in (Dai, 2021) that DFF can be synthesised from carbohydrate derived HMF through oxidation, or from fructose by dehydration reactions. Using similar reasoning to that of which was applied to furfural and levulinic acid, DFF can be considered a substance which is of high availability (Dai, 2021). However, due to the fact that DFF is currently mainly produced from HMF, the price of DFF is €1000 per tonne (Shaanxi Dideu Medichem Co. Ltd), greater than that of furfural and levulinic acid. With regards to malonic acid, it can be produced through the fermentation of glucose, as stated by (Peters et al, 2018). However, conventionally malonic acid is synthesised through esterification of carboxylic acids with alcohol which use petroleum feedstocks (Peters et al, 2018). Currently, the latter process is the industry norm with commercial malonic acid production from the fermentation of glucose presenting promise for future developments but, remaining theoretical. Therefore, unlike levulinic acid, furfural and DFF, malonic acid cannot be considered to be derived from biomass. As a result of this, the costs of malonic acid are €1000 per tonne (Alibaba.com).

Where the second synthetic route differs from the first is with respect to the additional substances inputted in the reaction at each step. While the first synthetic route requires three additional substances to produce FDPA, the second route requires eight including, pyridine, piperidine, methanol, sodium chloride, tetrahydrofuran, copper (I) chloride, sulfuric acid and sodium borohydride (Serum, 2018). The result of this is that the material cost of the process increases while the complexity of the process is also increased, leading to greater plant costs.

4.1.2. Reaction steps and conditions

The reaction steps for both synthetic routes have been discussed briefly in the research context and synthesis of FDPA sections however, a detailed description of the reaction steps and conditions has not been presented. The process details for synthetic routes one and two are provided by (Hachihama & Hayashi, 1954) and (Li et al, 2018), and (Serum, 2018) respectively and may be used to produce basis on which a preliminary design for commercial FDPA production can be formed.

As stated by (Hachihama & Hayashi, 1954), synthetic route one begins with producing two solutions, one containing a mixture of furfural and ethanol, and the other containing levulinic acid diluted in water and a condensing agent, sodium carbonate, although alternative condensing agents may be used, this will be discussed in section 4.1.3. Both solutions were added together slowly over a period of 2 hours while heated by boiling water bath before being refluxed for an additional hour. The product of the reaction as stated by (Hachihama & Hayashi, 1954) and (Li et al, 2018) was δ-furfurylidenelevulinic acid which was purified through dissolution, filtration, and crystallization to give isolated yields of 60% and 58% respectively. It should be noted

that within this reaction a by-product of (3Z, 5E)-6-(furan-2-yl)-3-(furan-2-ylmethylene)-4-oxohex-5-enoic acid is produced with an isolated yield of 30% (Li et al, 2018).

The second step of synthetic route one is described as using the raw condensation product from step one (Hachihama & Hayashi, 1954). Therefore, the δ-furfurylidenelevulinic acid product from step one is refluxed with ethanol at a 6.6 ethanol to δ-furfurylidenelevulinic weight ratio for eleven hours at 95˚C along with hydrochloric acid (37% diluted with water) at a 7.0 hydrochloric acid to δ-furfurylidenelevulinic acid molar ratio (Hachihama & Hayashi, 1954). It is then stated that the solvent, ethanol, and water, is evaporated before being twice recrystallized from water (Hachihama & Hayashi, 1954) (Li et al, 2018). The product from this step of the synthetic path is dilevulinic acid with a reported isolated yield of 79% by (Hachihama & Hayashi, 1954) and 77% by (Li et al, 2018).

The final step of synthetic route one describes producing FDPA by heating dilevulinic acid in a stream of nitrogen at a temperature of between 180˚C and 190˚C for five hours (Hachihama & Hayashi, 1954). FDPA is then separated with ether, removing dilevulinic acid which is insoluble in ether. It is then stated that the ether is removed via evaporation and the remaining FDPA is crystallized for an isolated yield of 93% (Hachihama & Hayashi, 1954).

The details of synthetic route two are obtained from (Serum, 2018) and begin in step one with DFF and malonic acid as the starting materials for the process. DFF is described as the limiting reactant and the malonic acid is added with a molar ratio of 2.4 moles for each mole of DFF. It is then stated that pyridine and piperidine were added to the mixture with respective molar ratios of 4.4 and 0.2 in comparison to DFF. The mixture was then reported to be heated for eight hours at 50˚C. After the eight hours had elapsed, the mixture was then heated for a further eight hours at an increased temperature of 100˚C. Once left to cool to room temperature, furan-2,5-diacrylic acid was produced with a crude yield of 88%.

In step two, furan-2,5-diacrylic acid is used from step one and is considered the limiting reactant of this second step (Serum, 2018). A solution was formed with the addition of methanol, sulfuric acid and sodium chloride which had molar ratios to furan-2,5-diacrylic acid of 3.4, 0.24 and 0.34 respectively. This mixture was then refluxed for nineteen hours and left to crystalize. To purify the dimethyl 3,3'-diacrylate product, the crystals are dissolved, filtered, and recrystallized to provide an isolated yield of 98% (Serum, 2018).

In the final step, FDPA is produced by first cooling a solution of dimethyl 3,3'-diacrylate, tetrahydrofuran, methanol and copper (I) chloride to a temperature of 10˚C. Sodium borohydride was added slowly in order to order to ensure that the reaction mixture did not exceed 10˚C (Serum, 2018). Once all the material had been added to the reaction mixture, the temperature was raised to room temperature over eleven hours to produce FDPA with a 93% crude yield.

4.1.3. Aldol condensation catalysts
As discussed in previous sections, an aldol condensation reaction occurs in step one of synthetic route one. An aldol condensation reaction is known as a reaction where an

enol or enolate ion reacts with a carbonyl compound to form a carbon-carbon bond between the two species. In order for the reaction to proceed, a condensing agent/catalyst is required to dehydrate the aldol condensation product (Liang et al, 2016). For the aldol condensation of levulinic acid with furfural (synthetic route one) there are three condensing agents/catalysts which are reported with yields of greater than 60%. These include sodium carbonate (Hachihama & Hayashi, 1954) and (Li et al, 2018), magnesium oxide (Su, 2019) and (Liang et al, 2016), and hierarchical MFI zeolite (Su, 2019).

Sodium carbonate is provided in (Hachihama & Hayashi, 1954) and (Li et al, 2018) as having an isolated yield of 60% and 58% respectively as discussed in section 4.1.2. The selectivity is also stated to be high with a value of 57.7% (Liang et al, 2016) while the conversion of furfural was 100% (Hachihama & Hayashi, 1954) (Liang et al, 2016).

With regards to magnesium oxide, it is reported that the yield of furfurydilevulinic acid from the aldol condensation reaction is 70.6% (Liang et al, 2016) and 75.3% (Su, 2019). While these findings suggest that magnesium oxide has a higher yield than sodium carbonate, the values provided are crude yields which contain an undesired β-furfurydilevulinic acid isomer along with the desired δ-furfurydilevulinic acid isomer. Using selectivity data from (Liang et al, 2016) a value of 56.5% for the isolated yield of δ-furfurydilevulinic acid can be obtained with 100% conversion of furfural (Su, 2019) and (Liang et al, 2016).

A comparable situation can be found between the yield results of the hierarchical MFI zeolite catalyst and magnesium oxide. While the crude yield of furfurydilevulinic acid is reported as being high at 70.6% (Su, 2019), the presence of β-furfurydilevulinic acid in these findings makes the value misleading for the purposes of FDPA production. Using the selectivity data of both isomers, as was done with magnesium oxide, it can be determined that the isolated yield of δ-furfurydilevulinic acid is 50.4% with 100% conversion of furfural (Su, 2019).

As a result of obtaining three promising options for the condensing agent/catalyst in the aldol condensation reaction, synthetic route one is split into three secondary synthetic routes, each with a different condensing agent/catalyst, to find which route is optimal for FDPA production. An overview of the yield and selectivity data is provided in table 2.

Table 2- An overview of the yield and selectivity data obtained for the aldol catalysts from literature

	Isolated yield (%)	Selectivity (%)
Synthetic route 1.1 (MgO)	56.5	61.8
Synthetic route 1.2 (Na2CO3)	60	57.7
Synthetic route 1.3 (K/H-MFI)	50.4	54.9

4.2. Principals of green chemistry

Green chemistry is defined as the "design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances" (Anastas & Warner, 1998) (Anastas & Warner, 1996). The focus of this field is to improve the safety of processes and products for humans while reducing the impact of these processes and

products on the environment. This aspect of the chemical industry has grown over the years as environmental concerns have escalated and now most new processes consider this way of thinking in the design process. In order to provide a basis so that industry can easily apply this concept, twelve criteria have been developed to produce the Twelve Principals of Green Chemistry. These principles include: prevention measured by E-factor, atom economy, less hazardous chemical synthesis, designing safer chemicals, safer solvents and auxiliaries, designing for energy efficiency, use of renewable feedstocks, reduce derivatives, catalysis, designing for degradation, real-time analysis for pollution prevention, and inherently safer chemistry for accident prevention (Anastas & Eghbali, 2010). These twelve principals can be split into three more general categories of waste reduction, process safety, and environmental impact reduction.

The factors which contribute to waste reduction are atom economy, prevention, derivative reduction, and catalysis. The latter three of which all refer to reducing the materials which are inputs for the process. Catalyst presence reduces the need for stoichiometric reagents, derivative reduction removes the reagents required for derivatization, and waste prevention focuses on removing unnecessary materials before they enter the process. Atom economy on the other hand refers to maximising the materials used in the reaction so that the product contains as much of the input materials as possible.

In order to improve the process safety, the principals which should be considered are less hazardous chemical synthesis, designing safer chemicals, safer solvents and auxiliaries, and inherently safer chemistry for accident prevention. These principals cover the whole process from the chemicals used, to the product, and the production method itself. In general, this means that it is preferable for the chemicals involved in the process to be of low toxicity and have low risk chemical characteristics, such as being inflammable.

Reducing environmental impact is mainly focused on acquiring materials from sustainable sources, to not deplete resources through use of the process, and preventing pollution by creating degradable products and monitoring pollution so that the process can be altered if it determined that the process is too polluting. An additional aspect of environmental impact which the twelve principles consider is that the energy consumption of the process should be as low as possible as, the majority of energy that is supplied to the process will originate from fossil fuel sources, contributing to polluting the environment.

5. Synthetic route selection

The aim of the following section is to use information from literature to select the most promising synthetic route for a preliminary process design of FDPA production. This includes, the method used and each of the factors which will be used to make an assessment. To conclude the section a result in the form of an average rank across all factors will be made from the data collected.

5.1. Method

In order to produce a preliminary design for the production of FDPA, a selection needs to be made over which specific route of synthesis is most suitable for scaling up to

commercial production. This selection process will be conducted by ranking each of the four synthetic routes, three secondary routes derived from primary synthetic route one and synthetic route two, against the principles of green chemistry and other typical factors, such as yield and cost of starting materials, which contribute to the economic potential of a commercial process. Once the ranks of each route have been determined for each factor, an average rank will be calculated for each route and the highest-ranking route, with the average rank closest to one, will be chosen for the preliminary design.

While it is stated that the synthetic routes will be evaluated against the Principles of Green Chemistry, many of the principles are unsuitable for this process as, it is either not possible to calculate values/rank the synthetic routes against these principles from the information provided in literature or it is not possible to differentiate between any of the synthetic routes. An example of this is that 'designing for degradation' cannot be used as a ranking criterion because FDPA is the same product in all cases. Therefore, the Principles of Green Chemistry which have been chosen to assess the synthetic routes are waste prevention measured by E-factor, atom economy, chemical toxicity, and process risk. An analysis of the method and results of ranking each synthetic route for each principle will be presented in the following sections.

As discussed previously, in addition to the Principles of Green Chemistry, typical measures of the performance of a chemical process are considered. These include conversion, yield, selectivity, and cost of starting materials as, they give an indication of the economic potential of the process. An analysis of the method and results of ranking each synthetic route for each measure will be presented in the following sections along with the Principles of Green Chemistry. A final overview of the synthetic route selection process and the outcome of the selection process is provided in section 5.7.

5.2. Chemical toxicity and process safety

To rank the synthetic routes based on chemical toxicity and process risk the chemical substances used in each route were entered into the OECD eChemPortal to obtain toxicology and risk assessment reports from the GHS Classification Guidance by the Japanese Government and ECHA C&L inventory for each of the twenty substances. The data collected is presented in the appendix in table 1. Six of the substances were not present in the database and therefore their toxicity and process risk could not be assessed. For the remaining fourteen substances, data was collected on their toxicity and process risk. These chemicals were then ranked from one to fourteen, with one being the safest, based on their chemical toxicity reports. With regards to process risk, many of the chemicals shared the same level of process risk. For substances where this was the case, the substances were given an equal rank. The final ranking for process risk was in groups of one to five, with one being considered the lowest level of risk.

With the chemical toxicity and process risk ranked for each substance, each step of the synthetic routes assessed was assigned a rank for toxicity and process risk based on the substances involved in the corresponding steps. For steps which included the same substances, steps two and three of the synthetic route one variations, equal ranks were assigned. These values can be seen in table 2 in the appendix.

The overall chemical toxicity and process risk ranks are determined from the ranks assigned to each reaction step for each synthetic route. These results illustrate that for chemical toxicity, synthetic route one with hierarchical MFI zeolite as a condensation catalyst in step one is ranked the safest followed by, with increasing toxicity, synthetic route one with magnesium oxide and sodium carbonate as condensing agents. Synthetic route two was ranked highest with respect to chemical toxicity. Regarding process risk, it was determined that synthetic route one was ranked with the lowest process risk, with each of the different condensing agents/catalysts ranking equally low risk. As a result, synthetic route two was ranked with the highest process risk. The overall ranking values for chemical toxicity and process risk for each synthetic route are presented in table 2 of the appendix and a summary of the values is presented in table 3 below.

Table 3- A summary of the chemical toxicity and process risk ranks for each route

		Chemical toxicity (1 = safest)	Process risk (1 = safest)
Synthetic route 1.1 (MgO)	Step 1	5	3
	Step 2	7	2
	Step 3	1	1
	Overall	**2**	**1**
Synthetic route 1.2 (Na2CO3)	Step 1	6	3
	Step 2	7	2
	Step 3	1	1
	Overall	**3**	**1**
Synthetic route 1.3 (K/H-MFI)	Step 1	3	3
	Step 2	7	2
	Step 3	1	1
	Overall	**1**	**1**
Synthetic route 2	Step 1	2	3
	Step 2	4	3
	Step 3	8	4
	Overall	**4**	**4**

5.3. Atom economy

The atom economy of a process describes the number of atoms from the raw materials which are incorporated into the desired product and is defined as the percentage molecular mass of the reactants which is present in the molecular mass of the desired product (Anastas & Eghbali, 2010). In order to calculate the overall atom economy of each synthetic route, the atom economy of each reaction step for each synthetic route is calculated first. The formula used to calculate the atom economy is presented in equation 1.

$$Atom\ economy\ \% = \frac{Mr\ of\ desired\ product}{Mr\ of\ reactants} \times 100 \quad (1)$$

It is important to note that for the reaction steps with at least two organic reactants, inorganic reactants are not considered in the calculation. Therefore, the different condensing agents/catalysts of synthetic route one do not have an impact on the atom economy. Furthermore, with reaction steps two and three of synthetic route one being identical, the overall atom economy of the three variations of synthetic route one are the same. The results of the atom economy for each step of each synthetic route are presented in table 3 of the appendix.

The overall atom economy of each synthetic route is calculated by multiplying the atom economy of each reaction step within the corresponding route. Ranking of the synthetic routes, based on the atom economy, use these overall values. The results of the overall atom economy illustrate that synthetic route one is most atom efficient with a value of 66.4% for all three condensing agents/catalysts, and synthetic route two is approximately half as atom efficient with a value of 31.2%. As a result, the three variations of synthetic route one are ranked equally with a value of one and synthetic route two has the lowest rank with a value of four. The rankings and atom efficiency values are presented in tables 2 and 3 in the appendix and an overview is presented in table 4 below.

Table 4- Overview of the atom economy for each step and each synthetic route

		Atom economy (%)
Synthetic route 1.1 (MgO)	Step 1	75.2
	Step 2	95.8
	Step 3	92.2
	Overall	**66.4 (1)**
Synthetic route 1.2 (Na2CO3)	Step 1	75.2
	Step 2	95.8
	Step 3	92.2
	Overall	**66.4 (1)**
Synthetic route 1.3 (K/H-MFI)	Step 1	75.2
	Step 2	95.8
	Step 3	92.2
	Overall	**66.4 (1)**
Synthetic route 2	Step 1	53
	Step 2	86.7
	Step 3	67.9
	Overall	**31.2 (4)**

5.4. E factor

The environmental impact factor, or E factor, is defined as the amount of waste generated per kg of product produced (Anastas & Eghbali, 2010). In order to calculate the E factor for each synthetic route, so that they can be ranked, the mass of waste needs to be determined for each step. While it is relatively simple to do this for industrial processes by measuring the flow of waste from the process, this is not the case for experimental batch set ups as, some of the waste products from the experimental set up may be recycled when scaled up to an industrial process, and there is a lack of focus on waste products in literature. Therefore, the principal of the conservation of mass is used to obtain the value of waste mass from the processes, this means that waste is considered to be the total mass of raw materials subtract the mass of the product. The result of this is that the E factor obtained is not an accurate depiction of the performance of a scaled up industrial process, although it does provide

a value which can be compared relatively between the synthetic routes to provide a rank.

The data used for the calculations of the E factor is gathered from the literature on the experimental set up of each synthetic route, which includes the mass of product and raw materials for each reaction step. The mass values and E factor for each reaction step are illustrated in table 3 of the appendix. The overall E factor for each synthetic route is determined by summing the waste mass of each reaction step and dividing by the mass of FDPA produced in the final reaction step. The lowest E factor value calculated, lowest environmental impact, was 35.7 for synthetic route one with sodium carbonate condensing agent which was followed closely by synthetic route one with magnesium oxide catalyst and a value of 36.2. As a result, these routes were given ranks of one and two respectively. Synthetic route two was ranked third with a large E factor of 186.9 due to the first reaction step utilizing a large amount of reagents. An overall E factor was not able to be determined for synthetic route one with a hierarchical MFI zeolite catalyst because the experimental set up provided in the literature used a different scale of experiment, on a millimole basis rather than a mole basis, as was used in the other set ups. Despite this, the E factor associated with each step of the reaction could be determined and is can be seen that they are larger than that of synthetic route two. Therefore, synthetic route one with a hierarchical MFI zeolite catalyst was ranked fourth. The results of the ranking and E factor values are presented in tables 2 and 3 of the appendix and a summary is provided in table 5 below.

Table 5- Summary of the E factor values calculated for each synthetic route

		E factor
Synthetic route 1.1 (MgO)	Step 1	15.9
	Step 2	12.4
	Step 3	0.2
	Overall	**36.2 (2)**
Synthetic route 1.2 (Na2CO3)	Step 1	17.3
	Step 2	12.4
	Step 3	0.2
	Overall	**35.7 (1)**
Synthetic route 1.3 (K/H-MFI)	Step 1	49.8
	Step 2	12.4
	Step 3	0.2
	Overall	**N/A (4)**
Synthetic route 2	Step 1	4.2
	Step 2	6.8
	Step 3	45.1
	Overall	**186.9 (3)**

5.5. Yield, selectivity, and conversion

As stated previously, the yield, selectivity and conversion of a reaction have an impact on the economic potential of a process as, they affect the amount of product formed

for a given amount of raw materials used. Selectivity and conversion data is obtained, where possible, from the literature containing the synthetic routes and experimental set up. However, due to the fact that FDPA is a novel substance, much of this data is not available. Selectivity and conversion data could only be obtained for the better documented aldol condensation reactions in step one of synthetic route one. Furthermore, selectivity and conversion values could not be calculated for the remaining steps of synthetic route one and the entirety of synthetic route two as, the lack of data in the literature presented too many unknowns. Therefore, ranks were assigned to synthetic route one based on the aldol condensation reaction conversion and selectivity values while synthetic route two was left unranked. With regards to selectivity, the aldol reaction with magnesium oxide catalyst performed the best with a value of 61.8%, the reaction with sodium was ranked number two with a value of 57.7%, and the reaction with hierarchical MFI zeolite catalyst was ranked third with a value of 54.9%. As for conversion, it was obtained that all three aldol condensation reactions with different catalysts reported a 100% rate of the limiting reactant, furfural, and therefore, the synthetic routes are left unranked with respect to conversion.

Regarding the yield of the synthetic routes, there was more data which was provided in the literature. However, as stated in the synthetic routes section, the yields reported in the aldol condensation reactions with magnesium oxide and hierarchical MFI zeolite catalysts were crude yields which are misleading when ranking the synthetic routes. Therefore, these values were converted to isolated yields using the selectivity data from the aldol reactions stated above so that the ranks could be determined. As a result, the isolated yields of the synthetic route one variants were 44.1%, 41.5%, and 37.0% for synthetic route one with sodium carbonate, magnesium oxide and hierarchical MFI zeolite catalyst respectively. Synthetic route two had the highest overall yield with a value of 80.2% however, the yields of steps one and three were crude yields which could not be converted due to a lack of selectivity data. Despite this, synthetic route two was ranked number one as, the yields reported were significantly greater than the crude yields of the other synthetic routes. Therefore, the final rankings for yield are synthetic route two first with synthetic route one with sodium carbonate, magnesium oxide and hierarchical MFI zeolite catalyst taking ranks two, three, and four respectively.

An overview of all the yield, selectivity, and conversion results are presented in table 3 of the appendix and an overview is provided below in table 6.

Table 6- Overview of the conversion, yield, and selectivity results for each synthetic route

		Conversion (%)	Isolated yield (%)	Selectivity (%)
Synthetic route 1.1 (MgO)	Step 1	100	56.5	61.8
	Step 2	-	79	-
	Step 3	-	93	-
	Overall	-	**41.5 (3)**	**1**
Synthetic route 1.2 (Na2CO3)	Step 1	100	60	57.7
	Step 2	-	79	-
	Step 3	-	93	-
	Overall	-	**44.1 (2)**	**2**
Synthetic route 1.3 (K/H-MFI)	Step 1	100	50.4	54.9
	Step 2	-	79	-
	Step 3	-	93	-
	Overall	-	**37 (4)**	**3**
Synthetic route 2	Step 1	-	88 (crude)	-
	Step 2	-	98	-
	Step 3	-	93 (crude)	-
	Overall	-	**80.2 (1)**	-

5.6. Cost of starting materials

The cost of starting materials is an important criterion on which to base the selection of a synthetic route for an industrial process as, this will contribute to the majority of variable costs. As discussed previously, the price of furfural, levulinic acid, hydrochloric acid, and ethanol had been found to be €700, €750, €250, and €500 per tonne respectively (Alibaba.com) for synthetic route one. However, the cost of catalyst/condensing agent should also be considered as, the contribution to the variable costs of the process from these substances is not negligible. The prices of sodium carbonate and magnesium oxide obtained are €150 and €200 per tonne (Alibaba.com). The hierarchical MFI zeolite catalyst could not be bought from a supplier and had to be produced in house. Therefore, it is assumed that the cost of this process is greater than the price of sodium carbonate and magnesium oxide.

Regarding synthetic route two, it has already been discussed that the price of DFF and malonic acid is €1000 per tonne for both (Shaanxi Dideu Medichem Co. Ltd) (Alibaba.com). The prices per tonne for the remaining materials required as input for the reaction pathway are €740 for piperidine, €1500 for pyridine, €110 for methanol, €30 for sodium chloride, €900 for tetrahydrofuran, €1000 for copper (I) chloride, €350 for sulfuric acid, and €1500 for sodium borohydride (Alibaba.com). It can be determined from these values that synthetic route two has a far greater cost in raw materials than any of the synthetic route one variants.

Based on the prices of starting materials found, it was concluded that synthetic route one with sodium carbonate condensing agent was ranked first followed by, in order of rank, synthetic route one with magnesium catalyst, and synthetic route one with hierarchical MFI zeolite catalyst, with synthetic route two being ranked fourth. An overview of these results is presented in table 3 of the appendix.

5.7. Result of selection

As stated in the method section, the synthetic route which is selected for the preliminary process design is the synthetic route with the average rank, across all factors, closest to one. The results of this analysis determine that synthetic route two

and synthetic route one with hierarchical MFI zeolite catalyst are the least promising synthetic routes with respective average rank values of 3.3 and 2.4. The variants of synthetic route one with magnesium oxide catalyst and sodium carbonate condensing agent rank more highly with corresponding values of 1.7 and 1.6. While both these synthetic routes indicate a promising performance potential, synthetic route one with sodium carbonate condensing agent is ranked highest and is therefore the synthetic route will be selected for the preliminary process design. An overview of the results is presented in table 3 of the appendix.

6. Preliminary process design

In order to determine whether FDPA economically feasible for commercial production, a process design is required to represent a continuous industrial production plan on which an economic evaluation can be made. With the most promising synthetic route selected, this section will scale up the experimental batch set up obtained from literature to a continuous process design.

6.1. Method of approach

To produce the preliminary process design, two main steps are performed. These steps involve producing a small-scale batch process diagram from the experimental procedure described in literature, and producing a continuous process design, from the batch design, on an industrial scale suitable for market introduction. Both designs will include process operations with the continuous process design offering further insight into potential equipment selection than the batch design. Furthermore, mass balances are utilized with yield data from literature in both designs to find mass and composition data throughout the batch process, and to obtain the mass flowrates and flow composition in the continuous design. Where possible, recycle streams are incorporated into the continuous design in order to reduce the waste of the system and reduce the cost of raw materials.

In the following section, the preliminary batch design is formulated together with the accompanying process details for this design. In this study, experimental testing is not conducted therefore, all process data is obtained from sources discussed in the literature review.

6.2. Batch process design

The batch process design follows the specifications provided in the experimental setup provided in the synthesis of FDPA and reaction steps and conditions sections for synthetic route one with sodium carbonate condensing agent. The mass of furfural, levulinic acid, hydrochloric acid, and ethanol are used as stated by (Hachihama & Hayashi, 1954) and (Li et al, 2018). The product from each reaction step is determined using the yield data and the moles of limiting reactant. The limiting reactants in each of the three steps are found to be furfural for step one, furfurydilevulinic acid for step two, and dilevulinic acid for step three. Knowing the amount of limiting reactants also allowed for the composition of the reaction mixtures to be calculated. This method provides the composition of the reaction mixture with a high degree of certainty for reaction step one as, the conversion data is provided in literature. However, for reaction steps two and three, as discussed in the route selection section, conversion data was not available in the literature reviewed. Therefore, an assumption was made

that the limiting reactants for steps two and three were fully reacted, with a conversion of 100%.

The batch process diagrams for reaction steps one, two and three are presented in figures 7, 8, and 9. These diagrams illustrate, as stated above, the mass inputs, outputs and compositions for each process block. While the equipment required for each process block is not included, the conditions required for each process block is incorporated into the design. To increase the readability, the overall process is split into three reaction steps however, the mass of product from steps one and two are used as the mass of reactant in the proceeding steps, two and three respectively, so that the overall process can be brought together without a discrepancy in mass transfer. The mass of waste from process blocks is also included in the diagrams but determination of whether a portion of this waste can be recycled will be left for the continuous process design.

It can be seen from the figures that the yields and masses obtained from the mass balances corroborate with the literature and that the conservation of mass of the process is satisfied, providing validation for the calculations performed. With this in mind, the next section will focus on producing a continuous process design on a market introduction scale from this batch process design.
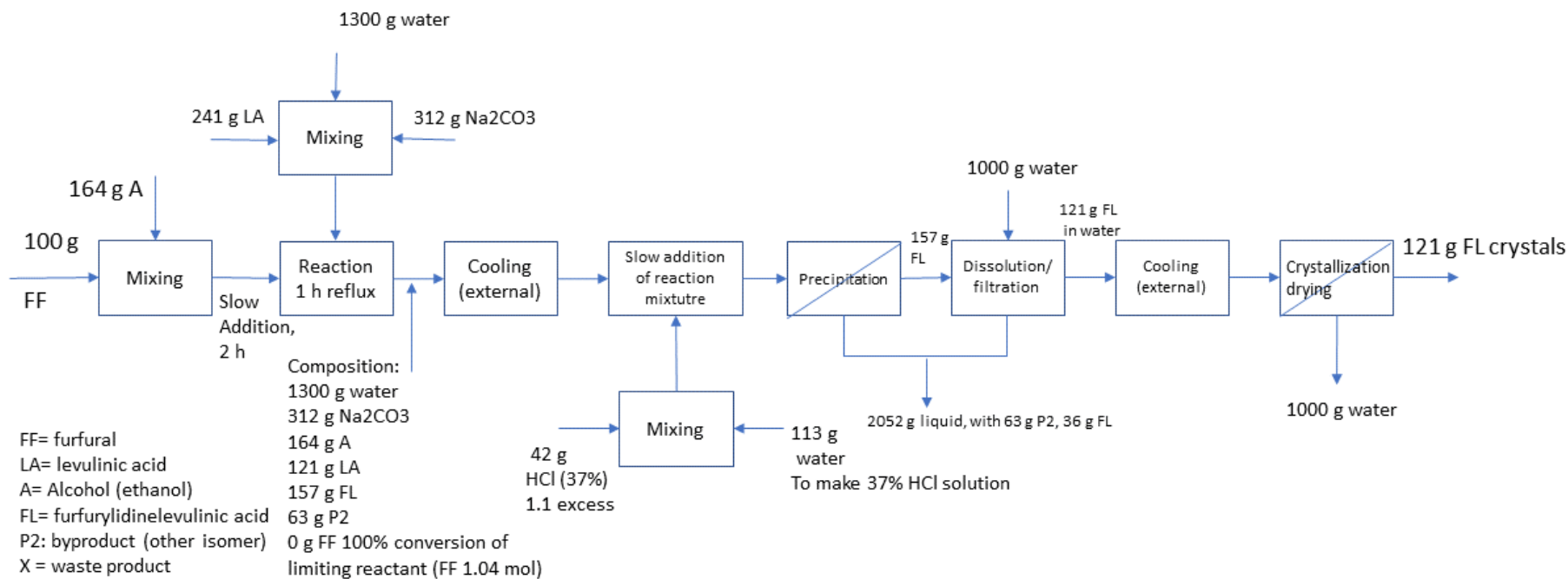
Figure 7- Batch process design for step 1

Figure 8-Batch process design for step 2

430 g water
To make 37% HCl solution

Mixing

159 g HCL (37%)

799 g A

1000 g water with activated carbon

121 g

FL

Mixing

Reaction
11 h reflux
(95°C)

Cooling
(external)

Evaporation
of solvent

Cooling
(external)

143 g
DA

113 g DA
in water

Dissolution/
filtration

Cooling
(external)

Crystallization
drying

113 g DA crystals

1396 g X

1000 g water

Composition:
430 g water
799 g A
143 g DA
137 g HCl
0 g FL assumed 100%
conversion of limiting
reactant (FL 0.62 mol)

FL= furfurydilevulinic acid
A= Alcohol (ethanol)
DA= Dilevulinic acid
X = waste product
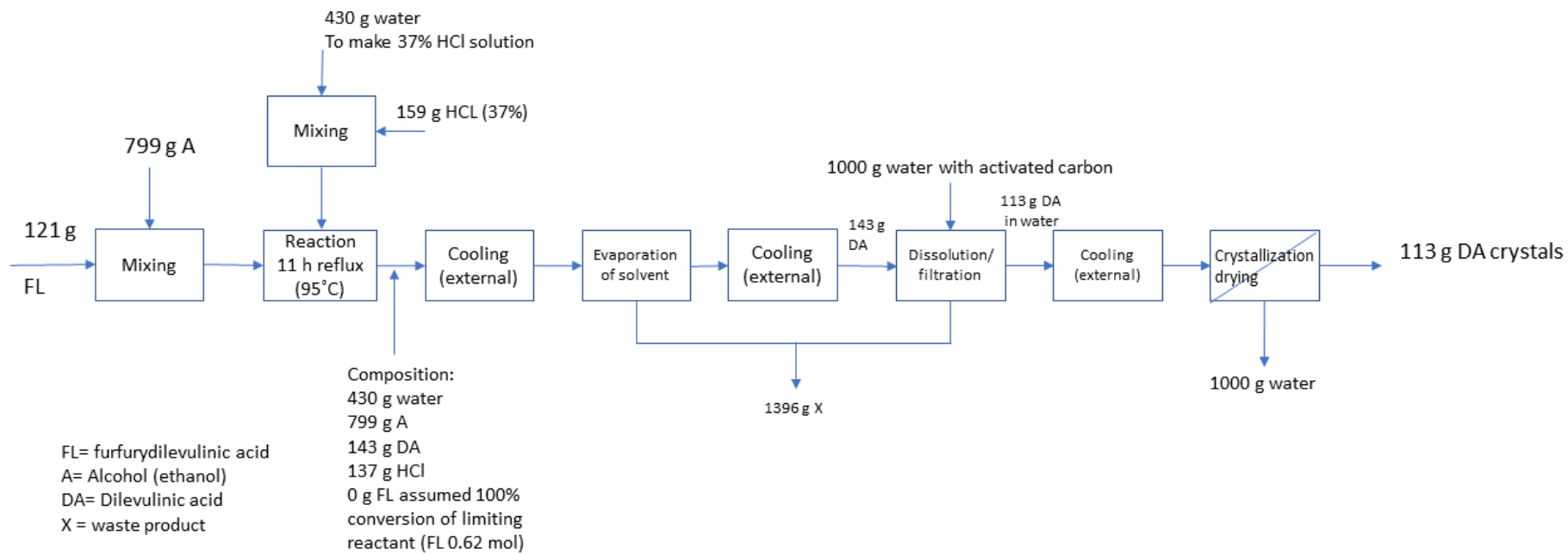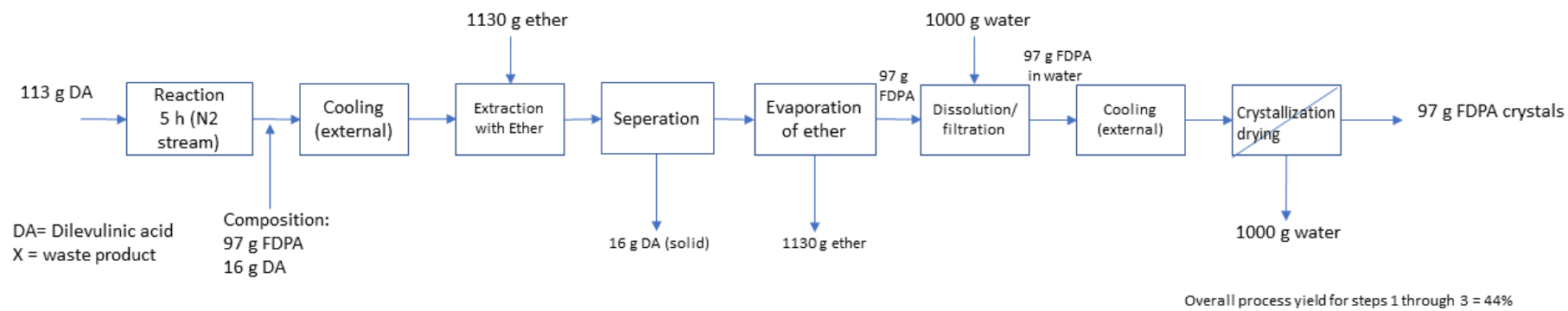
Figure 9-Batch process design for step

6.3. Continuous process design

In order to produce the continuous process design from the experimental batch design, first a scale of production needs to be determined. As stated previously, the continuous design is required to produce FDPA on an industrial scale suitable for market introduction. Therefore, the production rate of FDPA should be comparable to other existing biobased monomers such as FDCA. As a result, the production rate that is selected for this design is 10 ktonne per annum. It is assumed that the operational hours of a plant such as this are 8000 per year (Westerhout & Koningsbruggen, 1998). From this data, a production rate of 1.25 tonnes/hour for FDPA is calculated.

With the determination of the FDPA production rate, through use of mass balances, the feedstock and process mass flowrates can be calculated for a given process layout. As a result, the process layout needs to be produced. This includes the process blocks, equipment, and recycle stream configurations. The process block and equipment choices are made based on the function they perform in the batch design, but they are adapted for a continuous process. The processes and equipment which need to be adapted from the batch design to the continuous design are the reaction vessels, solid-liquid separation, liquid-liquid separation, and the crystallization/drying method. To adapt the reaction vessels of the batch design to that of the continuous design, continuously stirred tank reactors (CSTR) operated at high conversion are selected so that a continuous stream can enter and exit the reactor. Regarding the separation methods, distillation columns and settler are chosen for liquid-liquid and solid-liquid separation respectively with the distillation column efficiency assumed to be 95%. As for the crystallization/drying method, solids are dissolved in a CSTR with water before utilizing an industrial dryer for moisture removal. While these equipment choices have been made and incorporated into the design, the specific details, regarding size for example, have not been included and may determined in future research to further develop the process.

Since the layout of the processes has been determined, flowrates are calculated for the process design by use of mass balance. These flowrates are scaled up from the batch process in order to produce the desired production rate of FDPA at 1.25 tonnes/hour. An important part of this process is incorporating recycle streams, where possible, to reduce the production costs and waste produced. Recycle streams have been included where solvents have been separated from the reaction mixture. This occurs with ethanol and hydrochloric acid in reaction steps one and two, and ether in reaction step three.

The final continuous process design is illustrated in figures 10, 11 and 12. Like the batch process design, the continuous design has been divided into its three reaction steps in order to improve readability of the process. However, the product outflow of steps one and two, and inflow of steps two and three are not disconnected. Instead, in reality, these flows will be connected in order to produce a truly continuous process. From the process diagram the feedstocks of the substances required are determined. The results show that flows of 1.29 tonne/hour, 3.12 tonne/hour, 4.02 tonne/hour, 0.13 tonne/hour, 0.63 tonne/hour, and 0.73 tonne/hour of furfural, levulinic acid, sodium carbonate, hydrochloric acid, ethanol, and ether respectively are required to produce the 1.25 tonne/hour of FDPA with a yield of 44%. These results will be utilized in the

Techno-economic analysis of the production of FDPA to acquire and estimate for the manufacturing cost.
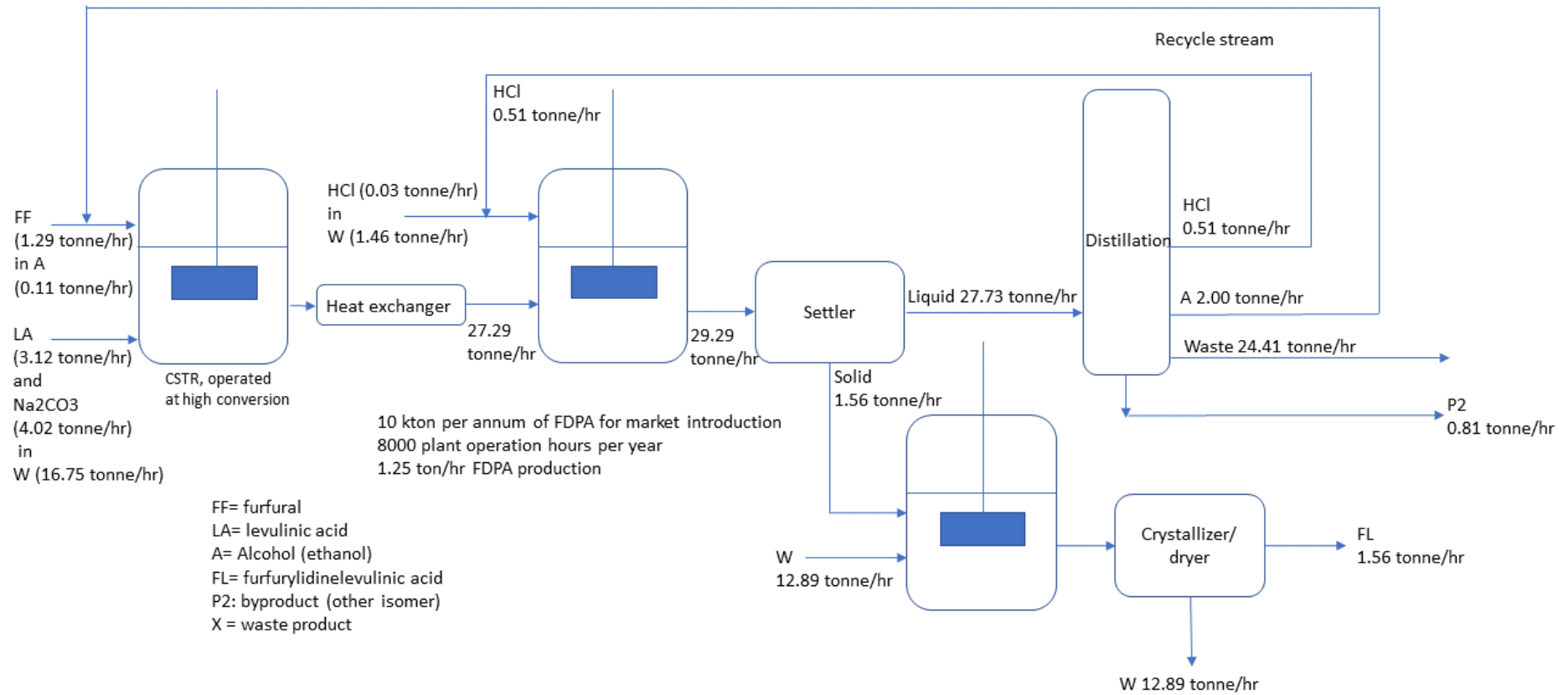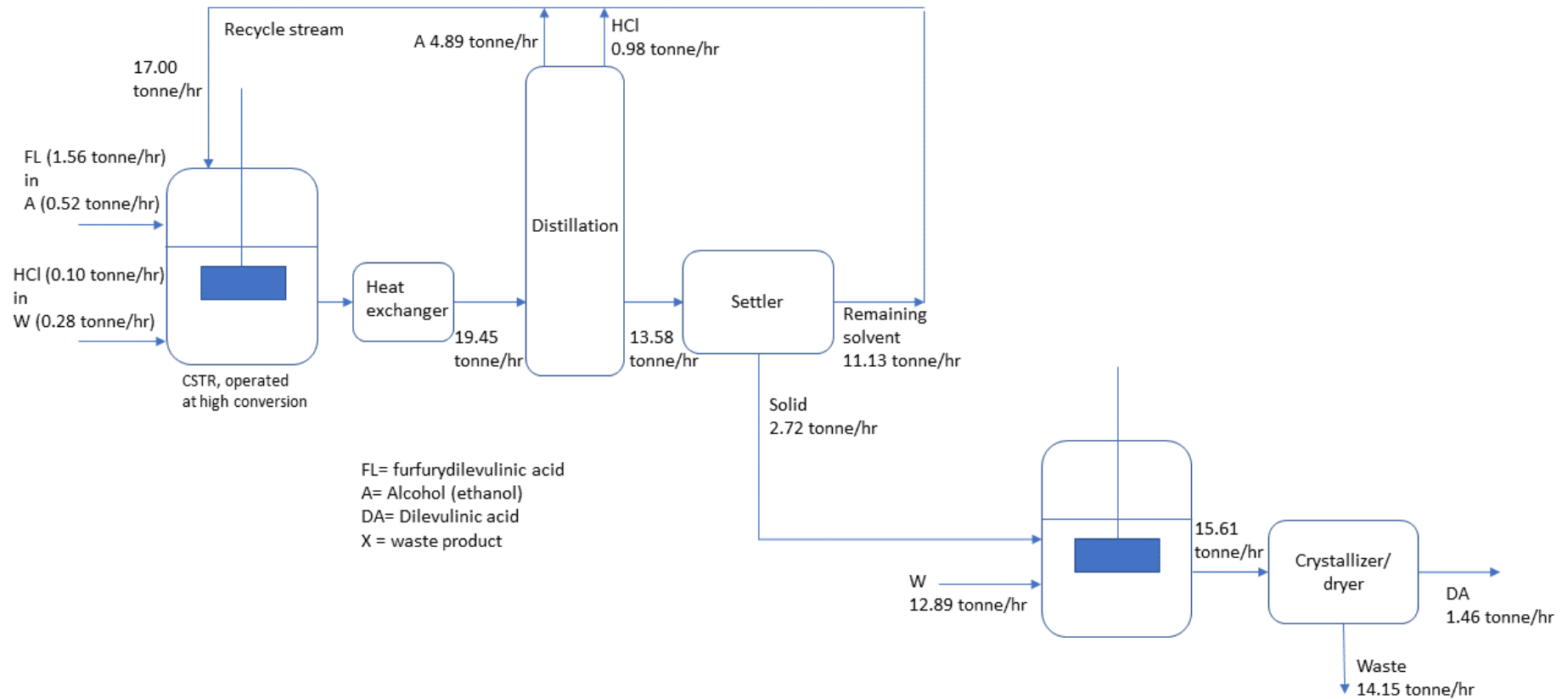
Figure 10- Continuous process design for step 1

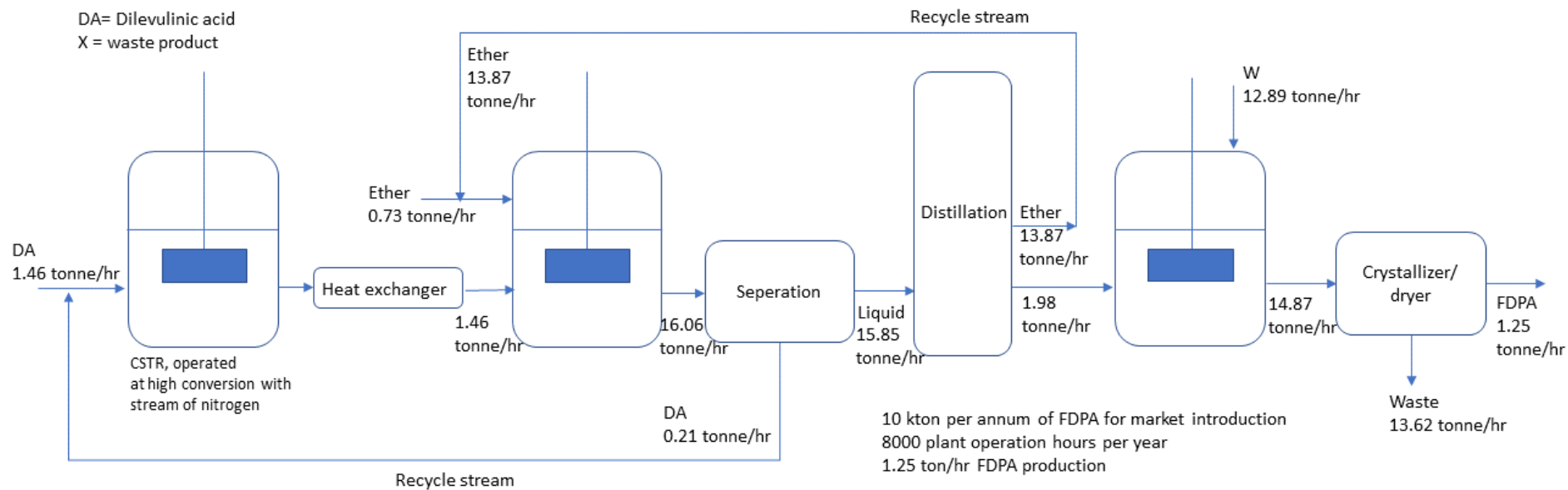*Figure 11-Continuous process design for step 2*

FL= furfurydilevulinic acid
A= Alcohol (ethanol)
DA= Dilevulinic acid
X = waste product

Figure 12-Continuous process design for step 3

7. Techno-economic analysis

7.1. Preliminary economic analysis

In order to determine whether the production of FDPA is feasible and competitive in the biobased monomer market in the future, an economic analysis is made on the preliminary process design. This analysis is made using assumptions and a preliminary design therefore, it is not highly accurate source of information but, it will provide a good insight into the potential minimum selling price range that FDPA could be placed around and provide a basis for future research. The analysis includes the expected variable, fixed, and investment costs associated with the production of FDPA.

To conduct this analysis, the total production costs per tonne of FDPA are determined. This is composed of variable costs, which follow the change in production volume, such as cost of raw materials and utility expenses. The raw material costs for the production of FDPA are generated from the starting materials which are required to produce FDPA. These include the cost of furfural, levulinic acid, ethanol, hydrochloric acid, ether, and sodium carbonate. On the other hand, utility costs are generated from supplying the process with electricity, fuel, cooling and process water, and air which may be needed. In addition to variable costs, fixed costs can be allocated per tonne of FDPA produced in order to account for payment over time. These fixed costs are generated through the purchasing of equipment, land, and licenses. Transport of materials is another cost which contributes to the cost of FDPA per tonne however, these vary with plant location and relative distance to suppliers/buyers. Therefore, the cost of transporting material is neglected.

7.1.1. Variable costs

As stated previously, variable costs are composed of two main groups, cost of raw materials and utility costs. In order to calculate the variable costs, first the cost of raw materials are computed. The method of obtaining this cost involves finding the mass, in tonnes, of each raw material required to produce one tonne of FDPA. These values are then multiplied by the cost of the respective material, in euro per tonne- pricing data is taken from Alibaba.com. Once these values have been calculated they are summed together to obtain the cost of raw materials to produce one tonne of FDPA. This method is illustrated in table 7.

Table 7- Pricing and mass data for material cost calculations

Component	Cost (€/tonne)	Source of cost information	Amount required per tonne of FDPA (tonne)	Cost per tonne of FDPA (€/tonne FDPA)
Furfural	700	Alibaba.com	1.03	721
Levulinic acid	750	Alibaba.com	2.5	1875
Hydrochloric acid	250	Alibaba.com	0.1	25
Sodium carbonate	150	Alibaba.com	3.21	481.5
Ethanol	500	Alibaba.com	0.50	250
Ether	770	Alibaba.com	0.58	446.6
			Total material cost:	**3799**

Regarding the cost of utilities, it is stated that for an industrial chemical plant, similar to the plant proposed in this study, the cost of utilities typically contributes to between

5-10% of the total production costs of a process (Towler and Sinnott, 2013). For the purposes of this study, a mid-value of 7.5% will be assumed in order to provide a estimate of this cost. The result of this calculation will be presented alongside the results of the cost of raw materials and the remainder of the economic analysis in section 7.2.

7.1.2. Fixed costs

For the purposes of attaining an estimate for the production costs of the production of FDPA, an explicit value of fixed cost will not be calculated. Instead of calculating the costs of equipment, land, and licensing, a percentage of the variable costs will be used as the contribution of fixed costs to the overall production costs. It is stated that this percentage of variable to fixed costs is 80/20% for variable/fixed for large scale chemical production plants (Towler and Sinnott, 2008). However, due to the scale of the preliminary design, a ratio of 75/25% will be assumed. The value of fixed costs was found to be €1021 per tonne.

7.1.3. Capital investment

In order to obtain the capital investment of creating a 10 kilotonne per annum FDPA plant, the known investment costs of a similar plant are used and adjusted to create an estimate. This method uses the 'sixth-tenths rule' shown in equation 2 (Towler and Sinnott, 2013) where C2 is the capital cost of a plant with capacity S2, and C1 is the capital cost of a plant with capacity S1, with n as an exponent relating to the type of plant which is being analysed.

$$C_2 = C_1 \left(\frac{S_2}{S_1}\right)^n \text{ (2)}$$

Plant two is the FDPA plant in this study, while plant one, the plant with known capacity and capital costs, is an FDCA plant. The capital costs of a 5 kilotonne per annum plant are known to be €41.4 million (Triebl, 2013). The exponent, n, which is selected for this calculation is 0.6 as, this is typical of a plant in the chemical production industry (Towler and Sinnott, 2013). The result of this calculation gives an estimated capital cost of €62.8 million. This value includes all the costs associated with building the production plant such as, land acquisition and equipment costs (Towler and Sinnott, 2013). Capital investment is important when analysing the economics of chemical plant as, it can be used in return on investment (ROI) calculations to determine the profit required for a desired ROI. The profit can then be added to the production costs in order to obtain a selling price. This will be discussed in the following section.

7.1.4. Return on investment

ROI is an economic performance measure indicating the efficiency of investment. It is represented as a percentage which is calculated using the net profit over total investment, illustrated in equation 3 (Towler and Sinnott, 2013).

$$ROI = \frac{net\ annual\ profit}{total\ investment} \times 100 \text{ (3)}$$

As stated previously, in order to obtain the selling price of FDPA for this process design, the net annual profit is required. To perform this calculation, a desired ROI

percentage is needed. A value for desired ROI for a FDCA plant is 15% (Triebl, 2013). Therefore, as a market competitor, this value will be used as the desired ROI for the production of FDPA. Using this value of desired ROI and the total investment cost obtained earlier, a net annual profit is found to be €9.42 million. When it is considered that 10 kilotonnes of FDPA is produced per year with the proposed design, this net annual profit equates to a desired profit of €942 per tonne of FDPA produced.

7.1.5. Internal rate of return

Internal rate of return, or IRR, is another common economic performance indicator. It is defined as the interest rate at which the cumulative net present value at the end of the project is zero and is illustrated in equation 4 where CFn is the cash flow in year n, i is the discounted cash-flow rate of return, and t is the plant life span (Towler and Sinnott, 2013).

$$0 = \sum_{n=1}^{n=t} \frac{CF_n}{(1+i)^n} \ (4)$$

In order to calculate the IRR, the cash flow of each year of the plant's operation and the life span of the plant need to be determined. The plant life span can be found by looking at plants of a similar nature, such as an FDCA plant. It is stated that a FDCA production plant has an operational life span of 20 years therefore, this value is assumed for a FDPA plant in this study (Triebl, 2013). The annual cash flow is determined by taking the total annual revenue and subtracting the total costs. This value is calculated to be €9.42 million per year with the exception of year one, where the investment costs are also included, returning an annual cash flow of €-53.4 million. Using Microsoft Excel's built-in IRR function, a value of 17% is obtained for the IRR. This is a reasonable value as it falls within the region of typical chemical plant IRR, between 14-18% as stated by Jan Wagenmakers (TU Delft). However, it should be noted that the value obtained is unrealistic due to the fact that the desire profit, attained from the desired ROI, is used in this calculation. The issue with this arises from the fact that the desired selling price of FDPA is calculated to be €6047 per tonne, which far exceeds the selling price of market competitor, FDCA, at €3700 per tonne (Triebl, 2013). Therefore, it is unlikely that FDPA will penetrate the market at this selling price and this IRR will not be achieved. This will be discussed further in the following section.

7.2. Economic analysis conclusion

Cost estimations and economic performance values have been determined in the previous sections for the production of FDPA, based on the preliminary process design. From this, the economic feasibility of the plant can be evaluated, with the aim of obtaining an estimate for the selling price of FDPA. To calculate this estimate, first the costs associated with producing FDPA were found using data from the preliminary process design. These costs included variable costs, raw material and utility, and fixed costs. With these costs accounted for, a value of €5105 per tonne of FDPA was calculated for the production costs of FDPA. In order to determine the selling price, desired profit was obtained from ROI calculations with a desired ROI value from an analysis of market competitor FDCA and was found to be €942 per tonne. When added to the production costs, this produces a selling price of €6047 per tonne of FDPA as illustrated in table 8.

Table 8- Summary of the calculations to obtain desired selling cost

Component	Cost (€/tonne)	Source of cost information	Amount required per tonne of FDPA (tonne)	Cost per tonne of FDPA (€/tonne FDPA)
Furfural	700	Alibaba.com	1.03	721
Levulinic acid	750	Alibaba.com	2.5	1875
Hydrochloric acid	250	Alibaba.com	0.1	25
Sodium carbonate	150	Alibaba.com	3.21	481.5
Ethanol	500	Alibaba.com	0.50	250
Ether	770	Alibaba.com	0.58	446.6
			Total material cost:	**3799**
Utility variable cost	7.5% of variable cost	(Towler and Sinnott, 2013)		284.9
			Total variable cost:	**4084**
Fixed cost	25% of variable cost	(Towler and Sinnott, 2008)		1021
			Total production cost:	**5105**
Desired profit	942	Internally calculated		942
			Desired selling price:	**6047**

While this result may seem economically feasible due to industry typical IRR of 17% calculated for FDPA, as discussed briefly in the IRR analysis, an issue arises when the selling price of FDPA is compared with that of FDCA. From this economic analysis is can be determined that the selling price of FDCA at €3700 per tonne (Triebl, 2013) is lower than the production costs of FDPA at €5105 per tonne. As a result, it could be suggested that FDPA will not be able to compete in this market as, its price will be undercut by FDCA and FDPA will be priced out of the market. However, it is important to consider that the molecules have a different chemical structure therefore, FDPA may have different properties to FDCA when polymerised. The potential value of these properties is not included in this economic evaluation as, these properties have not been determined in this paper. In order to compete in the biobased monomer market, the values of these properties should be determined in addition to a reduction in the cost of production, approximately 35-50% depending on the value of the properties. These cost reductions are unlikely to be attained however, to find which factors have the largest influence on cost, a sensitivity analysis can be performed. This will be discussed in the following section.

7.3. Sensitivity analysis

In order to determine which parameters related to cost have the largest effect on the production cost of FDPA, a sensitivity analysis can be conducted. This is performed by isolating a parameter and changing its value by a certain percentage while all other parameters remain constant. The output, or production cost in this case, is calculated along the range of the change. The range chosen in this study is from -50% to 50% of the value of the parameter. The parameters which will be included in this analysis are the price of individual raw materials, utility costs, fixed costs, and yield. A plot of the production cost for each parameter, y-axis, as their percentual value is changed, x-axis, is produced, with the steepest gradient indicating the most sensitive parameter. The results of the analysis are presented in figure 13.
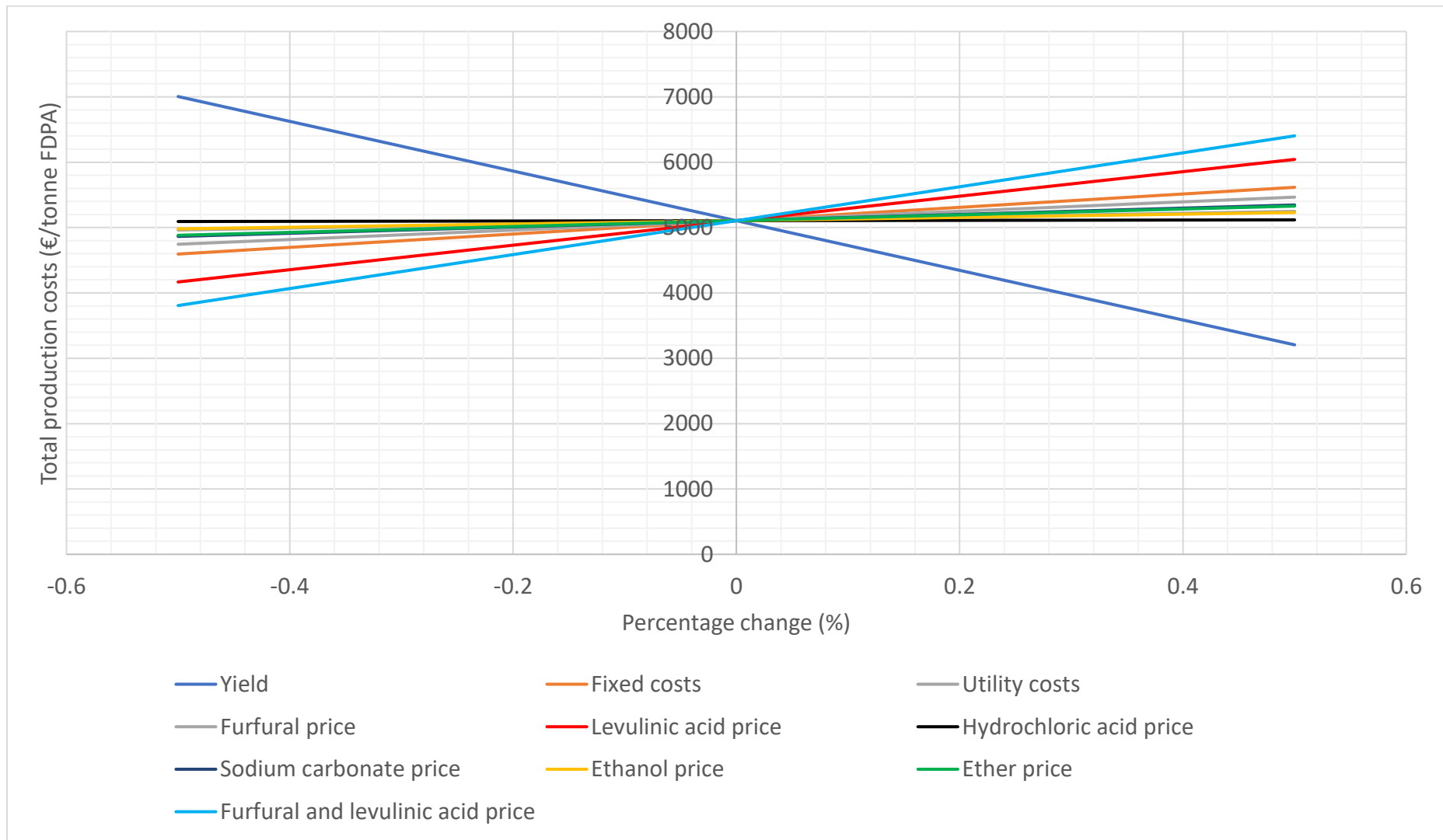
Figure 13- Plot of the results of the sensitivity analysis

From the results it can be determined that a change in yield is the most sensitive parameter, indicated by the steepest gradient, with production cost decreasing as yield increases, as expected. This is promising for the production of FDPA as, the process developed in this study is very immature and therefore, developments in the process and equipment may increase the yield, potentially leading to a large production cost reduction. Furthermore, it can be seen that the utility, fixed, and the raw material costs, excluding levulinic acid, have little effect on the production cost as, they all possess shallow gradients. On the other hand, levulinic acid presents a moderate level of sensitivity, increasing the production cost fairly significantly with increasing price. This is of high interest as, it is suggested that as the biobased monomer market grows, the cost of levulinic acid and furfural will become less expensive due to improvements in process design and manufacturing volumes increase. Therefore, this could result in further reductions to the production cost of FDPA. To illustrate the effect this may have on the production cost of FDPA, an additional line has been plotted indicating a scenario where both levulinic acid and furfural have their prices changed. While the sensitivity of production cost to this scenario is not as great as that of yield, it can be inferred that it may have a significant impact on production cost if it does occur.

The results observed from the sensitivity analysis fall in line with expectations however, that does not undermine the potential impact which the identified parameters could have on reducing the production costs of FDPA as the process is developed. As a result, it is concluded that improving the yield and reducing the cost of levulinic acid should be at the centre of focus for future research, while any price reduction of levulinic acid and furfural is an additional benefit.

8. Conclusion

The aim of this study was to determine whether the production of FDPA was technically and economically feasible. To achieve this, a preliminary process design was required so that financial calculations could be made for the production process and a production price for FDPA could be determined. In this study, a selection process based on key environmental and economic factors was produced in order to evaluate possible synthetic routes of FDPA with data acquired from existing literature in order to obtain the most promising reaction pathway. From this it was gathered that a synthetic route with furfural and levulinic acid feedstocks and a sodium carbonate condensing agent should provide a basis for which a process design could be made for. Using data from existing literature and mass balance calculations, a preliminary process design was created for a production rate of 1.25 tonnes/hour of FDPA, a 10 kilotonne per annum production plant. The mass flows associated with this design were used for the subsequent economic analysis where the production costs were calculated to be €5105 per tonnes of FDPA produced. Using a desired ROI and an estimated capital investment value of €62.8 million, a desired profit of €942 per tonne of FDPA was calculated, producing a selling price of €6047 per tonne of FDPA.

While comparison of the production price of FDPA, €5105 per tonne, with that of FDCA, €3700 per tonne, suggested that the production of FDPA may not be economically feasible due to the high production costs, a sensitivity analysis provided insights into which production parameters had the greatest impact on production costs. It was determined from this analysis that the yield and cost of levulinic acid were

the most sensitive parameters and therefore, should be the centre of focus for future research to make FDPA production economically viable in the future.

Currently, with the data and calculations provided in this study, the production of FDPA is economically unfeasible to produce. However, with determination of the potential property differences between FDPA and FDCA, and their respective value to the customer, along with future research directed into developing the production process and more robust calculations performed to provide an accurate depiction of the process, it is entirely possible that FDPA could penetrate the biobased monomer market.

9. Future research opportunities

The future research opportunities have been discussed briefly in previous sections. However, they have not been presented in their entirety. Firstly, a by-product of (3Z, 5E)-6-(furan-2-yl)-3-(furan-2-ylmethylene)-4-oxohex-5-enoic acid is produced in reaction step one of the process. This by-product, for which the value is not known, has not been included in the economic analysis for this reason and therefore would provide an additional contribution to reducing the selling price of FDPA. As a result, future product and application research should be conducted to assess the value of this by-product and this should be considered in the economic analysis as it is an added benefit of utilising the synthetic route selected.

As stated previously, extensive product and application research should be conducted for FDPA in addition to the by-product of the process. This research will allow for the true value of FDPA to be determined by providing information on the properties of FDPA and its corresponding polymer which customers may be willing to pay more for when compared to FDCA. With a better understanding of the value of FDPA, the high production costs of the monomer may become justified.

In addition to the future product and application research of the by-product and FDPA, further research should be conducted into more general areas such as equipment selection and process details, as mentioned before, because the overall yield of the process at 44% still leaves room for significant improvement when developments in equipment and processing techniques are implemented/accounted for. Furthermore, many of the financial details provided in this study are estimates based on industry norms therefore, more robust data and calculation of the cost and revenue values in future research may provide a significant improvement in economic performance of the process.

Finally, further research should be focused on the production of levulinic acid and furfural from biomass as, it was not included in this study due to the scope of the research. These substances are stated by various sources as having the potential to be produced for low cost from biomass. However, this is not currently common practice and this can be observed in the relatively high price. With the ongoing development of biobased monomer processes, these prices are expected to be reduced as the production process is refined but further research is still required in order to make this a reality.

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Appendix

Table 1- Presenting the chemical toxicity data, process risk data, and accompanying ranks

	Chemicals	Chemical toxicity	Chemical toxicity rank (1=safest)	Process risk	Process risk rank (1=safest)
Route 1 (shared components between 1.1, 1.2 and 1.3)	Furfural	Acute toxicity (oral, dermal, inhalation), Skin and eye irritation, Suspected carcinogen, Specific target organ toxicity (lungs and liver), Hazardous to aquatic life	14	Flammeable (L+V)	5
	Levulinic acid	Acute toxicity (oral), Skin and eye irritation	4	Low risk	1
	δ-furfurylidenelevulinic acid	Data not availible	N/A	Data not availible	N/A
	Hydrochloric acid	Acute toxicity (oral and inhalation), Skin, eye and respirtory irritation, Specific target organ toxicity (lungs), Hazardous to aquatic life	12	Gas under pressure may explode if heated	2
	Dilevulinic acid	Data not availible	N/A	Data not availible	N/A
	Nitrogen	Non toxic	1	Gas under pressure may explode if heated	2
Route 1.1	Magnesium oxide	Eye irritation, Specific target organ toxicity (lungs)	5	Low risk	1
Route 1.2	Sodium carbonate	Acute toxicity (inhalation), Eye irritation, Specific target organ toxicity (respirtory tract)	6	Low risk	1
Route 1.3	K/H-MFI-0.6	Non toxic	1	Data not availible	N/A
Route 2	2,5-Diformylfuran	Data not availible	N/A	Data not availible	N/A
	Furan-2,5-diacrylic acid	Data not availible	N/A	Data not availible	N/A
	Malonic acid	Acute toxicity (oral)	3	Low risk	1
	Piperidine	Acute toxicity (oral, dermal, inhalation), Skin and eye irritation, Reproductive toxicity, Specific target organ toxicity (central nervous system)	8	Flammeable (L+V)	5
	Dimethyl 3,3'-diacrylate	Data not availible	N/A	Data not availible	N/A
	Sodium chloride	Skin and eye irritation	2	Low risk	1
	Methanol	Acute toxicity (oral, inhalation), Eye irritation, Reproductive toxicity, Specific target organ toxicity (central nervous system, visual organs, kidney, liver)	9	Flammeable (L+V)	5
	Sulfuric acid	Acute toxicity (oral and inhalation), Skin and eye irritation, Specific target organ toxicity (respiratory system), Acute hazard to aquatic life	11	Low risk	1
	Tetrahydrofuran	Acute toxicity (oral, inhalation), Eye irritation, Carcinogenicity, Reproductive toxicity, Specific target organ toxicity (central nervous system, repiratory system)	10	Flammeable (L)	4
	Copper (I) chloride	Acute toxicity (oral, inhalation), Skin irritation, Specific target organ toxicity (haemal system), Hazardous to aquatic life	13	Low risk	1
	Sodium borohydride	Acute toxicity (oral), Skin and eye irritation, Specific target organ toxicity (repiratory tract irritation)	7	Produces flammable gases when in contact with water	3

Table 2- Presenting the E factor, atom economy, and corresponding ranks for the synthetic routes

		Mr of reactants (g/mol)	Mr of desired product (g/mol)	Atom economy (%)	Mass of waste (g)	Mass of product (g)	E factor
Synthetic route 1.1 (MgO)	Step 1	96.1 + 116.1 + 46.1	194.2	75.2	2095	114	15.9
	Step 2	194.2 + 46.1	230.2	95.8	1396	113	12.4
	Step 3	230.2	212.2	92.2	16	97	0.2
	Overall	-	-	**66.4 (1)**	**3507**	**97**	**36.2 (2)**
Synthetic route 1.2 (Na2CO3)	Step 1	96.1 + 116.1 + 46.1	194.2	75.2	2052	121	17.3
	Step 2	194.2 + 46.1	230.2	95.8	1396	113	12.4
	Step 3	230.2	212.2	92.2	16	97	0.2
	Overall	-	-	**66.4 (1)**	**3464**	**97**	**35.7 (1)**
Synthetic route 1.3 (K/H-MFI)	Step 1	96.1 + 116.1 + 46.1	194.2	75.2	39.8	0.8	49.8
	Step 2	194.2 + 46.1	230.2	95.8	1396	113	12.4
	Step 3	230.2	212.2	92.2	16	97	0.2
	Overall	-	-	**66.4 (1)**	-	-	**N/A (4)**
Synthetic route 2	Step 1	124.1 + 104.1 + 85.2 + 79.1	208.2	53	326.5	77.9	4.2
	Step 2	208.2 + 32	208.2	86.7	240.6	35.2	6.8
	Step 3	208.2 + 32 + 72.1	212.2	67.9	180.5	4.0	45.1
	Overall	-	-	**31.2 (4)**	**747.6**	**4.0**	**186.9 (3)**

Table 3- Containing all ranking data for the selection of synthetic routes

		Principals of green chemistry				Additional criteria				
		E factor	Atom economy (%)	Chemical toxicity (1 = safest)	Process risk (1 = safest)	Conversion (%)	Isolated yield (%)	Selectivity (%)	Cost of starting material rank (1=least expensive)	Average rank (1 = best)
Synthetic route 1.1 (MgO)	Step 1	15.9	75.2	5	3	100	56.5	61.8	2	N/A
	Step 2	12.4	95.8	7	2	-	79	-	N/A	N/A
	Step 3	0.2	92.2	1	1	-	93	-	N/A	N/A
	Overall	**36.2 (2)**	**66.4 (1)**	**2**	**1**	-	**41.5 (3)**	**1**	**2**	**1.7**
Synthetic route 1.2 (Na2CO3)	Step 1	17.3	75.2	6	3	100	60	57.7	1	N/A
	Step 2	12.4	95.8	7	2	-	79	-	N/A	N/A
	Step 3	0.2	92.2	1	1	-	93	-	N/A	N/A
	Overall	**35.7 (1)**	**66.4 (1)**	**3**	**1**	-	**44.1 (2)**	**2**	**1**	**1.6**
Synthetic route 1.3 (K/H-MFI)	Step 1	49.8	75.2	3	3	100	50.4	54.9	3	N/A
	Step 2	12.4	95.8	7	2	-	79	-	N/A	N/A
	Step 3	0.2	92.2	1	1	-	93	-	N/A	N/A
	Overall	**N/A (4)**	**66.4 (1)**	**1**	**1**	-	**37 (4)**	**3**	**3**	**2.4**
Synthetic route 2	Step 1	4.2	53	2	3	-	88 (crude)	-	4	N/A
	Step 2	6.8	86.7	4	3	-	98	-	N/A	N/A
	Step 3	45.1	67.9	8	4	-	93 (crude)	-	N/A	N/A
	Overall	**186.9 (3)**	**31.2 (4)**	**4**	**4**	-	**80.2 (1)**	-	**4**	**3.3**