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Conceptual Process Design

Postgraduate Designer Program in Bioprocess Technology

BODL - Faculty of Applied Sciences
Delft University of Technology

Subject

Biological Manufacture of Thioic Acid

FINAL REPORT

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Summary

This report is the Basis of Design report of Conceptual Process Design of the plant for the production of thiooleic acid ($C_{18} : 1$), which could be used as monomer in a polymerization process to produce polythioester.

It is aimed at designing an industrial plant with an annual production capacity of 5,000 tons of the long chain (C_{18}) thiooleic acid with (at least) one unsaturated bond. The proposed product selling price 3-4 EUR/kg. As side product, the plant produces 1364 tons/year of thiolinoleic acid and 293 t/a of saturated acid. The thiolinoleic acid is sold at the same price level as the main product, while the saturated acid is sold at 50 cents per kg.

The product, 99.5% pure thioomer acid, is formed during dynamic kinetic resolution in which the substrate (crude oleic acid) is continuously hydrolyzed and sulphurylated during enzymatic resolution. The dynamic kinetic resolution employs immobilized lipase as the catalyst for the reactions. With recycle structures, the process is expected to have a yield of 89%-w based on the substrate.

The economical life of the plant will be 15 years in which the first year is reserved for design and construction and 14 years of working period. For the 5000 t/a scale, the annual income is expected to be EUR 25M at the assumed product selling prices. The gross profit margin is EUR 16M. The maximum allowable investment is calculated at EUR 48-87M at 10% interest rate depending on the calculation method. At least based on the rough calculation the project seems to be profitable.

This report covers an introduction to the project, the available process alternatives, an analysis of the alternatives from black box to tasks levels, and an analysis of the chosen pathway at each level. For this moment in time, a rough block diagram of the proposed process has been developed. The options and decisions shall be discussed in detail during the Basis of Design defence.

1 Description of the design

This case comes from DSM Corporate Research in Geleen. They are interested in manufacturing monomers for a new polymer of the polythioester type.

Thioic acid is the monomer of polythioester. The polymer has the following advantageous properties:

- Hydrolytic stability comparable to hydroxy esters
- Material is more hydrophobic
- Polymer melting points are higher compared to hydroxy esters
- Slightly higher density of materials
- Aliphatic polymers are expected to be (bio)degradable
- Improved oxidative stability [37]

The novel polymer can be used for coatings, thermoplastic elastomers and can be also applied in the biomedical field. The new polymer has a major advantage over petrochemical-based polymers in the prevention of infection. Plastic implants tend to attract bacteria. These bacteria may not be pathogenic but they can cause the development of a film on the implant, resulting in blockages and delaying the healing process. [60]

The most important bottleneck for producing polythioester is the production of thioic acid. There exists no efficient chemical means to produce thioic acid. Therefore, a biological means is proposed to overcome this issue. However, the biological route is not well known, either.

The goal of the project is to design an industrial plant with an annual production capacity of 5,000 tons of the long chain (C_{18}) thiooleic acid with (at least) one unsaturated bond. The proposed product selling price 3-4 EUR/kg. If time permits, a pilot plant with an annual production scale of 10 tons would also be shown in the design.

The product specifications have been set by the client as follows:

- The product shall have at least one unsaturated bond and one thioic group to allow polycondensation mechanism in polymerisation. Appendix 1 explains the common mechanisms of polymerisation.
- The purity of the product must exceed 99.5% on molar basis

-
- The amount of polyunsaturated compounds must not exceed 5% on molar basis to prevent unwanted branching.

In this project, an enzymatic route is proposed to produce the thioic acid from crude, commercial fatty acid with lipase as the catalyst. The reaction route is analogous to fatty acid amidation reaction by lipase, which has been successfully developed at the Delft University of Technology. The designers will also present several different alternatives to the enzymatic route, as well as several different process options within the enzymatic route.

It is expected that the group will spend more time in theoretical work than the usual process design groups due to the relatively new production pathway.

2 Process definition

The following sections will describe the available options to manufacture thioic acid.

2.1 Raw Materials

Several possibilities exist for the raw materials. The thioic acid is basically an analogue of long chain carboxylic acid with a thioic group. Therefore, we will need a carbon source and a sulphur source.

2.2 Carbon source

As the client prefers long-chain thioic acid, it is of our advantage to use long chain carbon source as the starting raw material. Making carbon-carbon bond requires a lot of energy (≈ 30 kJ/bond) [40], therefore starting from a long chain carbon source will be preferred energetically.

In biological reaction, glucose is the most commonly used starting raw material for fermentation. Its metabolic fate in microbial cell is also well known. The by-products from fermentation with glucose can be predicted relatively well by going through the metabolic pathway of the wanted product. Therefore, glucose is an important alternative that we must take into account if we are considering fermentative pathway.

Some long chain carbon sources exist in the form of long chain fatty acids. These acids are available commercially as purified or crude acids. The esters of the acid are available commercially in animal fats and vegetable oils as triglycerides.

Another requirement from the client is that the product should contain at least one unsaturated bond. Taking this into account, it is found that along the fatty acid biosynthesis pathway there exists an unsaturated thioester compound. As the fatty acid synthesis originates from acetyl-CoA which is a compound found in the glycolysis pathway of glucose. Therefore, glucose is indeed a possible starting material.

Taking the second requirement into account, we can logically infer that the fatty acid or ester of choice should also have one unsaturated bond. If we are going to use natural fats as the source of acid, it is preferable to use vegetable oil rather than

animal fats because vegetable oil contains more unsaturated fatty acid than animal fats.

2.3 Sulphur source

After a screening of the literature two sulphur (HS^-) sources are proposed:

- Hydrogen Sulphide (H_2S).
- Sodium Sulphide (Na_2S).
- Elemental sulphur (S).

2.3.1 Hydrogen Sulphide (H_2S).

By putting in contact the hydrogen sulphide gas with an aqueous phase, by first its solubility and afterwards the dissociation reaction, H_2S (g) will become HS^- (aq.).

The dissociation reaction is as follows:

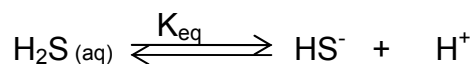


Figure 2.1 Dissociation of hydrogen sulphide

The equilibrium constant (K_{eq}) of this reaction is equal to 1.039×10^{-7} (at 25°C and 1atm (101.325 kPa) [5].

Since aqueous hydrogen sulphide is acidic, the effect of pH on its solubility is relevant to determine which will be the predominant species, either the molecular form (H_2S) or the ionic species (bisulphide ion, HS^-). The concentration of the molecular form is also dependent on the partial pressure of the H_2S within the gas phase and is related to its concentration in the aqueous phase by Henry's law.

The effect of the pH is presented on the next graph.

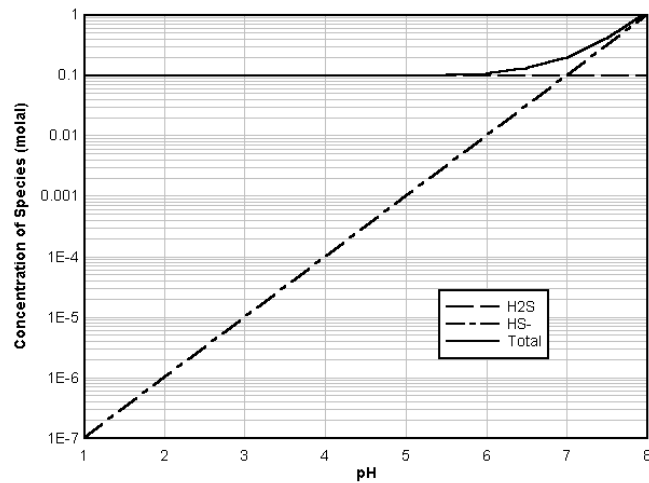


Figure 2.2 Solubility-pH relationship of hydrogen sulphide

It is then seen that at low pH values the predominant form of the sulphide species is the molecular one (See dissociation equilibrium). As the pH increases the dissociation is shifted towards the right side, hence increasing the bisulphide ion concentration. At pH values of slightly less than 7, there are equal amounts of both forms. At pH 8 the concentration of bisulphide ion is 10 times higher than the concentration of the molecular form.

For enzymatic reaction reaction pH is also affecting the enzyme optimal performance. It is known that for example in the case of lipases the optimal pH lies at pH values of between 6 and 8. This means that catalytic activity of the enzyme will be favoured at the similar pH at which we have the higher concentration of the ionic form of hydrogen sulphide. Then the sulphurylation will behave as follows:

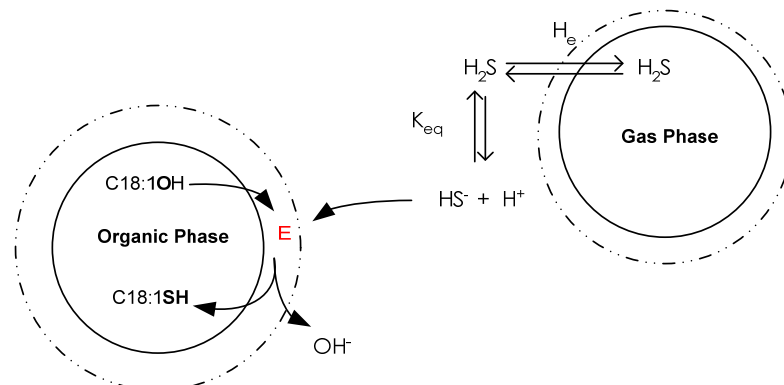


Figure 2.3 Reaction scheme involving hydrogen sulphide and enzymes

2.3.2 Economics

The commercial price of hydrogen sulphide is quite high. This is mainly due to the transportation and storage cost, due to the fact that it is considered as a hazardous compound and the environmental legislation is highly strict.

In spite of the previous facts, our supply of hydrogen sulphide will be considered to be available on site.

2.3.3 Environmental trends and regulations

The disposal of hydrogen sulphide gas is quite expensive and highly regulated. Industrial processes that produce it as a by product, normally chose to get rid of it by converting it to elemental sulphur, therefore we can get environmental royalties by being consumers of H_2S .

2.3.4 Sodium Sulphide (Na_2S).

This alternative raw material arose as a possibility due to economical reasons; its price is less than hydrogen sulphide. But then again to obtain our requested sulphur form starting from this raw material we need to include an extra raw material, an acid. The following reaction on aqueous solution will take place by the mixing of the two:

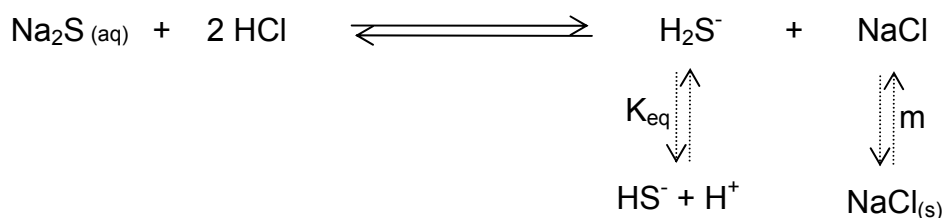


Figure 2.4 Reaction to obtain the nucleophile HS^- from Na_2S

By performing this reaction at low temperatures (reducing the solubility of the salt) the precipitation of the salt will shift the equilibrium towards the product side.

The disadvantage of this reaction lies on the formation of salts, due to possible regulations on the concentration of those in the wastewater.

One advantage of using this raw material is that we are getting rid of the gas phase within the reactor; which represents less investment cost on equipment.

2.3.5 Elemental Sulphur

Starting from this raw material requires a reduction reaction that needs as catalyst. The catalyst is usually a micro organism (sulphur reducing bacteria) and as reducing agent either hydrogen or methanol is required. It is not beyond the scope of this project and of this report to discuss further in detail this process.

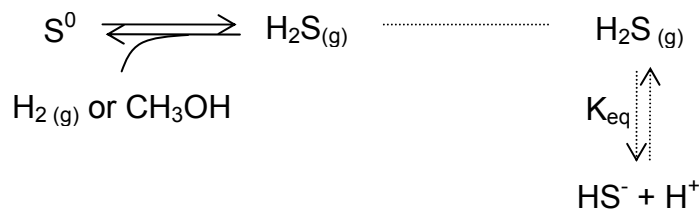


Figure 2.5 Reaction to obtain the nucleophile HS^- starting from elemental sulphur

2.3.6 Conclusion

Considering the possible costs, possible additional complexities resulting from the utilization of Na_2S and elemental sulphur and their impact on the economic feasibility of the project, it has been decided that the process shall employ hydrogen sulphide.

2.4 Technology

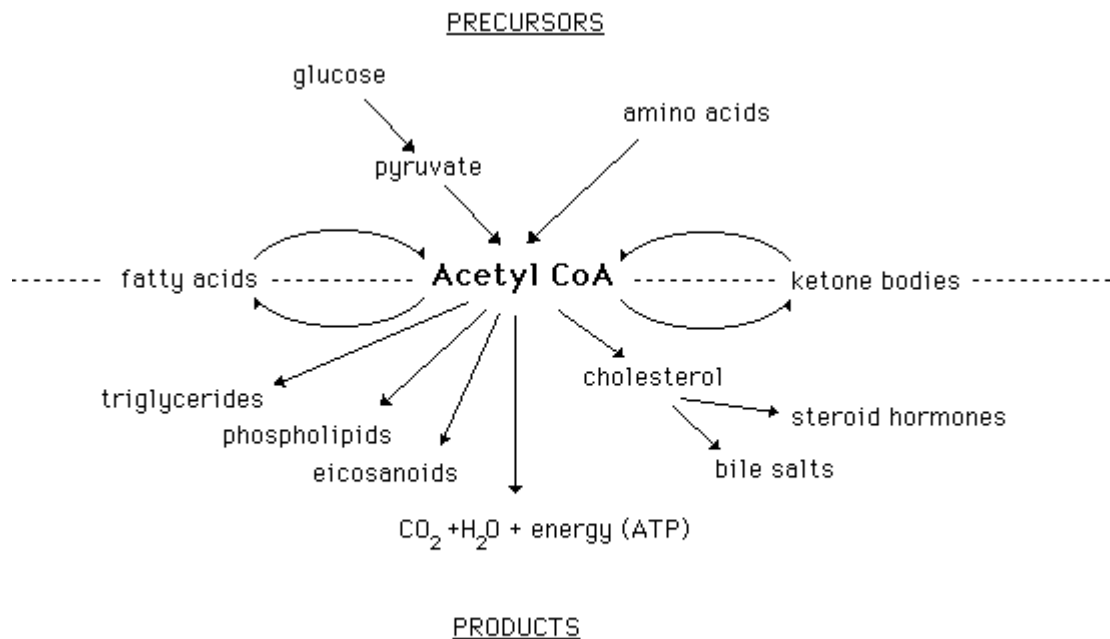
The technology that we are considering here are the enzymatic and fermentative conversion of carbon and sulphur source to thioic acid. Since the client excludes chemical pathway, this pathway will not be further discussed. Nevertheless, for completeness' sake, the chemical pathway has been included in the following discussion.

2.5 Fermentation alternative

The expected product is long chain thioic acid, which should serve as the monomer for the manufacture of polythioester. Long chain thioicesters are found in the fatty acid biosynthesis pathway. The pathway starts from acetyl-CoA is at the center of lipid metabolism which is obtained from:

- ✓ Fatty acids
- ✓ Glucose (through pyruvate)
- ✓ Amino acids
- ✓ Ketone bodies

Here are the major metabolic sources of acetyl CoA and some of the pathways for which it serves as a substrate (Figure 2.6).



Acetyl CoA is a central intermediate in lipid metabolism.

Figure 2.6 Metabolic sources of acetyl CoA [49]

Thus, the raw material for this pathway is actually glucose, which is converted along the glycolysis pathway.

The pathway is as follows

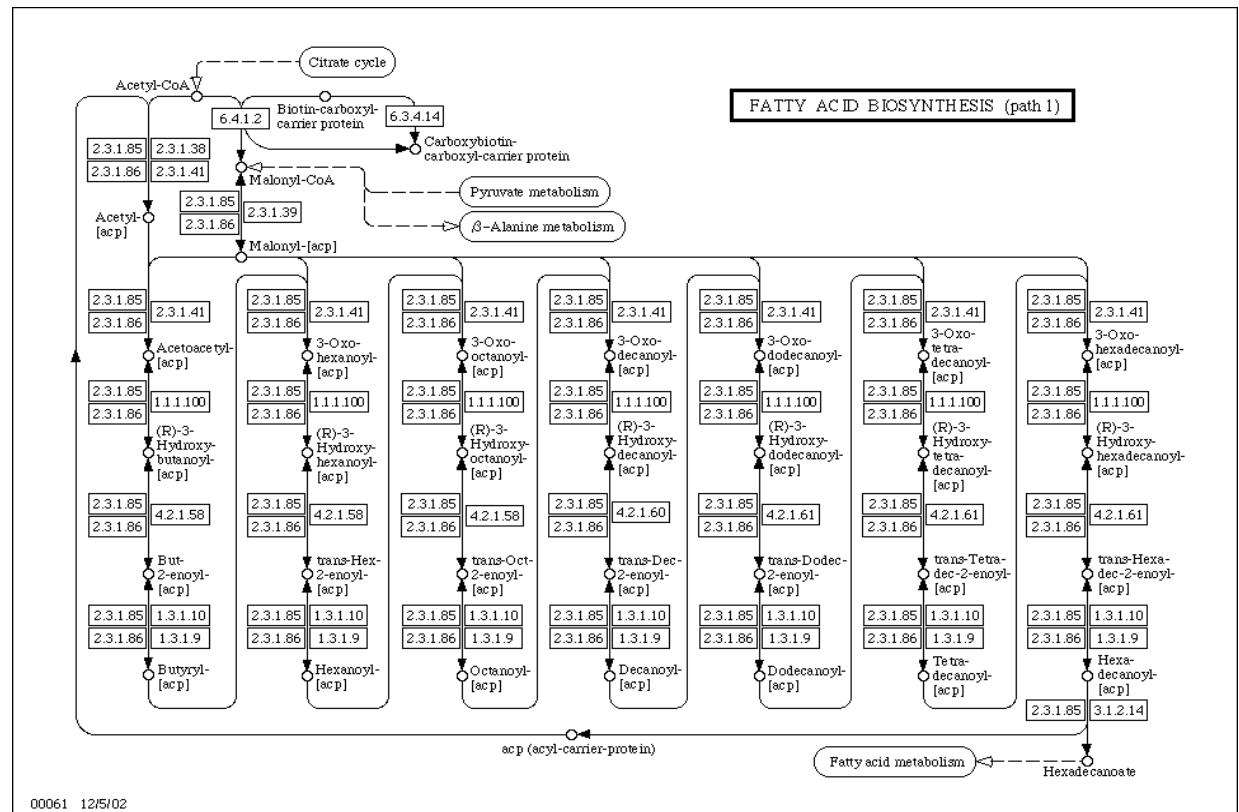


Figure 2.7 Fatty acid biosynthesis reference pathway [24]

The thioesters are found in the end of the pathway. The compounds are esters of C4, C6, C8, C12, C14 and C16 thioic acids and an acyl-carrier protein (acp).

To obtain the carboxylic acid, the ester should be hydrolysed, which is a common chemical reaction. The hydrolytic reaction can be done with either chemical catalysts or enzyme. Here, we propose a chemical hydrolytic reaction instead of an enzymatic one.

Details of the reactions involved in the pathway are as follows: [24]

The first step

The Acetyl-CoA is used as the substrate. The acetyl-CoA has the following structure.

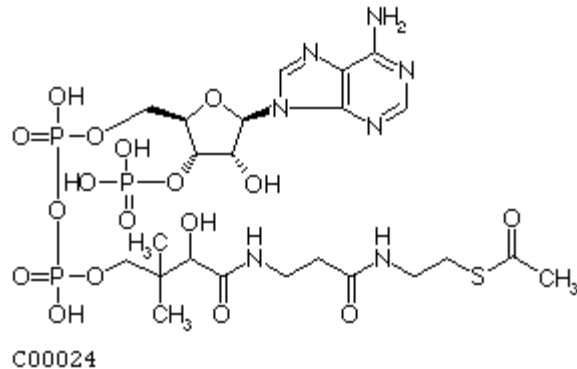


Figure 2.8 The structure of acetyl-CoA

The potential products as given in the pathways are:

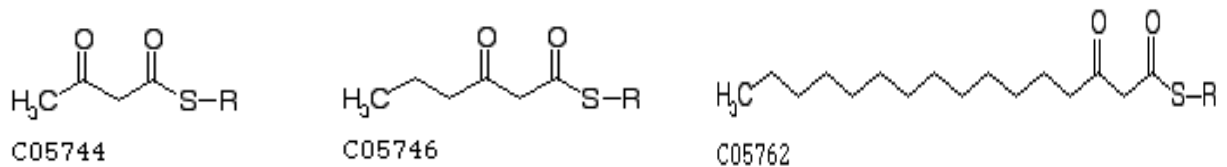
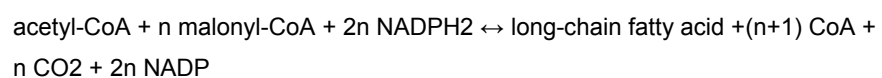
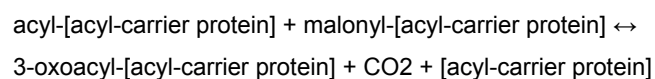
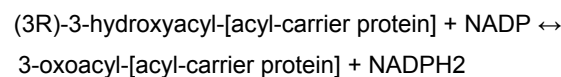


Figure 2.9 Potential products in the fatty acid biosynthesis pathway

The following enzymes are found in the first step.

ENZYME 1.1.1.100 2.3.1.41 2.3.1.85 2.3.1.86

REACTION:



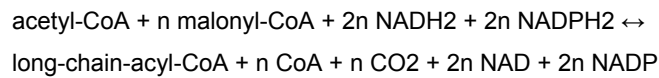


Figure 2.10 Reactions in the first step

The second step:

The following enzymes are used in the second step of the fatty acid pathway.

ENZYME 1.1.1.100 2.3.1.85 2.3.1.86 4.2.1.58

The following is the product of the second step.

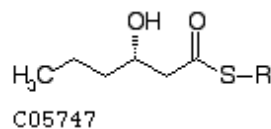


Figure 2.11 Product of the second step

Reaction:

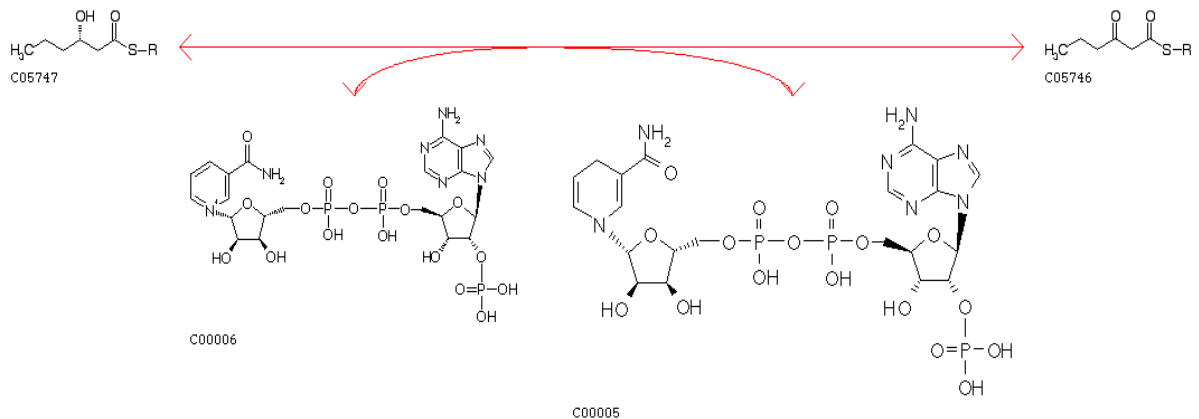


Figure 2.12 Reaction in the second step

The third step:

The following is the product of the third step

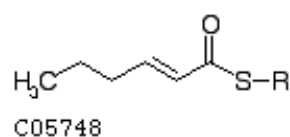


Figure 2.13 Product of the third step

The following enzymes are used in the third step.

ENZYME 1.3.1.9 1.3.1.10 2.3.1.85 2.3.1.86
 4.2.1.58

Reaction:

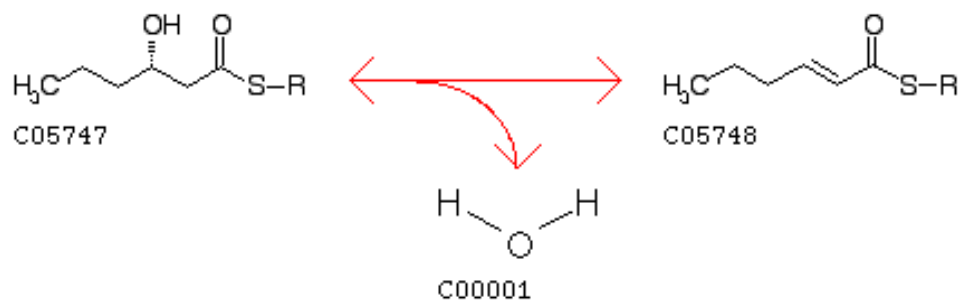


Figure 2.14 Reaction in the third step

The fourth step :

The fourth step is the hydrolysis step, which is carried out chemically.

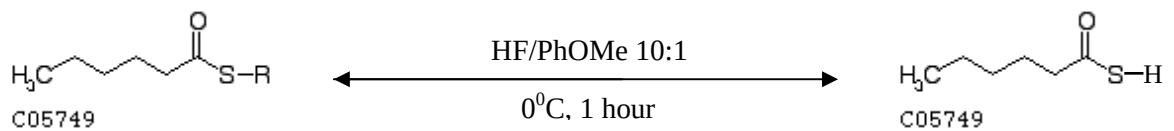


Figure 2.15 Reaction in the fourth step [12]

2.6 Enzymatic Conversion

2.6.1 Starting from an Ester.

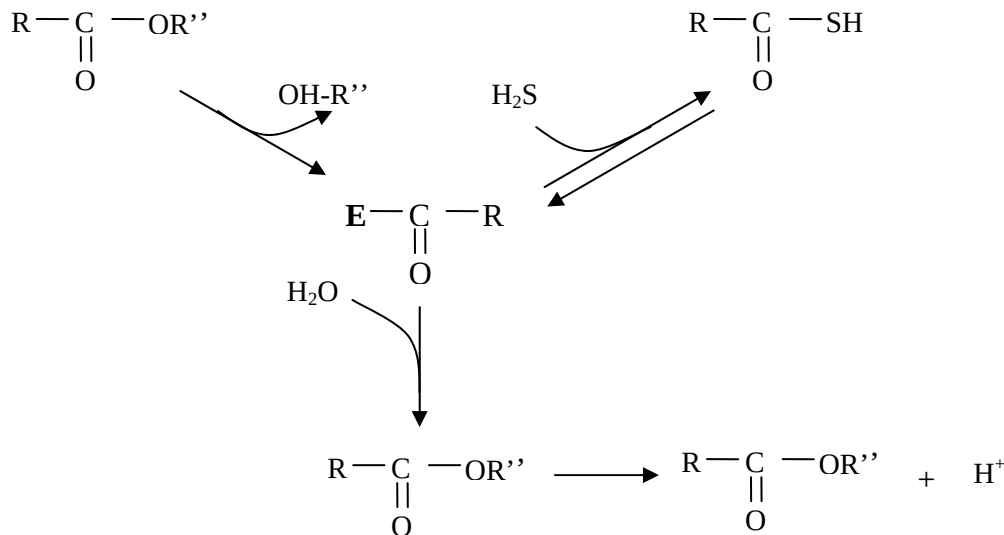


Figure 2.16 Enzymatic conversion by hydrolysis of carboxylic ester [53]

There is a potential problem if we use this reaction. The problems are as follows. If it is done on aqueous phase, then a competition between water and hydrogen sulphide will take place. This will be unfavourable for the reaction equilibrium, resulting in lower yields.

We can solve the problem by replacing the water by an organic solvent. The reaction can also take place in the organic solvent, as proven by E.M Anderson et al [1]. A potential substitute solvent is tert-butyl alcohol.

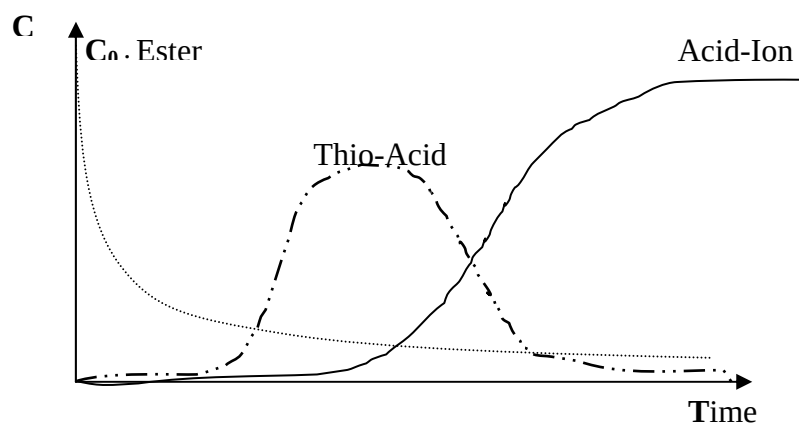


Figure 2.17 Typical Concentration Profile

A possible cheap starting material for this process is a mixture of long chain fatty ester. This mixture is easily found in a lot of lipids.

2.6.2 Starting from a Carboxylic Acid

The difference from the first reaction lies in the substrate type. In this case the process will begin from a purified carboxylic acid, the price of which is lower than the corresponding purified ester. The reaction will take place in oil-water interface with water content just as high as the enzyme requires, in order not to jeopardize its activity.

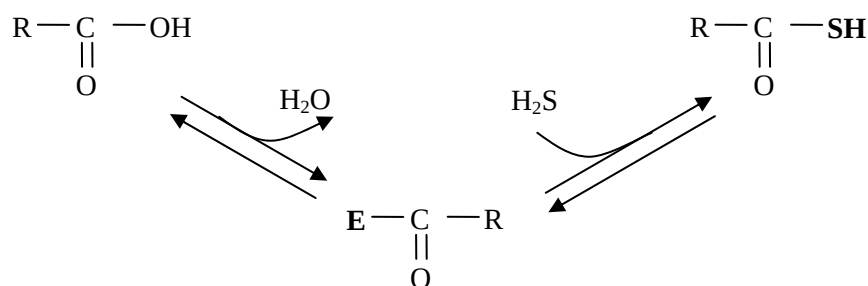


Figure 2.18 Enzymatic conversion by dehydration and substitution of carboxylic acid [53]

An application of this type of synthesis is already in use, and it is applied in the production of amides [30]. This is shown on the next figure:

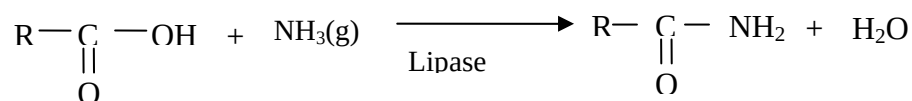


Figure 2.19 Analogous amidation reaction [30]

Analogously we can propose the following reaction.



Figure 2.20 Enzymatic group substitution of carboxylic acid [53]

2.7 Chemical Pathway

2.7.1 Chemical pathway starting from alkyl halides

The pathway shown here is the chemical pathway without using enzyme or bio-cycle.

Step 1:

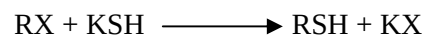


Figure 2.21 Reaction in the first step of the chemical pathway [62]

An alternative reaction for the first step is as follows.

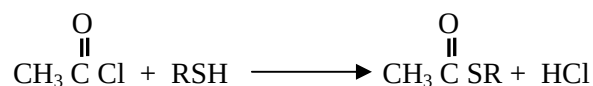


Figure 2.22 Alternative first step reaction [34]

X is the halide group such as: Cl^- , Br^- , and so on

For this reaction a large amount of KSH is required in order to inhibit the production of by product RSR.

Step 2:



Or

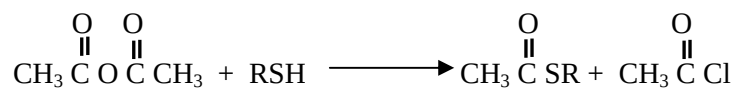


Figure 2.23 Reactions in the second step of the chemical pathway [62]

An alternative second step reaction is as follows.

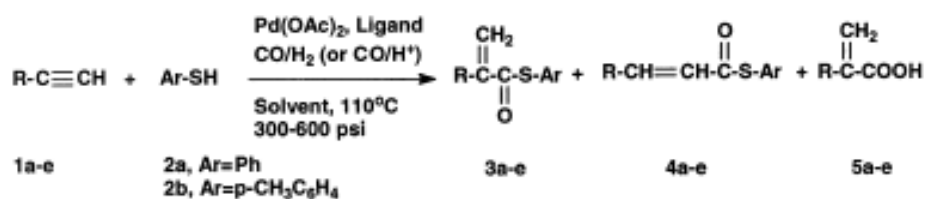


Figure 2.24 Alternative second step reaction [14]

Step 3:

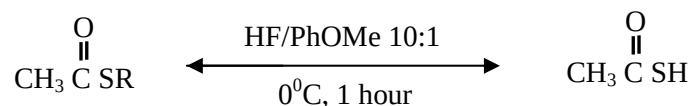


Figure 2.25 Reaction in the final step of the chemical pathway [12], [62]

2.7.2 Chemical pathway starting with commercial ester

The chemical pathway can also start with a commercial ester, such as the following.

- By using Ligand Exchanger Reaction of Sulf-oxides in Organic synthesis:

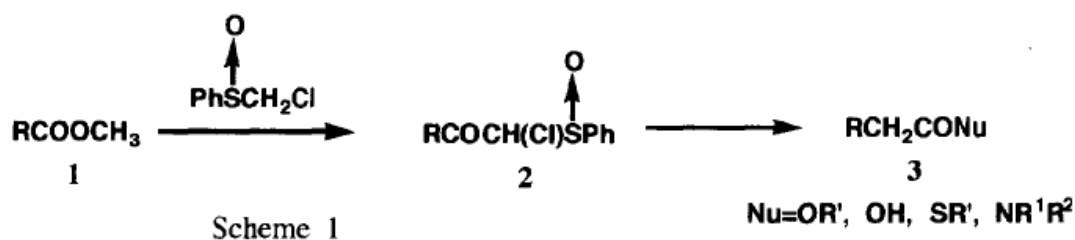


Figure 2.26 Ligand exchange reaction [44]

- By Using Horne –Wittig Reaction approach to the thiomers acid:

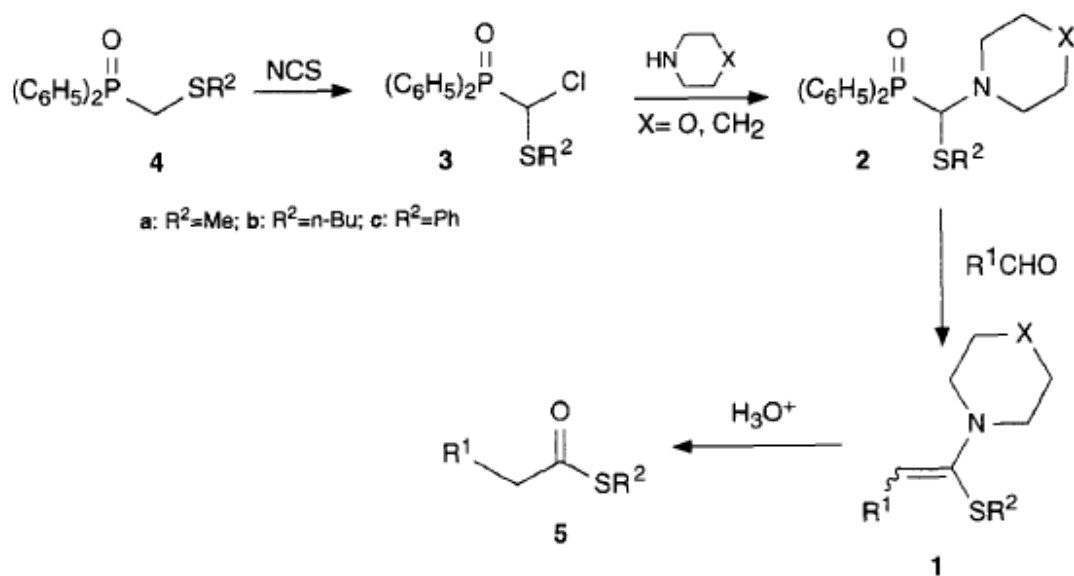


Figure 2.27 Horne-Wittig reaction approach [38]

The benefit of using this reaction is quite high yield and purity can be reached, some result is given in the table below:

Table 2.1 Synthesis of S,N-ketene acetyls [38]

Compound	R ¹	R ²	X	Yield
1a	Phenyl	Methyl	O	90
1b	Phenyl	n-butyl	O	88
1c	Phenyl	Methyl	CH ₂	80
1d	p-methoxyphenyl	Methyl	O	88
1e	p-methoxyphenyl	n-butyl	O	81
1f	p-methoxyphenyl	Methyl	CH ₂	80
1g	2-thienyl	Methyl	O	80
1h	2-thienyl	n-butyl	O	84
1i	m-bromophenyl	Methyl	O	89
1j	m-bromophenyl	Methyl	CH ₂	85

2.7.3 Black boxes

A number of black boxes have been developed to summarize the possibilities arising from the above technologies. The black boxes are useful to identify the possible by products that we have by employing a specific pathway.

Alternative 1: Fermentation alternative

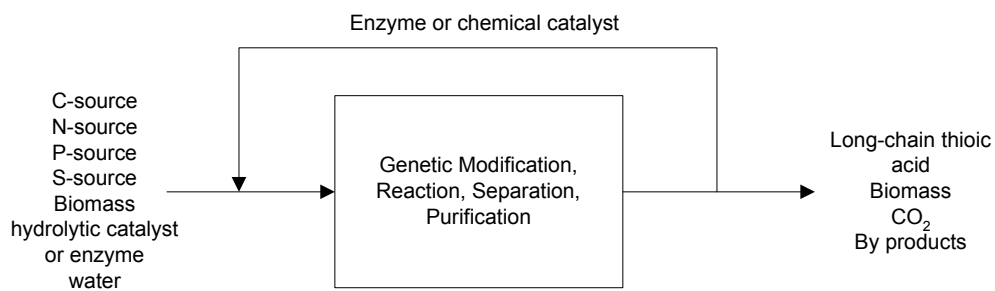


Figure 2.28 Alternative 1: fermentation alternative

Alternative 2: Enzymatic alternative 1

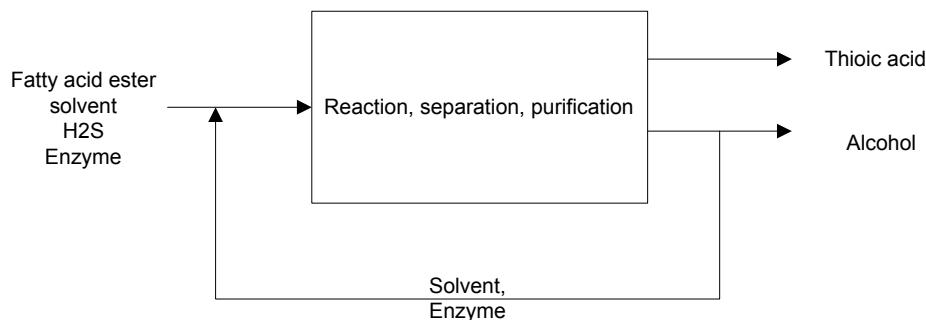


Figure 2.29 First enzymatic alternative

Alternative 3: Enzymatic alternative 2

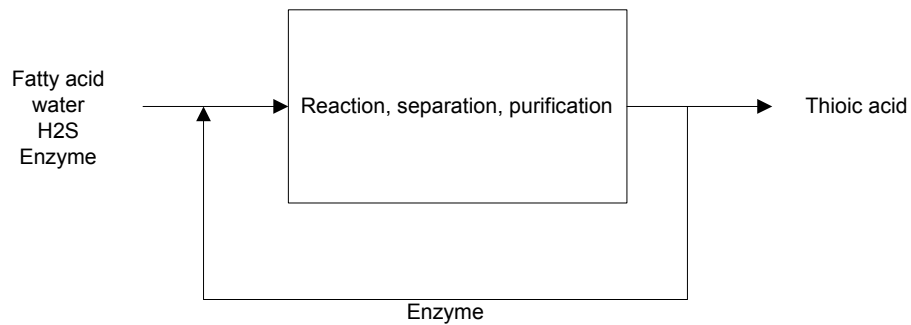


Figure 2.30 Second enzymatic alternative

A chemical alternative has been found and it is presented below.

Alternative 4: Chemical pathway 1

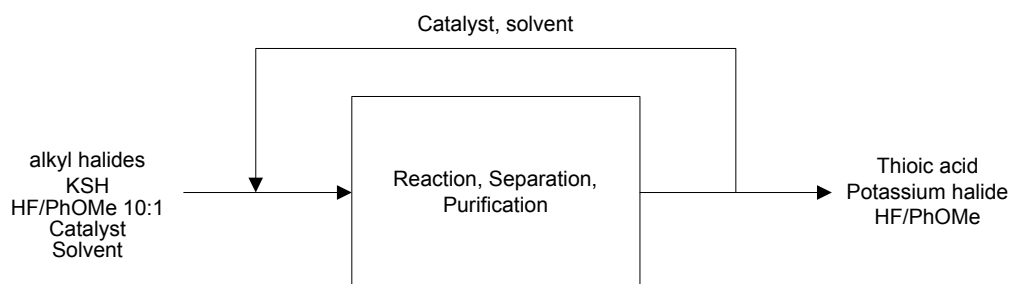


Figure 2.31 First chemical alternative

Alternative 5: Chemical pathway 2

This pathway differs from the first pathway in terms of its raw materials.

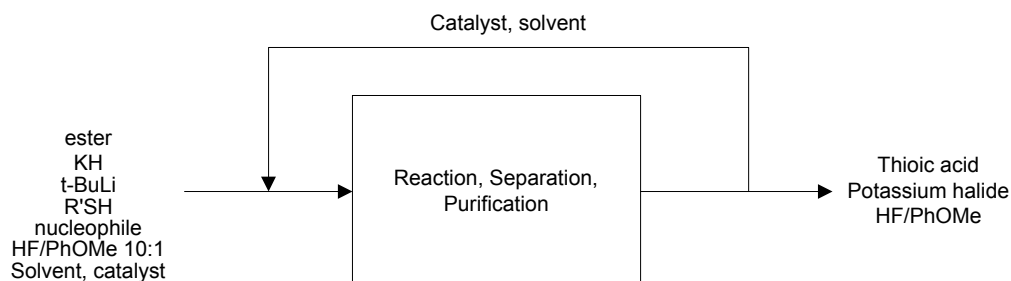


Figure 2.32 Second chemical alternative

A sixth alternative has been suggested by the team. The sixth alternative is a combination of the first and second enzymatic alternatives, and the black box is presented below. In this alternative, the triglyceride is first converted into glycerol and fatty acids by enzyme. After that, the fatty acid is sulphurylated using H_2S , catalysed by enzyme, to yield the thioic acid.

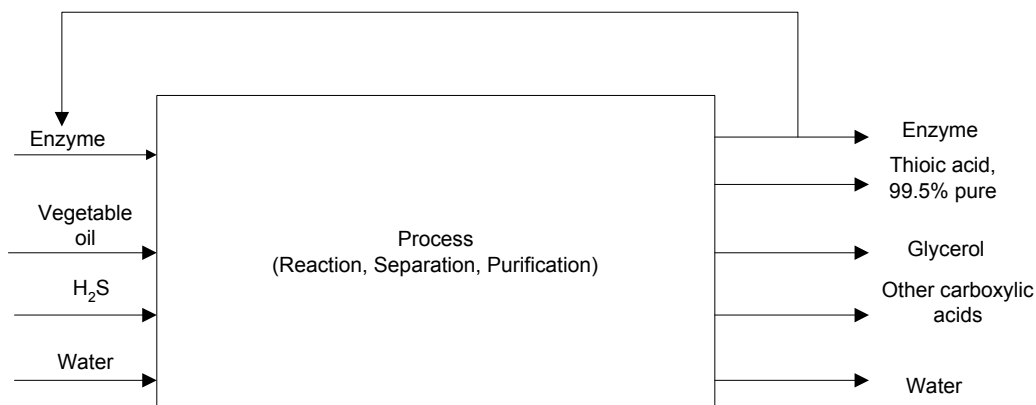


Figure 2.33 Sixth alternative, a combination of the first and second enzymatic alternative

2.8 Evaluation

Evaluation is made basically on the first quality criterion, which is economics. It is realized at this early stage that the plant economics shall not be determined by the costs of raw materials alone but also the costs of utilities. Therefore a comparison of utility costs shall also be carried out.

2.8.1 Raw materials

According to the price list (Appendix 4), some of the cheapest raw materials are the vegetable oils. The cheapest vegetable oil we could find is palm oil. Nevertheless, there is a lot of saturated fatty acid in palm oil, so that we expect to have some issues in downstream processing.

Glucose is more expensive than vegetable oils. An analysis of theoretical maximum yield from glucose has been carried out and the result is presented in Appendix 2. We can see that fermentation will give a maximum theoretical yield of 67% by weight,

which is relatively high. However good values for commercial production of chemicals using pathway engineering can be higher. Values around wt% yield of 95 for Succinic acid production have been reported [7].

But since enzymatic conversion can theoretically give 100% conversion, this is relatively low. In addition to glucose, the reactor should also be supplied with S-, P- and N-sources as well as trace elements to sustain the microbes.

Directly using the fatty acid is another possibility. The price of crude oleic acid which is a long chain monounsaturated fatty acid (C18:1) has been found to be around US\$ 1000 per ton in 2002. Since our product will be priced in the range of US\$3000-4000 per ton, direct use of the fatty acid seems feasible. Using the fatty acid also gives us the advantage of fewer steps in achieving our goal compared to using vegetable oil. The oil hydrolysis step can be removed, leaving only one reaction to the whole process. Thus, controlling the process becomes also easier because fewer operations are involved in the plant.

2.8.2 Catalyst

The catalysts used in the different pathways are different. In the fermentation pathway, we use genetically modified organisms. As GMO's are usually not very stable, we may expect problems when we decide to use continuous culture system. A failure in the flow rate control system may cause wash out of the microorganism of interest. It should also be kept in mind that the resulting product of fermentation, which is the thioester shall be obtained as intracellular product, which will also give some recovery and purification issues.

In the enzymatic pathway, we are going to use enzymes. The enzyme of choice for both enzymatic pathways is lipase. Lipase is a relatively cheap and stable enzyme. However, the enzyme shall preferably be immobilized to make the process more economical. Immobilising the enzyme brings the consequence that the investment for catalyst is higher because immobilised enzyme costs more than free enzyme. Nevertheless, immobilised enzyme can be used repeatedly, so that in the end the cost can be minimised.

2.8.3 Challenges to fermentation technology

Additional challenges would be faced if we use fermentation pathway; for instance for large-scale production some restrictions are related to host-strain physiology and fermentation technology. Large-scale processes impose restrictions on the expression system. Many promoters system that work well in small-scale systems cannot be implemented in industrial environment [21]. Regarding cultivation methods, three methods can be considered: batch, fed-batch and continuous cultivation. In order to be commercially viable, any cultivation method has to meet a number of criteria. These include a high volumetric productivity, a high final product concentration, stability and reproducibility of the process and applicability a low cost, high soluble substrate, and legal restrictions [21].

Batch cultures are not suited for large scale of production. High initial sugar concentrations cause catabolite repression phenomena and in some yeasts, trigger alcoholic fermentation even when oxygen is present [57]. In batch cultures, the growth rate cannot be controlled; and then growth rapidly becomes limited by oxygen. When sugars are used as a feedstock, this triggers alcoholic fermentation, resulting in a reduction of biomass yield and product formation.

During fed batch and continuous culture, the growth rate can be manipulated by controlling addition of substrate. Thus, by-product formation and catabolite-repression phenomena can be avoided and oxygen uptake and heat generation can be adapted to the limitations set by the reactor specifications. However, industrial applications of continuous cultivations are rarely used. During prolonged cultivation, accumulation of less or non-producing variants can lead to decrease productivity. Prolonged maintenance of axenic conditions may be also a problem. These considerations have resulted in fed-batch cultivation being the generally preferred method for large-scale production. However large-scale fed-batch fermentation involve a substantial number of generations. Therefore, even low expression-cassette instability has a profound effect on the overall productivity of the system [21].

Regarding the influence of physiological parameters involved, large scale of fed-batch processes are in principle aerobic and sugar limited (for instance in the case of production of heterologous protein). During large-scale cultivation of yeast at high biomass densities, it is virtually impossible to avoid local gradients in sugar and oxygen concentration. These have a profound effect on the occurrence of alcoholic

fermentation. Production of ethanol and others metabolites causes a diversion of substrate carbon from biomass and protein production and is therefore not desired. The reasons exposed before show the high risk involved in fermentation process that require genetic modified microorganisms. The fed batch fermentation constitutes the best option for large-scale production. However, this cultivation has problems regarding to gene expression. Studies on gene expression should be taken into account for the specific production rate of the product of interest (amount of product per unit biomass and per unit of time), and in particular its relation to the specific growth rate. The numerous physiological and technological restrains on large-scale fermentation processes should, at an early stage, be taken into account in studies on the expression in the host [21].

2.9 Comparison between processes

The comparison between the processes is given in the following table.

Table 2.2 Comparison between processes

Comparison factor	Enzymatic pathway 1	Enzymatic pathway 2	Combined enzymatic pathway	Fermentation pathway
Raw materials	Fatty ester	Fatty acid	Vegetable oil	Glucose, S-source, N-source, P-source
Raw material price	Expensive	Expensive, if pure US\$ 991/ton for 89%-w crude C18 UFA	Cheapest available US\$600/ton	US\$600/ton
Hazardous materials	Organic solvent	Acid	H ₂	GMO
Yield	100% achievable	100% achievable	50-70% w/w oil achievable	66.7% w/w glucose
Maximum gross profit margin	Not calculated	US\$2000/ton product	US\$2100/ton product	US\$2100/ton product
Catalyst availability	Commercially available	Commercially available	Commercially available	Tailor-made
Catalyst price	Low	Low	Low	Low, if genetic modification is successful
Catalyst stability	High	High	High	Low compared to wild type
Genetic modification	Not needed	Not needed	Not needed	Needed

Table 2.2 Comparison between processes

Comparison factor	Enzymatic pathway 1	Enzymatic pathway 2	Combined enzymatic pathway	Fermentation pathway
By product	None	Alcohol	Glycerol	Biomass, metabolites
Utilities to be used	Cold and hot utility	Cold and hot utility	Cold and hot utility, inert gas (N ₂ or Ar)	Cold and possibly hot utility
Solvent	Organic	Water	Water	Water
Controllability	High	High	Lower than the first two alternatives	Lower than all enzymatic alternatives

2.10 Technology of choice

Considering the advantages and disadvantages of the technologies that have been found so far, the team decided to focus its attention to the second enzymatic pathway. The commercial availability of the catalyst and the raw materials is one of the main reasons. Although it may seem that the third enzymatic pathway is cheaper in terms of raw material costs, it must be kept in mind that in this rough calculation we assume 100% hydrolytic conversion, which is hardly achievable.

Process controllability is another reason. The second enzymatic pathway involves the fewest number of steps, so that we can expect that the whole plant will be more controllable.

Taking commercial availability into account, the team decided to use crude oleic acid as its raw material. Oleic acid is commercially available as bulk chemical, so that we can expect no issue of raw material supply.

Legislative regulations of the raw materials can be found in Appendix 3.

2.11 Alternative schemes

Keeping the target product quality in mind, the team has come up with five different alternatives of the arrangement of subprocesses within the first enzymatic route. The alternative block diagrams are presented in the respective paragraphs below. Larger version of the block diagram can be found in Appendix 8.

2.11.1 First alternative

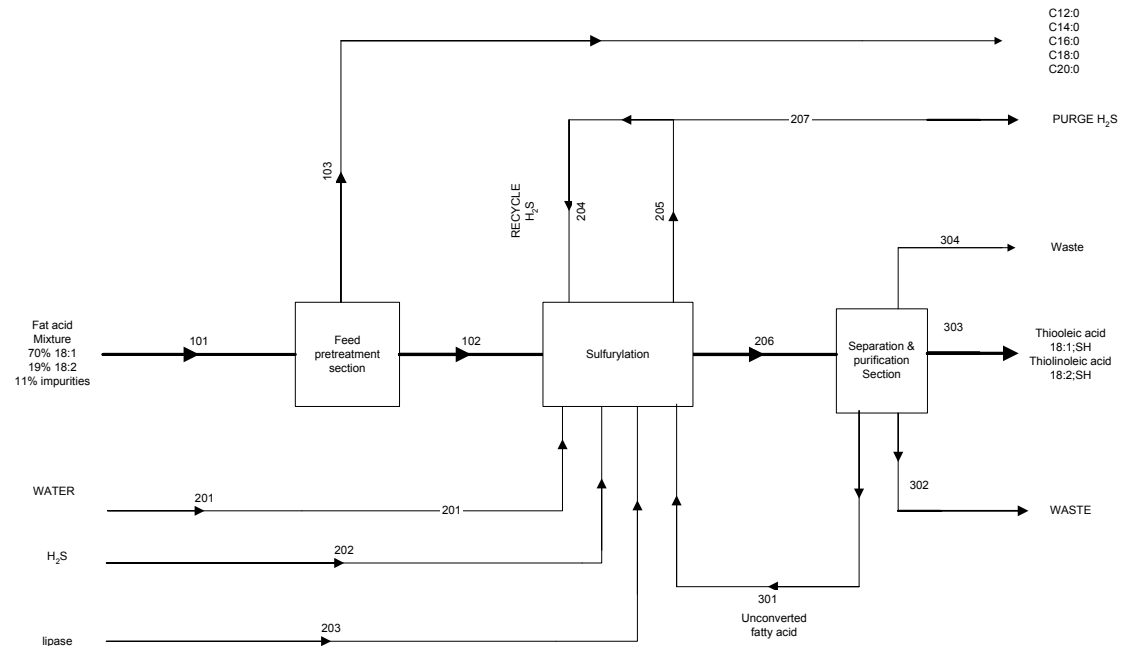


Figure 2.34 Alternative A

In this alternative, the feed is first pre-treated before entering the enzymatic reaction stage. The feed consists of saturated C12, C14, C16 and C18 acids as well as mono- and polyunsaturated C18 acids. The saturated and unsaturated fatty acids have very different melting points as presented in Table 2.3.

Table 2.3 Melting points of feed components

Characteristic	C18:1 (oleic)	C18:2 (linoleic)	Saturated fatty acid
Melting point	16°C max	-5°C	44°C min
Flash point	189°C		180°C

By exploiting the melting point difference we can infer that at room temperature (20°C), separation of unsaturated acids from the rest of the feed can be easily accomplished. The unsaturated acids will be liquid while the other components are in solid phase. Therefore, the first step in this alternative is to separate the unsaturated acids from the rest of the feed components.

In the first alternative, after feed pre-treatment, the linoleic and oleic acids are not separated from each other. The mixture of linoleic and oleic acid enters the sulphurylation section. The reaction with hydrogen sulphide is again catalysed by lipase. The result is a mixture of thiooleic and thiolinoleic acid. As the customer only specifies at least one unsaturated bond, this mixture is still acceptable.

2.11.2 Second alternative

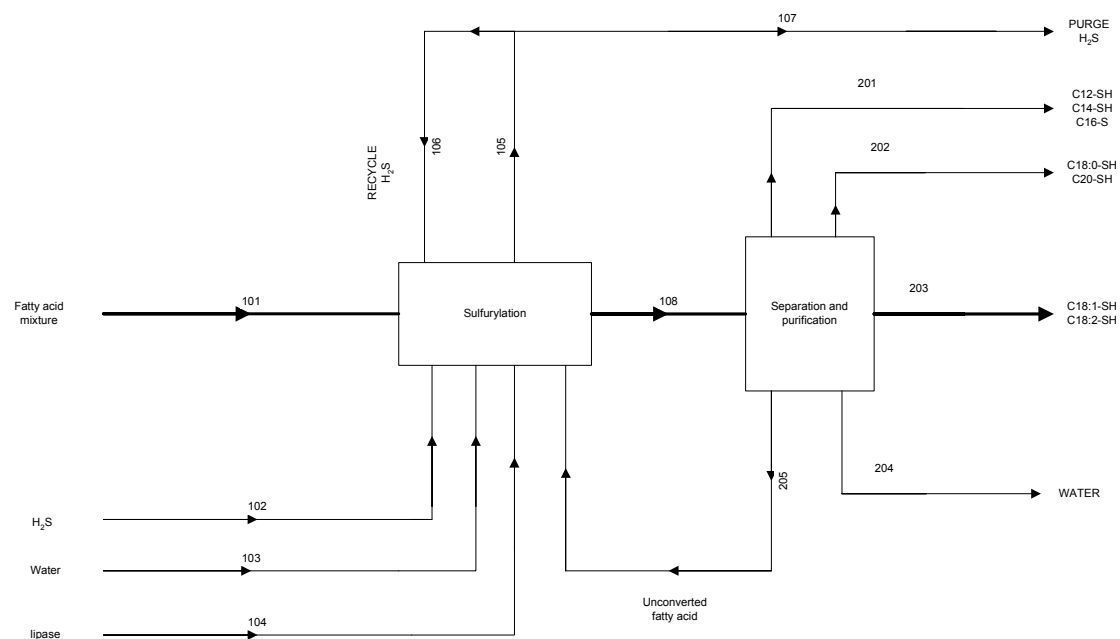


Figure 2.35 Alternative B

In the second alternative, the feed is not pretreated. The whole stream enters the sulphurylation section and reacts with H₂S, catalysed by lipase. After that, the stream is separated in a separation section. Two-step separation will probably have to be carried out. In the first step, the unsaturated thioic acid is recovered from the rest of the stream. After that the thiooleic and thiolinoleic acids are separated from each other.

2.11.3 Third alternative

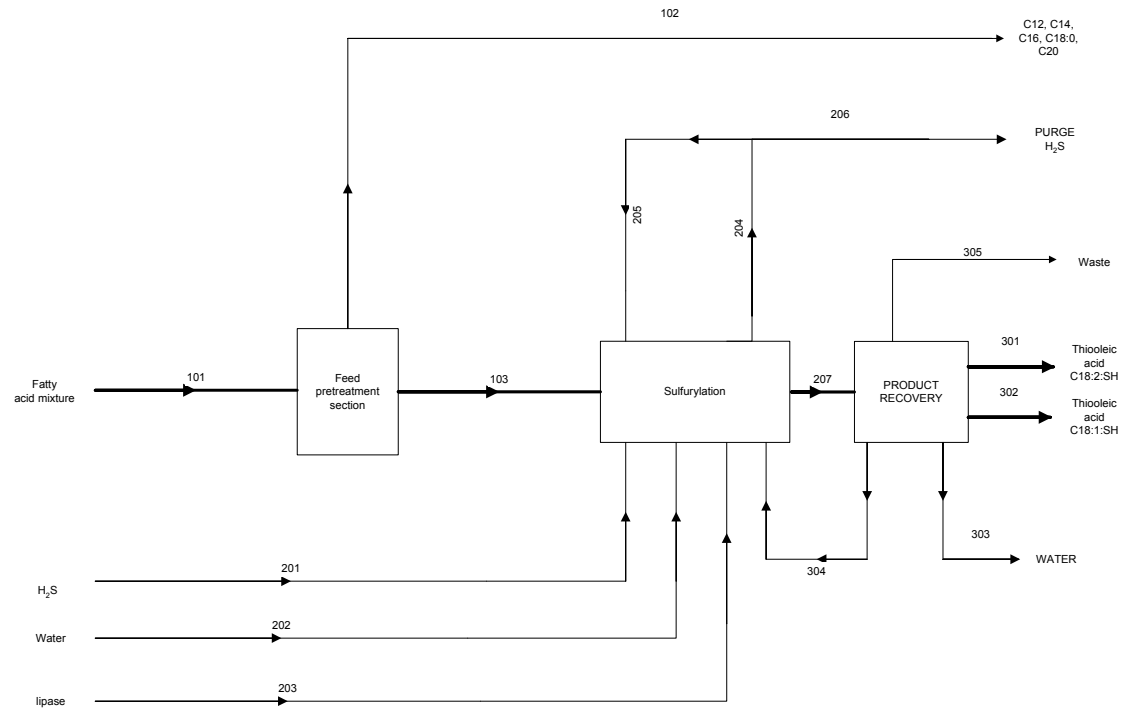


Figure 2.36 Alternative C

The third alternative is basically similar to the first alternative. The mixture of unsaturated C18 acids enters the sulphurylation section after being recovered from the rest of the feed stream. After sulphurylation, the thioleic and thiolinoleic acid are separated from the unreacted acids, separated from each other and purified. Thus, we have two purified streams of thioleic and thiolinoleic acids.

2.11.4 Fourth alternative

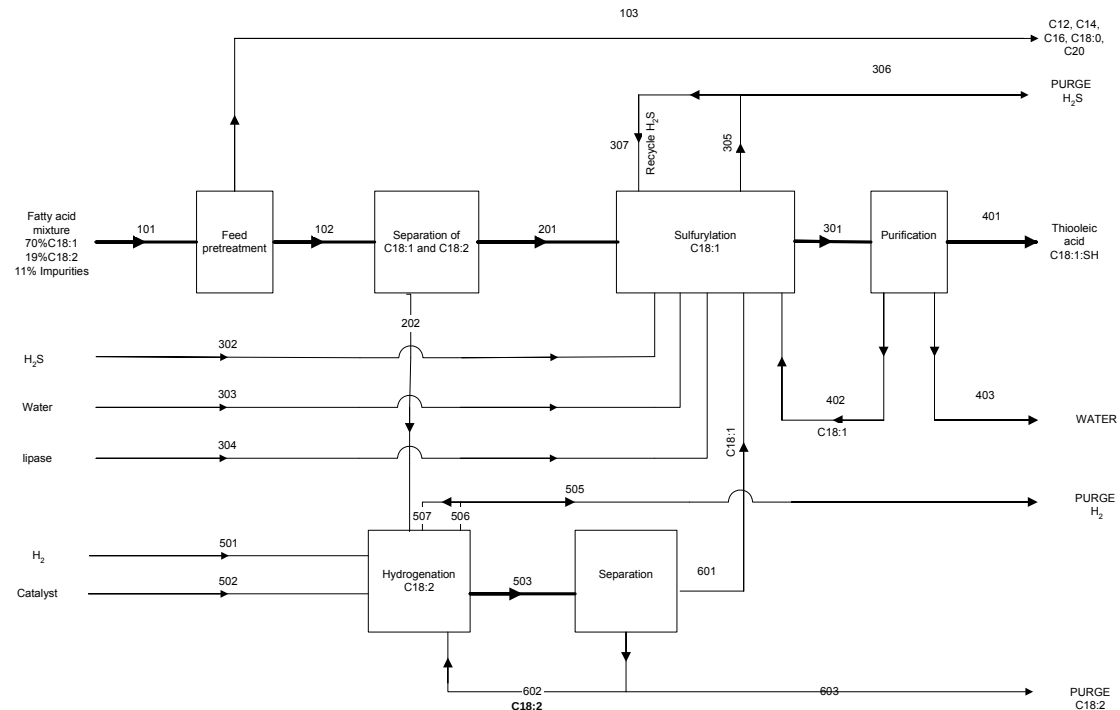


Figure 2.37 Alternative D

In this alternative, C18:1 and C18:2 are recovered from the rest of the feed component, exploiting the physical property difference. C18:1 and C18:2 are again separated from each other in the second step.

Rather than directly reacting C18:2, the linoleic acid stream is first hydrogenated to yield oleic acid using chemical catalyst and hydrogen. The resulting oleic acid stream is first purified before entering the enzymatic sulphurylation step. This oleic acid stream will flow into the sulphurylation reactor, combined with the original oleic acid stream to yield thiooleic acid. After sulphurylation, the stream is purified before being sold. With this process, we will produce only one product, the thiooleic acid.

2.11.5 Fifth alternative

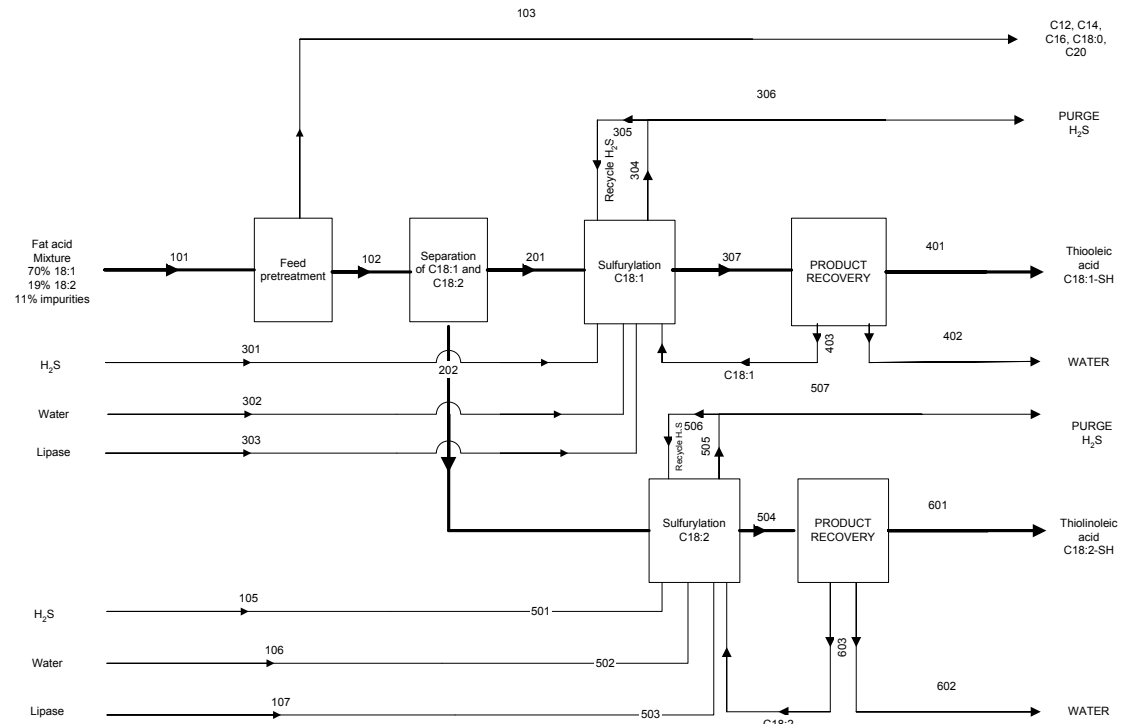


Figure 2.38 Alternative E

The fifth alternative is basically similar to the fourth alternative. After separation of the unsaturated acids, we separate the oleic acid and the linoleic acid. This separation can be easily accomplished by exploitation of the melting point.

Recovered C18:1 will react with H₂S to yield thiooleic acid. Separated stream of C18:2 will also react with H₂S to yield thiolinoleic acid in another reactor or in the same reactor within different batch. The thiooleic and thiolinoleic acids are purified and later sold. Thus we have two different products, pure thiooleic acid and pure thiolinoleic acid.

2.11.6 Mass balances

The mass balances for all the alternatives have been solved with a maximum error of 2%. The complete balances and the assumptions are given in Appendix 6. From the balances, the raw material requirements can be calculated for each individual process. The results are as follows.

Table 2.4 Raw material requirements (in tons/year)

Raw materials	A	B	C	D	E
Fatty acid mixture	7260	7115	7188	5831	6828
H ₂ S	771	887	774	608	731
H ₂	0	0	0	8	0

All processes give product purities which exceed 99.5% on molar basis

2.12 Evaluation of alternatives

The five alternatives proposed by the team were submitted to an evaluation based on the criteria stated on the PIQUAR matrix. The PIQUAR matrix can be found in Appendix 21. Each member of the team make an assessment of each alternative, and afterwards the team came together and make the final evaluation. The best alternatives found were A, C and E. The results of the individual evaluations are presented in Appendix 8.

The following table summarizes the result of PIQUAR analysis on a 5-point scale.

Table 2.5 Results of PIQUAR analysis

Alternative	Final Score
A	3.70
B	3.29
C	3.70
D	2.84
E	3.42

From the table it can be seen that alternatives A, C and E are the ones that scored closest to 5. Moreover alternatives A and C scored equal values, therefore a further evaluation is required, for this, three scenarios will be established, and each of the selected alternatives will be tested on them. The three scenarios are as follows:

1. The client only wants the C18:1-SH
2. The client suggested that the plant must be built on existing site (space restriction).
3. There are side reactions in the sulphurylation step.

Detailed results of the three-scenario analysis can be found in Appendix 9. A summary of the results is given in the following table.

Table 2.6 Scenario analysis results

Scenario	Alternatives		
	A	C	E
1. The client wants only the C:18:1 SH	2.88	3.93	3.8
2. The client suggested that the plant must be built on an existing site	3.99	3.96	3.47
3. "Presence of side reactions in the sulphurylation step"	3.74	3.65	3.88

2.12.1 Scenario 1

This scenario is closely related to the two most important quality factors. In order to make money, the product must be sellable, which means it must fulfil the demand of the market. The product must be of sufficiently high quality to fulfil this demand.

At first, the product specifications were defined as follows. The product shall have at least one unsaturated bond and one thioic group. However, the existence of more than one unsaturated bond is not preferred because of branching possibilities. Based on these specifications, the mixture that we produce from alternative A would have been acceptable.

In this scenario, we propose a market situation where only one unsaturated bond will be acceptable. Under this scenario, we found that alternative A will not be acceptable because there is simply too high level of C18:2 which will be present in the product. Therefore alternative A scored the lowest in this respect. This scenario turned out to be realistic as after further consultation with the company, we found out that the maximum level of C18:2 in the product is 5%-mol.

In this first scenario, alternative C seems to be performing best. Alternative C has the same number of sub-processes as alternative A but its product is of higher quality. However, the final separation and purification section of alternative C is expected to be more complex than alternative A because more streams will be produced in this section of alternative C.

Alternative E performs a bit worse than alternative C, however the difference is not significant. The main issues which cause this difference are the space saving and the number of equipment involved.

2.12.2 Scenario 2

In the second scenario, the preferred process should require the least space, energy and water as the new plant should be built as part of an existing industrial complex. In this respect, alternative E performs the worst and alternatives A and C, which have the same number of equipment, perform equally well. The small difference between A and C is related to the expectation that alternative C will have a more complex separation section, and thus require more space, energy and water.

2.12.3 Scenario 3

In this scenario we consider the possibility of having an unselective catalyst. The catalyst will be somewhat less selective towards the sulphurylation of the carboxyl group so that a number of by products is expected to increase. Under this scenario, scenario C scored lowest despite the fact that the product quality will be probably similar to alternative A. In alternative C, the final separation section would probably involve more equipment if there were a lot of by-products. Therefore alternative C scored lower in terms of having the fewest number of equipment. Alternatives A and C score lower than alternative E in terms of controllability because there is hardly any way to control by-product formation. Therefore alternative E scored the best under this scenario.

2.12.4 Conclusion

After carrying out the above evaluation, alternative C is chosen for the next step of design. However, alternative E still has some advantages, thus it remains an option when an obstacle is faced in the future. This alternative will be analysed in depth. Mass balance as well as battery limits will be given for each of the subprocesses.

2.13 Analysis of chosen alternative

As described above that the alternative C is chosen as our favourite process at the moment, which is based on scenario 1.

From Figure 2.34 it is clear that the whole process in alternative C is separated into three parts, *Feed Pretreatment*, *Sulphurylation*, and *Product Recovery*. The detailed discussion on each sub-process is given in the following sections.

2.13.1 Feed Pretreatment

First, the raw material stream S-101 (fatty acid) is fed into the *Feed Pretreatment* sub-process. In this process, the fatty acid mixture is separated into two streams, which are by product stream S-102 (C_{12} , C_{14} , C_{16} , $C_{18:0}$, C_{20} mixture), and the process stream S-101 ($C_{18:1}$, $C_{18:2}$, small impurity). In that case most of the impurity has been separated into S-102 and relatively pure raw material will be used into next step. As it is shown in Figure 2.36, the by product stream will go outside the process, and process stream will come into the second sub-process *Sulphurylation*.

Purer raw material stream will require lower amount of hazardous gas H_2S , and a simpler reaction medium in the following reactor. This is the main aim of this sub-process.

The keys technologies which may be used in this sub-process are crystallization, vacuum distillation and filtration, which are based on the physical properties of the fatty acids. All those properties have been given in Appendix 5. It is well known that the relatively big difference on the melting points of different fatty acids makes the crystallization method possible. If crystallization is used in the process, filtration has to be used to separate solid phase and liquid phase. The relatively low flash points make the normal distillation technology become too dangerous to be used, thus we must lower the boiling point by using vacuum distillation. The key technologies chosen will be discussed in the next space.

The mode of operation in this sub-process depends also to some degree on the separation method chosen to purify the raw materials. If crystallization plus filtration are chosen, in biotechnological cases the process will be operated in batch wise. However, according to Belter et al. [3], continuous crystallisation is also the norm in the production of bulk chemicals. If vacuum distillation column is used, the sub-process will run continuously as a normal requirement of distillation technology.

The mass based ports of the sub-process is given in the Table 2.7.

2.13.2 Sulphurylation

After pretreatment of raw materials as described in the previous paragraphs, a mixture, which only contains $C_{18:1}$ and $C_{18:2}$ and very little impurities, is injected into the second sub-process *Sulphurylation* section from the first sub-process *Feed pretreatment* in stream S-103. Other inlet streams are, S-201, the H_2S gas stream;

S-202, the water stream, which will be used as solvent in the reactor; S-203, the lipase stream, which probably will stay in the reactor and be regenerated after certain period. The outlet streams are S-206, the purge stream for H_2S ; S-207, the reacted stream, which contain thioester acids ($C_{18:1} SH$, $C_{18:2} SH$, impurities-SH), will leave the section and go to next sub-process *Product Recovery*.

In this section the fatty acid will be converted into thioic acid. This is the main reaction in the whole process. The reaction in the reactor is given as:

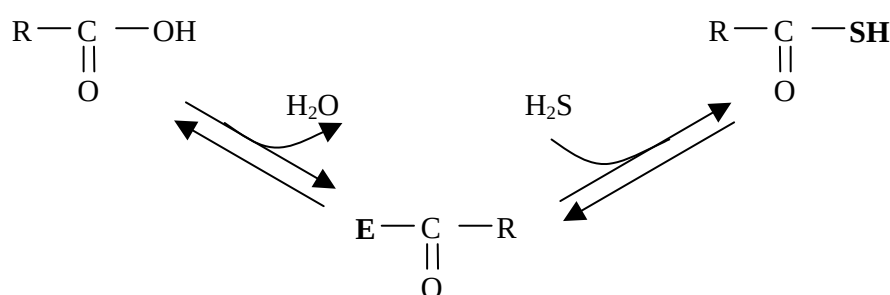


Figure 2.39 Reaction in the sulphurylation section

Besides the reaction part there are two other parts included in this sub-process. First, the recycle of H_2S , it is well known that the H_2S is a quite harmful gas. As it has to be used in the reaction, the amount used should be kept to the minimum. As shown in the figure, streams S-204 and S-205 indicate the H_2S recycle section. Second, we have the recycle of the un-reacted reactant, which is S-304. It comes from the third sub-process. By using this recycle, a higher yield could be expected. In the mass balance calculation, the recycles are not yet considered at the moment. The aim of this sub-process is to obtain the final product thiooleic acid.

The key technology using in the sub-process is enzymatic technology, the reason for choosing this technology has been detailed discussed in 2.10.

The mode of operation in this sub-process depends on the kinetic information of the enzyme reaction. If the reaction is slow, the operation should use the batch mode. Otherwise, the continuous mode would be used in the process. The time available of this sub-process will also be given after the research on the reaction kinetic finished.

The mass based ports of the sub-process is given in the Table 2.7.

2.14 Product Recovery

The stream S-207 from *Sulphurylation* section is the only inlet stream of the third sub-process *Product Recovery*. In this process the main aim is to purify the product $C_{18:1\ SH}$ to the requested quality, 99.5 mol%. There are five streams leaving the sub-process, including one recycle stream S-304, which is the un-reacted reactant stream and which has been mentioned in the previous discussion. The other four streams are S-301, main product stream with 99.5% pure $C_{18:1\ SH}$; S-302, main by product stream with 99.5% pure $C_{18:2\ SH}$; S-303, water stream, which is different from another water stream S-202, in this stream, the water is the product from the thioester reaction, which occurs in the previous sub-process *Sulphurylation*; S-305, the waste stream, of which the waste impurity_{SH} is the main component.

The key technologies which may be used in this sub-process are similar to the key technologies, which have been discussed in the first sub-process *Feed Pretreatment*. The chosen of technology will also be discussed in the next Delft Matrix space. Accordingly, at this moment it is impossible to decide whether continuous or batch mode will be applied in this sub-process.

The mass based ports of the sub-process is given in Table 2.7 below.

Table 2.7 Mass-based ports of the subprocesses

MASS BALANCE FOR STREAMS TOTAL						
IN			SPACE IDENTIF.	OUT		
PLANT				PLANT		
Mass Tons/year	Heat kW	Stream Nr.		Stream Nr.	Mass tons/year	Heat kW
7260		S-101	1	S-102	855	
				S-103	6405	
7260			Total		7260	
6405		S-103	2	S-206	48	
782		S-201		S-207	7138	
7187			Total		7186	
7138		S-207	3	S-301	5010	
				S-302	1384	
				S-303	386	
				S-305	359	
7138			Total		7140	
8042			Total		8043	

2.14.1 Economic evaluation

A preliminary economic evaluation has been carried out. The following are the results of this evaluation.

Table 2.8 Key economic evaluation parameters

Proposed selling price (US\$/kg product)	3-4
Raw material cost (US\$/kg product)	1.30
Gross profit margin	57-68%
Minimum selling price based on raw material cost (US\$/kg product)	3.60

Taking into account the proposed selling price, we can conclude that the process seems to be profitable.

2.15 Physical and chemical task sequence

After deciding on the sequence of subprocesses, the team has developed two alternatives of task sequence to achieve the required product specifications. The difference between the two lies in the recycle structure as we will discuss below.

2.16 First alternative

The block diagram for the first alternative task sequence is given in Figure 2.40.

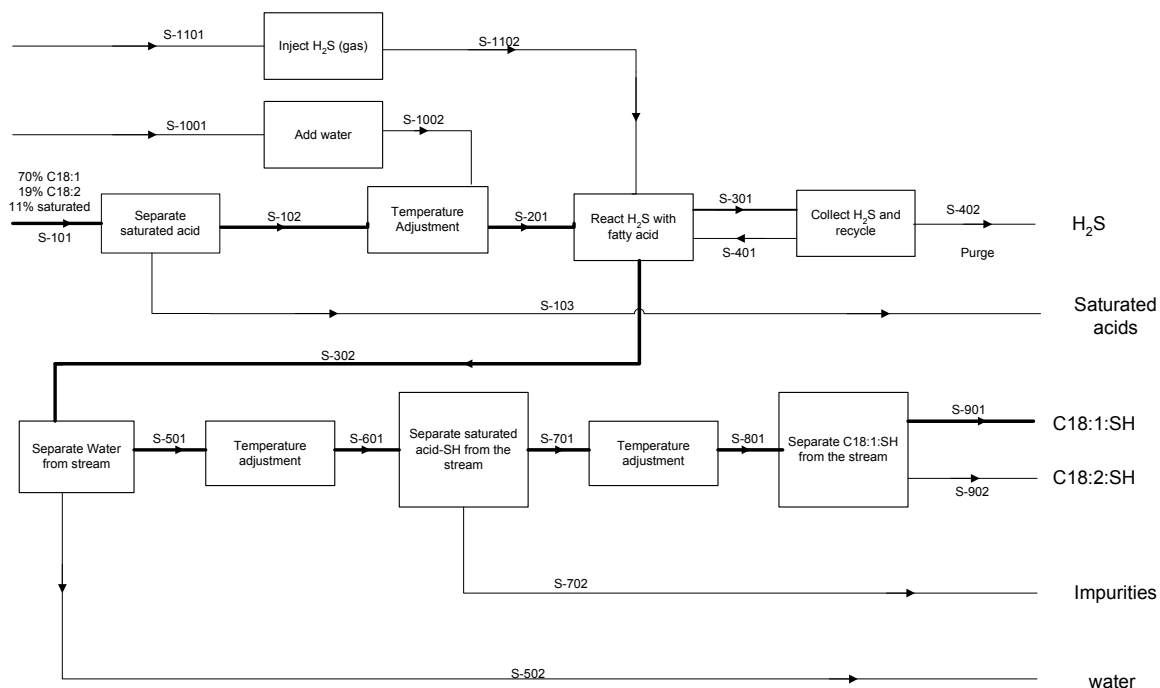


Figure 2.40 First alternative of task sequence

2.16.1 Feed purification

The objective of this sub process is to reduce the amount of hydrogen sulphide (H_2S) which will be required in the subsequent sulphurylation step. The feed consists of both unsaturated and saturated fatty acids. As unsaturated fatty acids are undesired, their amount should be reduced to the minimum.

In this subprocess, the saturated and unsaturated fatty acids are separated based on their different physical properties. The different phase change temperatures of the substances will be exploited for separation. The boiling points could be used to separate the acids. However, the normal boiling points of several compounds far exceed their flash points. Therefore, only vacuum operation can be a safe option.

If we consider the melting points, we can find that, at room temperature, linoleic and oleic acid will be in the liquid phase. All other components are in solid phase. Therefore the compounds can be separated by filtration at room temperature.

2.16.2 Reaction

In this step, the purified acid is fed into the reactor. The feed will be emulsified in water; therefore sufficient amount of water will also be injected into the reactor. This emulsification step is essential to keep a high enzymatic activity. There is an optimum water/organic ratio, which will ensure the high enzymatic activity. A sufficient amount of H_2S is subsequently fed into the reactor. The hydrogen sulphide gas will be bubbled through the reactor. Some temperature adjustments are necessary to obtain the optimum equilibrium concentrations.

The reaction will be an equilibrium reaction taking place in the interface between the organic and aqueous phase. The reaction is given in the following equation.

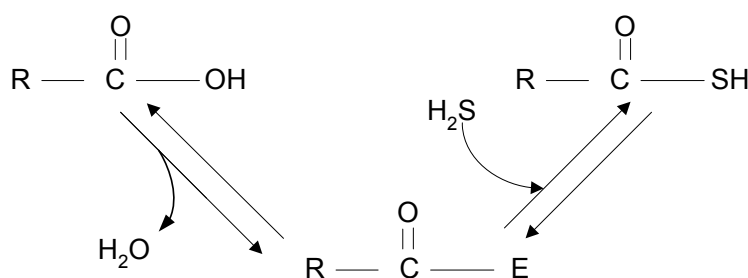


Figure 2.41 Reaction at oil-water interface

Equilibrium will be established in this interface. After equilibrium is established, no further conversion will take place. If no suitable means of product separation can be found, it will mean that our yield will be considerably lower than 100%. However, in this reactor water is continuously transferred out of the interface, thus shifting the equilibrium towards the product. A very high yield on substrate can be expected. In the first alternative water is not recycled. The price of water is much less than the price of H_2S , so in this alternative water recycle is not considered.

2.16.3 Separation and purification

In this section we will again exploit the different phase change temperatures of the components. A temperature adjustment is necessary to facilitate the separation of saturated thioic acid from the rest of the stream. The saturated acid will be in a different phase from the unsaturated acid. There are two options to achieve this phase difference. The stream can be either cooled down for crystallisation or heated up for distillation. In the subsequent section, the options and decision made will be explained in detail.

The second task to be accomplished in this section is to separate the thiooleic acid from thiolinoleic acid. Thiolinoleic acid level in the final product stream should be kept below 5% on molar basis. As the monounsaturated and polyunsaturated fatty acids also possess different phase change temperatures, we can exploit these to separate them from each other. Again, some temperature adjustments are necessary to realize the different phases of components.

2.17 Second alternative

The block scheme for the second alternative is given in Figure 2.42 below.

In this alternative, the produced water from the reaction section is not wasted. Water is recycled back into the reactor after separation following the reaction. In this way, fresh water requirement is reduced. However, further evaluation and analysis will be needed to justify the additional equipment requirement against the saving in water costs.

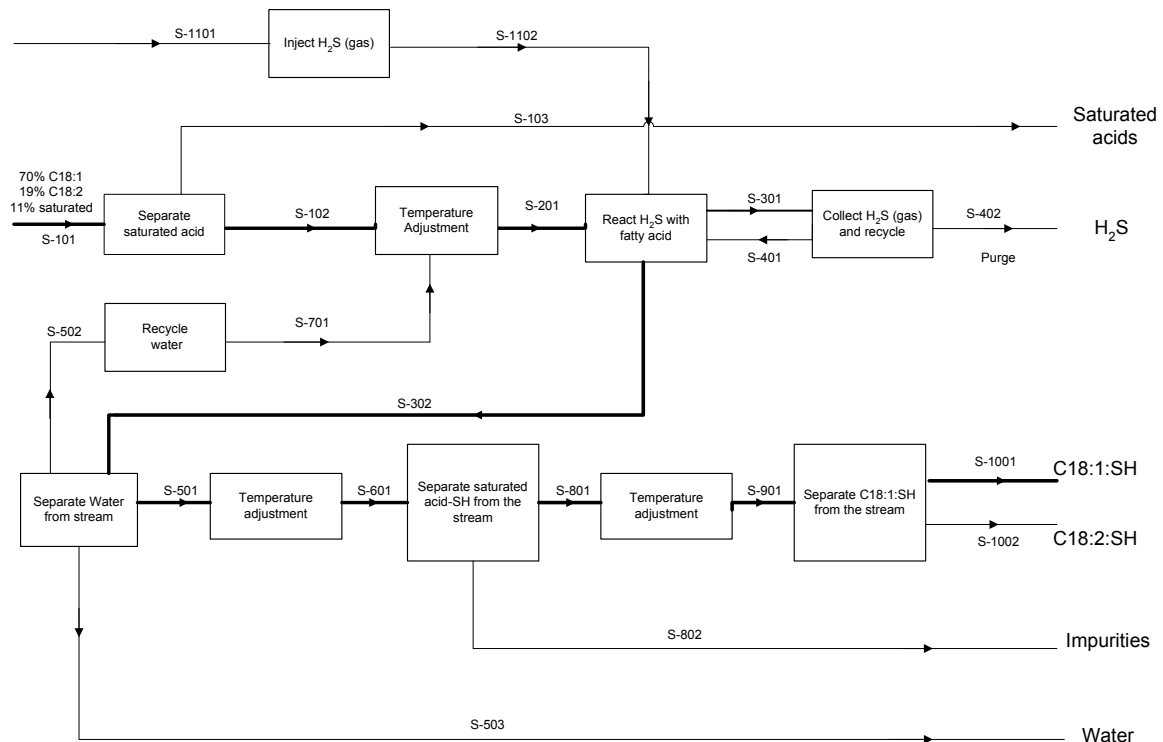


Figure 2.42 Second alternative of task sequence

2.18 Analysis of alternatives

In this section options shall be evaluated and compared to each other. The available options are given in the table below.

Table 2.9 Available options

Type of options	Alternatives
Recycle structure	With water recycle (A) Without water recycle (B)
Separation technology	Crystallisation-filtration (C) Vacuum distillation (D)

The advantages and disadvantages of the four alternatives are analysed using the PIQUAR factors.

All four alternatives have been submitted to an evaluation based on the criteria stated on the PIQUAR matrix. The procedure followed was similar to that used in choosing the best available subprocess sequence. The alternatives have scored as in Table 2.10. Details of the individual scores are given in Appendix 21.

Table 2.10 PIQUAR analysis scores

Alternative	Average score
A	4.19
B	4.16
C	4.11
D	3.94

Combining the alternatives, we have the following results.

Table 2.11 PIQUAR scores of combined options

	Separation mode	Crystallisation (C)	Vacuum distillation (D)
Recycle structure	With water recycle (A)	4.15	4.06
	Without water recycle (B)	4.14	4.05

The difference between the recycle structure options is not significant. Therefore, we first consider the separation technology options. It is quite clear that crystallisation scores better than vacuum distillation. Therefore *crystallisation is chosen*.

Another approach must be taken to decide on the recycle structure. Considering that DSM is an environmentally-conscious company, it is decided that the process to be employed shall incorporate water recycle. Therefore, *water recycle is chosen*.

The chosen option will then be *an enzymatic reaction, following a feed purification step in the form of crystallisation-filtration, followed by product purification using crystallisation-filtration, incorporating water recycle*.

However, there is actually another option which we have not so far discussed in detail. Alternative E from the subprocesses step can be developed into a third alternative sequence which is depicted in the figure below.

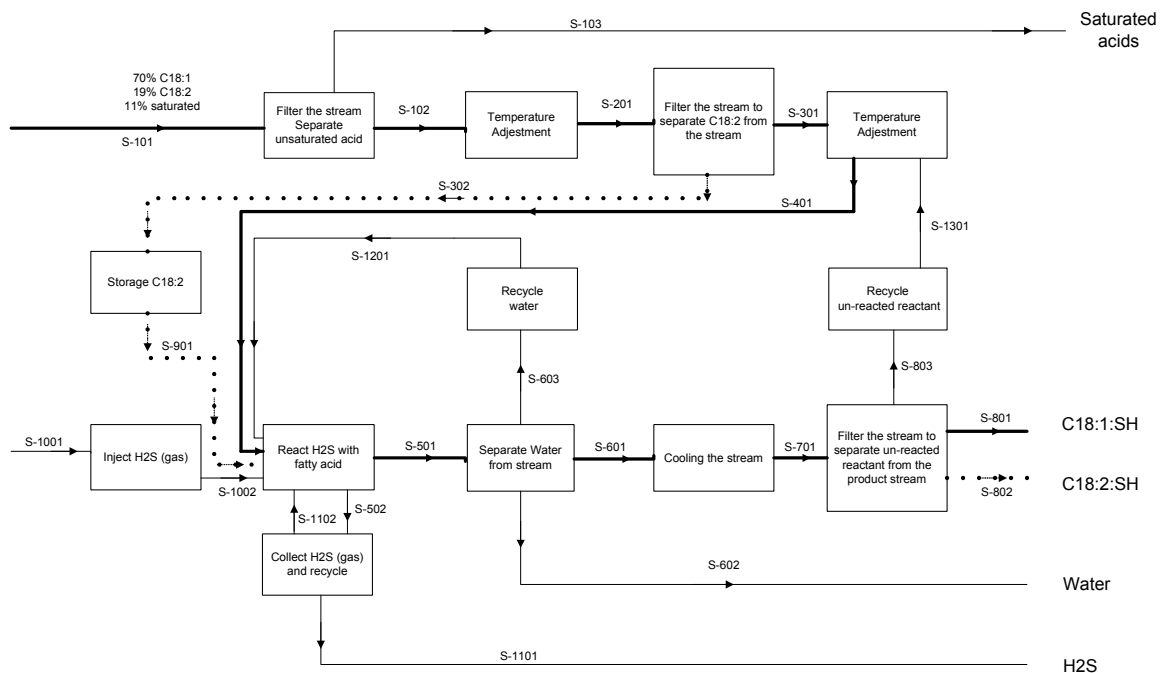


Figure 2.43 Third alternative of task sequence

Figure 2.43 shows the third alternative, which is developed from the alternative E in design space 2. Instead of using two parallel reaction and purification systems, we decided to use semi-continuous mode to operate the plant, in order to save the capital investment of the project, assuming that the costs of reactor are very high.

This alternative is given here because of the issue of missing melting point data (paragraph 2.20) In this alternative, because we already have most of the experimental physical properties of the fatty acids, the designs of the feed pre-treatment tasks are closer to reality compared to previous alternatives.

Compared to the first two alternatives (11 tasks), which have been discussed in the previous part, the alternative contains more tasks (13 tasks), that means the operation cost of this alternative is probably higher than the other two alternatives. Because of the semi-continuous mode, applied in it, the controllability of this process is more complex than the previous ones. Moreover, the use of additional storage tank may cause loss of raw materials, because of the degradation of fatty acids. But by comparing the sustainability of all three alternatives, due to the recycle systems of water and un-reacted reactants; this alternative has the best performance in terms of

the environmental friendliness issue. Also because of the missing information on product melting point, this alternative has the lowest risk in designing.

It has to be noted that we will not have further discussion on this alternative in this space, except when the client requires us to do so, due to the worse economic performance.

2.19 Mode of operation

Douglas in [13] listed the factors that favour batch operation while considering the option between batch and continuous. According to that, *continuous process should be chosen* because the production scale for this process is 5000 tons/yr (which is nearly 11,000,000 lb/yr more than 1×10^6 lb/yr).

2.20 Pure component properties

The following components are involved in the process:

- fatty acids:
 - lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, arachidic acid.
- Thioic acids:
 - Thiooleic acid, thiolinoleic acid
- Sulphur source
 - Hydrogen sulphide (H_2S)
- Solvent:
 - Water
- Catalyst:
 - Lipase

The properties of the components are given in Appendix 5.

Most of the chemical & physical properties have been found in literature research or have been estimated by using ASPEN +. The results are discussed in the Appendix 15. However, there are several data still which cannot be found. The most important ones are melting points of the products. We try to estimate the melting point by using Joback's method. But unfortunately, because of the inaccuracy of the model, it is impossible to get acceptable melting point estimations (Appendix 14). In this case, in order to reduce the risk of wrong estimation of the melting point, another alternative

process will be considered in later spaces and the tasks sheet is given in Figure 2.43. However, in order to decide the purification temperature, melting point of thio-oleic acid still need to be determined, regardless of which alternative we will choose.

2.21 Process stream summary and mass balances

The process stream summaries are given in Appendix 12 and Appendix 13. Mass balances for processes A and B are given in Table 2.12 and Table 2.13.

Table 2.12 Mass and Heat Balance for alternative A

HEAT & MASS BALANCE FOR STREAMS TOTAL										
IN					TASK IDENTIF.	OUT				
Plant		TASK				TASK			Plant	
Mass ton/year	Heat kW	Mass ton/year	Heat kW	Stream Nr.		Stream Nr.	Mass ton/year	Heat kW	Mass ton/year	Heat kW
7188	0	7188		<S-101>	1	<S-102> <S-103>	6341 847	847		
7188	0	7188	0		Total		7188	0	847	0
0	0	12682		<S-701>	2	<S-201>	19023			
	A2	6341		<S-102>						
0	A2	19023			Total		19023	0		
		19023		<S-201>	3	<S-301>	48			
0		774		<S-1102>		<S-302>	19748			
		0		<S-401>						
0		19797			Total		19796	0		
		48		<S-301>	4	<S-401>	0			
						<S-402>	48	48		
0		48			Total		48	48		
		19748		<S-302>	5	<S-501>	6676			
						<S-502>	12682			
0		19748			Total	<S-503>	390	390		
							19748	390		
		6676		<S-501>	6	<S-601>	6676	B		
0		6676			Total		6676	0		
		12682		<S-502>	7	<S-701>	12682			
0		12682			Total		12682	0		
		6676		<S-601>	8	<S-801>	6381			
						<S-802>	295	295		
0		6676			Total		6676	295		
		6381		<S-801>	9	<S-901>	6381	C		
0		6381			Total		6381	0		
		6381		<S-901>	10	<S-1001>	5018	5018		
						<S-1002>	1363	1363		
0		6381			Total		6381	6381		
774		774		<S-1101>	11	<S-1102>	774			
774		774			Total		774	0		
15924	A				Total			15922		
OUT - IN :								B+C		
								-2		
								A2-B-C		

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Table 2.13 Mass and Heat Balance for alternative B

HEAT & MASS BALANCE FOR STREAMS TOTAL										
IN					TASK IDENTIF.	OUT				
Plant		TASK				TASK			Plant	
Mass ton/year	Heat kW	Mass ton/year	Heat kW	Stream Nr.		Stream Nr.	Mass ton/year	Heat kW	Mass ton/year	Heat kW
7188	0	7188		<S-101>	1	<S-102> <S-103>	6341 847		847	
7188	0	7188	0		Total		7188	0	847	0
0	A1	12682		<S-1002>	2	<S-201>	19023			
	A2	6341		<S-102>						
0	A1+A2	19023			Total		19023		0	
		19023		<S-201>	3	<S-301>	48			
0		774		<S-1102>		<S-302>	19748			
		0		<S-401>						
0		19797			Total		19796		0	
		48		<S-301>	4	<S-401>	0			
						<S-402>	48		48	
0		48			Total		48		48	
		19748		<S-302>	5	<S-501>	6676			
		19748			Total	<S-502>	13072		13072	
0							19748		13072	
		6676		<S-501>	6	<S-601>	6676			B
0		6676			Total		6676		0	B
		6676		<S-601>	7	<S-701>	6381			
						<S-702>	295		295	
0		6676			Total		6676		295	
		6381		<S-701>	8	<S-801>	6381			C
0		6381			Total		6381		0	C
		6381		<S-801>	9	<S-901>	5018		5018	
						<S-902>	1363		1363	
0		6381			Total		6381		6381	
12682		12682		<S-1001>	10	<S-1002>	12682			
12682		12682			Total		12682		0	
774		774		<S-1101>	11	<S-1102>	774			
774		774			Total		774		0	
41288	A				Total				41286	B+C
OUT - IN :									-2 A1+A2-B-C	

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2.22 Reaction kinetics

2.22.1 Introduction

Reaction kinetics equations express a reaction rate as a function of temperature, pressure and concentration. As a matter of simplicity the reaction kinetics are described using the law of mass action for a reversible reaction, given at the end the reaction rate (r [kg/m³*s]) for the production of the thioic acid as a function of the enzyme concentration and the concentration of the reactants.

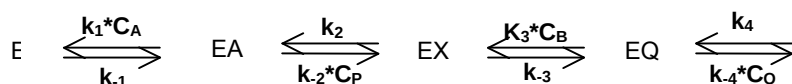
$$r_{olethioacid} = f(C_E, C_{H_2O}, C_{H_2S}, C_{OleicAcid}, C_{ThioOleicacid}, K_{eq}) \text{ Equation 2.1}$$

2.22.2 Reaction mechanism, kinetic model and rate equation.

Our reaction works by means of the Bi-bi ping pong mechanism, which is the one shown by reactions catalyzed by serine proteases (i.e. lipases) [30].

2.22.3 Kinetic model

The kinetic model is:



Equation 2.2

Due to the lack of experimental data the reaction rate constants can not be determined, they have to be assumed. The assumed values will come from the analogous amidation process performed by lipases in an organic solvent [53]. For this analogous process, there are tabulated reaction constants in literature.

2.22.4 Reaction rate expression

As a matter of simplicity and also mainly due to the lack of experimental data, the terms that represent inhibition effects are neglected. We will consider only the effect of enzyme concentration, products concentrations, reactant concentrations and the equilibrium constant, hence the rate expression is:

$$r_{ThioOleicAcid} = k \cdot C_{Enzyme} \cdot \left(C_{OleicAcid} \cdot C_{H_2S} - \frac{C_{H_2O} \cdot C_{ThioOleicacid}}{K_{eq}} \right) \quad \text{Equation 2.3}$$

Where:

C_{Enzyme} : Enzyme concentration [gr / L]

$C_{OleicAcid}$: Oleic acid concentration [kg/m^3]

C_{H_2S} : Hydrogen sulfide Concentration [kg/m^3]

C_{H_2O} : Water Concentration [kg/m^3]

$C_{ThioOleicacid}$: Thio Oleic acid concentration [kg/m^3]

K_{eq} : Equilibrium constant

Equilibrium Constant is

$$K_{eq} = \frac{C_{Thio-Oleic Acid} \cdot C_{H_2O}}{C_{Oleic Acid} \cdot C_{H_2S}} \quad \text{Equation 2.4}$$

The reaction rate only describes the consumption of oleic acid, because it is the main compound in the feed (70 – 89% w/w). For the other consumed fatty acids, the same rate expression applies.

2.22.5 Assumptions

As it has been previously stated the process from which our kinetic data will be assumed is the amidation process. The kinetic analysis of this process has been published by Straathof et.al (2002) [53].

2.22.6 Reaction rate constant (k)

An analogous reaction can be found on the literature, this is the production of oleamide. Starting from oleic acid and ammonia (gas) and using a lipase as catalyst the amidation of the fatty acid takes place. The reaction rate constant (k) reported for this process was

$$k = 1 \cdot 10^{-7} \text{ m}^6 / \text{kg} \cdot \text{mol} \cdot \text{s}$$

Ref: [30]

2.23 Thermodynamic properties

Phase behaviour involving the solid and liquid states is the basis for separation processes (e.g. crystallization) in chemical engineering. Crystallization is widely used to separate and purify materials in the pharmaceutical and specialty chemical industries. Successful design of crystallization processes depends upon knowledge of the equilibrium solid-liquid phase behavior of the mixture to be separated.

2.23.1 Model for solid/liquid equilibrium

For solid-liquid equilibrium several models are useful. They are:

- NRTL. Non-Random Two Liquid model is an extension of the Wilson equation. Used with mixtures which can form two immiscible liquid phases.
- UNIQUAC. Universal Quasi Chemical. It can also be used in cases where there are two liquid phases present.
- UNIFAC. Universal Quasi-Chemical (UNIQUAC). This method can predict phase equilibrium for systems for which no experimental data are available. It doesn't depend on binary interaction parameters, but is based upon the so-called group contribution method. Since the thermodynamic data for thiolinoleic acid, thioleic acid, thiododecanoic acid (products) is hardly available; The UNIFAC method is chosen to predict solid/liquid equilibrium for this system, using ASPEN SIMULATION engine.

None of these models should be used under critical conditions.

The thermodynamic properties for the fatty acids, water, and hydrogen sulfide were obtained from ASPEN PLUS engine (Appendix 15). For short introduction about how the calculation is carried out in ASPEN, the following reference was useful:
<http://www.chems.msu.edu/resources/aspenprops.html>

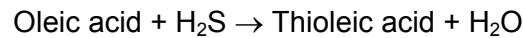
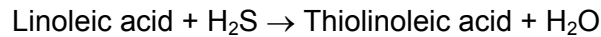
2.23.2 Reaction enthalpy data

Since the reaction proceeds at 35°C, then the reaction enthalpy is calculated from the heat of formation of each component at 35°C. (Note: Data of heat of formation at 35 °C for each component are taken from ASPEN SIMULATION engine)

Table 2.14 Heat of formation of the components at 35°C (from ASPEN)

Component	$\Delta H_{f, 35^\circ\text{C}} \text{ (kJ/kmol) } \text{ at } 1 \text{ atm}$
Linoleic acid	-667805
Oleic acid	-816245
Hydrogen sulfide	-20345.6
Thiolinoleic acid	-338502
Thioleic acid	-450958
Water	-284978

The reactions are:



Hence the heat of the reaction can be calculated as:

First reaction:

$$\Delta H_{\text{reaction at } 35^\circ\text{C}} = \Delta H_{\text{product}} - \Delta H_{\text{reactant}}$$

$$\Delta H_{\text{reaction at } 35^\circ\text{C}} = -338502 - 284978 - (-667805 - 20345.6)$$

$$\Delta H_{\text{reaction at } 35^\circ\text{C}} = 646760 \frac{\text{kJoule}}{\text{kmol}}$$

Hence, the reaction is endothermic.

Second reaction:

$$\Delta H_{\text{reaction at } 35^\circ\text{C}} = \Delta H_{\text{product}} - \Delta H_{\text{reactant}}$$

$$\Delta H_{\text{reaction at } 35^\circ\text{C}} = -450958 - 284978 - (-816245 - 20345.6)$$

$$\Delta H_{\text{reaction at } 35^\circ\text{C}} = 100654 \frac{\text{kJoule}}{\text{kmol}}$$

Hence, the reaction is endothermic.

3 Basic assumptions

3.1 Plant capacity

The plant capacity is 5000 tons per year of thiooleic acid. The process will run continuously for 300 days per year, 24 hours a day. The turn-down ratio is 17%.

3.1.1 Feed stock

The conditions and composition of feedstock entering the process are as in the tables below.

Table 3.1 Feed stock inlet conditions

Temperature	298 K
Pressure	1 bar

Table 3.2 Feed stock composition

Components	Stream number	Feed stream (t/a)	Weight percentage (%)	Notes	Additional information (ref. note number)
Oleic acid	S-101	5031	70%	Min. conc	
Linoleic acid	S-101	1366	19%	Max. conc	
Lauric acid	S-101	791	11%	Total: max 11%, taken as saturated acid	For calculation, worst-case scenario is assumed. All the impurities are taken as lauric acid
Stearic acid	S-101				
Palmitic acid	S-101				
Myristic acid	S-101				
Arachidic acid	S-101				
H ₂ S	S-1101	774			
Water				For start-up only	
Lipase				For start-up only	

Table 3.3 Feed stock specifications

Components	Stream number	Specifications
Crude oleic acid	S-101	Supplier: VVF-Limited Supply form: Liquid in plastic drums of 150 kg each Appearance: Pale yellow liquid
Lipase		Supplier: Juellich Chemicals
H ₂ S	774	Supplier: Scott Gas Company
Water		Supplier: utility company Quality: process water

3.1.2 Product

The plant produces 5000 tons of thiooleic acid and 1357 tons of thiolinoleic acid per year. The purity of thiooleic acid is 99.5% on molar basis (as design parameter).

The product will be sold as liquid in drums. The expected buyers of this product are polymer manufacturers. DSM has several customers who are interested in buying this product.

Table 3.4 Product purity

Components	Stream number	Feed stream (t/a)	Weight percentage (%)
Thiooleic acid	S-901	5000	99.64
Thiolinoleic acid	S-902	1357	99.56

3.1.3 By products

The by-product of the process is technical grade saturated fatty acid mixture (S-102).

The mixture can be sold as biodiesel raw material.

Table 3.5 By product

Components	Stream number	Feed stream (t/a)	Weight percentage (%)
Lauric acid	S-102	783	89.7
Myristic acid			
Palmitic acid			
Stearic acid			

3.2 Plant location

The main suppliers of crude oleic acid are found in China and India. However, the main suppliers of H_2S , are found in Europe. As transporting H_2S is more expensive than transporting the fatty acid, we decide that the plant should be located closer to the supplier of H_2S . The majority of the main consumers of the product are also located in Europe. Coupled with the good industrial infrastructure in most western European industrial complex, this seems to be a reasonable choice.

3.3 Battery limits

3.3.1 Processes inside battery limits

The designed processes will only consist of feed-pretreatment, reaction and product purification sections. The wastewater treatment plant will not be designed in detail and is assumed to be available on-site. Utilities are assumed to be supplied from outside utility generating companies. Utility generating units will not be designed.

3.3.2 Utilities

The utilities that will be used in the plant are *Electricity, Dry utilities, Hot utilities and Cold utilities*. There are several options for choosing utilities. Dry utilities, which are Nitrogen and air. Cold utilities, which can be chosen are HFC, CW_{Salt} , CW and CA (cooling air). Hot utilities, which are HW, LP, MP, HP and hot oil, are available.

Depending on the properties of the raw materials, intermediate product, product and by product and on the separation methods which will be used in the process; and also the result from heat integration evaluation, different utilities will be chosen in the process.

The following table gives the normal utilities cost.

Table 3.6 Utility costs

UTILITY COSTS PER UNIT (Euro.)		
Utility	Unit	Cost per Unit (Euro.)
Electricity	kWh	0.0462
Steam (LP)	Ton	13.64
Steam (MP)	Ton	-
Steam (HP)	Ton	-
Boiler Feed Water	Ton	0.6818
Hot oil	Ton	-
Nitrogen (gas)	m ³	3.41
Cooling Water	Ton	0.0455
Cooling Air	Ton	-
HFC	Ton	-

3.3.3 Streams crossing the battery limits

Table 3.7 Streams crossing the battery limits

<i>Component</i>	<i>Stream number</i>	<i>Density kg/L</i>	<i><u>Price</u></i>			<i><u>IN</u></i>	
			<i>Euro/lb</i>	<i>Euro/kg</i>	<i>Euro/t</i>	<i>kg/year</i>	<i>t/a</i>
<u>Feed stock</u>							
Lipase (1)	< >						
Oleic Acid (2)	<S-101>		0.46	1.01	1,014	7,188,000	7,188
Process water (3)	<S-1001>	1		0.5	500	1,268,000	1,268
H ₂ S (4)	<S-1101>		0.8	1.76	1,764	774,000	774
<i>Total raw materials cost</i>							
<u>Product</u>						<u>OUT</u>	
Thiooleic Acid (5)	<S-901>			4.00	4,000.00	5,025,000	5,025
Thiolinoleic Acid (6)	<S-902>			4.00	4,000.00	1,364,000	1,364
<i>Total product value</i>							
<u>By products</u>							
Saturated Acid (7)	<S-103>			0.5	500	293,000	293
<i>Total by-products value</i>							

4 Financial margin

Table 4.1 Available financial margin

Component	Stream number	Density kg/L	Price			IN		Value
			Euro/lb	Euro/kg	Euro/t	kg/year	t/a	Euro/year
<u>Feed stock</u>								
Lipase (1)	< >							
Oleic Acid (2)	<S-101>		0.46	1.01	1,014	7,188,000	7,188	7,289,418
Process water (3)	<S-1001>	1		0.5	500	1,268,000	1,268	634,000
H ₂ S (4)	<S-1101>		0.8	1.76	1,764	774,000	774	1,365,079
Total raw materials cost								9,288,497
<u>Product</u>						<u>OUT</u>		
Thiooleic Acid (5)	<S-901>			4.00	4,000.00	5,025,000	5,025	20,100,000
Thiolinoleic Acid (6)	<S-902>			4.00	4,000.00	1,364,000	1,364	5,456,000
Total product value								25,556,000
<u>By products</u>								
Saturated Acid (7)	<S-103>			0.5	500	293,000	293	146,500
Total by-products value								146,500
MARGIN (= product value + by-products value – raw materials cost)			16,414,002.65					

Assumptions for the above calculation can be found in Appendix 16.

The maximum investment is defined as the maximum amount of money that one can spend in order to have a Net Present Value of zero at the end of the project at an annual interest rate of 10%. In this project, it has been found that if tax and depreciation is not considered and construction takes 1 year, the maximum amount of investment is EUR 44M. Using the method of Asselbergs [2], which takes into account tax and depreciation, with construction period of 2 years, the maximum allowable investment has been found to be EUR 87M. Details on maximum investment calculation can be found in Appendix 17.

5 Creativity and group tools

Creativity and group tools form design space 0. The results of this part are as follows.

5.1 Objective

In this design space, the designer team tries to define a structure of the team in order to make it function.

5.2 Group interaction

The system we look at is the group (design team) comprising four members and its internal workings.

The group interacts with:

- The principal (Atze Nijenhuis of DSM Corporate Research-Geleen) who will function as the client commissioning the design.
- Its creative coach, Pieter Swinkels.
- Its departmental coach: Mark van Loosdrecht
- Its supervisor: Luuk van der Wielen
- The design tools (DDM, design quality monitor (Piquar))
- Austine Ajah, who will assist in the use of the design tools.
- Work process tools (AAA, timetable Gantt chart, blackboard)
- The domain knowledge and information

5.3 Exchange streams with the outside:

Basically the exchange streams will be streams of information. The streams of information may take different forms, which are outlined in the table below.

Table 5.1 Exchange streams with the outside

Point of contact	Stream
Principal	- E-mails - Monthly meetings - Progress reports - Phone calls - Basis of design (written report and subsequent defense) - Final report
Creative coach	- E-mails - Weekly meetings - Progress reports

Table 5.1 Exchange streams with the outside

Point of contact	Stream
Departmental coach	- Basis of design
	- Final report
	- E-mails
	- Monthly meetings
	- Progress reports
Austine Ajah	- Basis of design
	- Final report
Luuk van der Wielen	- Meetings as needed
	- Progress meetings
	- Basis of design
	- Final report

5.4 Constraints

The group has identified the following constraints:

- Dates set for BoD, and Final report which are as follows:
 - o Basis of design report shall be sent to all coaches by April 28, 2003 at 08:00 AM.
 - o Final report shall be finished on August 15, 2003 before 05:00 PM.
- Requirements on the contents and format of the memos, BoD and Final report (given in the CPD-manual)
- Requirements on the quality of the design
- On the design method:
 - o The Delft Design Matrix is to be used.
 - o For evaluation the Piquar quality control tool is to be used.

5.5 Variables

To achieve a satisfactory result in terms of design quality within the constraints, the team has to analyse the following variables in the current space.

- Creative methods to be used.
- Time planning of actions.
- Application of team capabilities through group profile.
- Group rules.
- Use of tools.
- Piquar quality factors

5.6 Building blocks

The object of this section, group functioning, can be divided into:

- Creativity methods. They are designed to stimulate the generation and application of creativity during the design process. This will enable the creation of a more innovative (plant) design
- Time planning of the project is performed to ensure that the project is finished in time and to prevent loss of time especially because the team is not working full-time in this project.
- Team capabilities and personal capabilities are examined, by group profiling, to use the capabilities of the group to maximum extent.
- Internal structure is defined by establishing group rules to enable smooth operation of the group.
- The design method employed is defined. The evaluation of the design is done using the Piquar quality control tool; evaluation factors have to be chosen for this.

5.7 Available knowledge

Knowledge available on these objects:

- Creativity methods: A number of articles on creative method have been supplied [[4][55][9][29][11][8][22]]; each member of the design team has read these. Additional knowledge was attained by performing a creativity assignment.
- Time planning: Constraints put on the group by the principal (delivery dates, personal schedules of all involved parties, and requirements for reports/ presentations) and the delft design method.
- Team capabilities: Members were asked to analyze their strengths and weaknesses in a predetermined format. These are combined to assess overall strengths and weaknesses of the group.
- Internal structure: Apart from some experience-based knowledge of the members some rules were established using the outcome of the creativity methods development.
- The design method is specified in [17].

5.8 Tools

The tools we use are:

- Synthesis and analysis, evaluation:
 - o Brainstorm sessions to create ideas.
 - o Group meetings. During these meetings an open discussion is held to analyze and evaluate options. Group-wide consensus is the deciding factor.
 - o Individually assessing articles on creative method and reporting the findings to the group

5.9 Synthesis, analysis and evaluation

The results of this design space are given in the following appendices.

1. Group profile is given in Table 5.2
2. Gantt chart is given in Appendix 18
3. Schedule of meetings is given in Appendix 19
4. Group rules are given in Appendix 20
5. Creative methods and articles are given in individual reports.
6. PIQUAR factors are given in the Appendix 21

Table 5.2 **Group profile**

Technical Insight	Systematic Thinking (st2 3 4)	Deep interest in CT topics(st 3 4) Deep interest in CT topics(st 2)
Economics(st2) Economics(st1 4)	Accuracy (st1 4)	Reporting (st2 4) Reporting (st1)
Creativity (st1) Creativity (st2)	Being connections various courses CT curriculum	Hard working (st3)
Mathematics(st1 3) Mathematics(st2 4)	Intuition	Persistent in problem situations (st1)
Long-term vision(st3)	Cooperation(st1) Cooperation(st4)	Planning(st2) Planning(st3)
Making right choices	Achieve Solid (but not creative) Results	Leadership(st4)
Coordination (st1)	Domain Knowledge (st3)	Self-criticism(st3)
presentation skill (st2)		

Date: 11th March 2003

Name:

CPD-team number: CPD 3291

Other participants: Beatrix (st1)

Edwin Habeych (st2)

Esteban J.Freydell (st3)

Xiaonan Li (st4)

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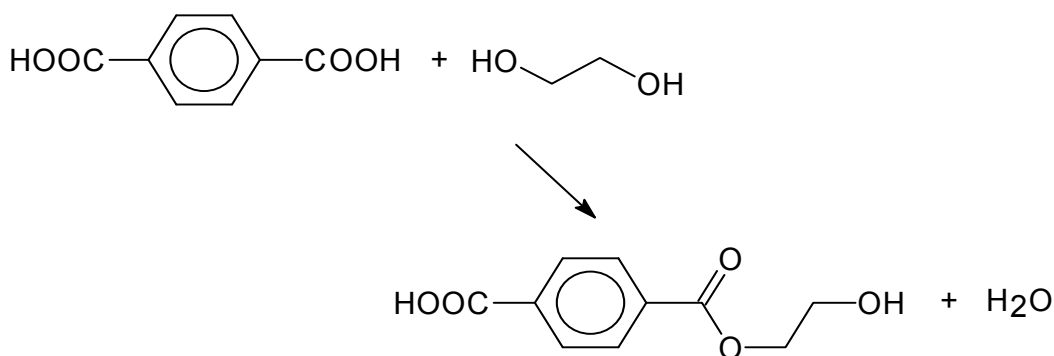
Appendix 1 Polymerisation Mechanisms

Polymerisation reactions can be classified as either step-growth or chain growth reactions. Polymer physical properties can differ significantly depending on the polymerisation mechanism, and this is often due to the difference in molecular masses, i.e. polymers synthesised by chain growth polymerisation often have higher molecular masses.

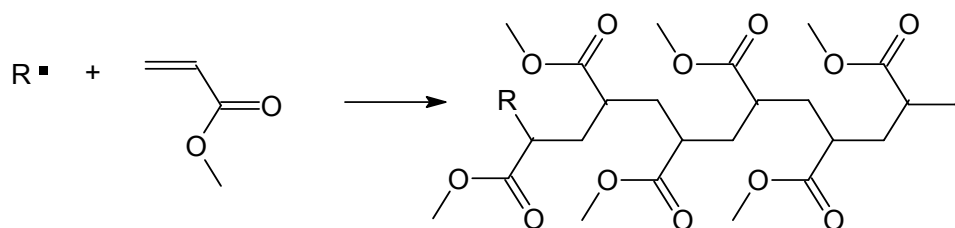
These two types of growth reaction differ basically in terms of the time scale of various reaction events, namely the size of polymer molecules increases at a relatively slow rate over a much longer period of time in step growth polymerisation. With step-growth polymerisation, the reactions that link monomers, oligomers and polymers involve the same reaction mechanism and any two molecular species (monomer, oligomer, or polymer) can be coupled. The growth of a polymer chain proceeds slowly from monomer to dimer, trimer, tetramer, and so on, until full-sized polymer molecules are formed at high monomer conversions. Polymer chains continue to grow from both ends throughout the polymerisation and, therefore, both chain lifetimes and polymerisation times are usually of the order of hours,

In chain growth polymerisation, polymer molecules generally grow to full size in a time-scale which is much smaller than the time required for high conversion of monomer to polymer. The lifetime of a growing polymer molecule may be less than a few seconds for a free-radical polymerisation, while a typical polymerisation time to obtain high monomer conversion may be several hours. Chain-growth polymerisation require an active center, which may be a free radical, cation, or anion. Once an active center is created, a polymer chain grows extremely rapidly, and when the growing chain is deactivated by a termination reaction, the polymer chain is dead and no longer takes part as a reactant. With free-radical polymerisation, however, the so-called dead polymer chain is not always truly dead, because under certain circumstances it may itself react with radicals. The active center may initiate the growth of many polymer chains.

The two mechanisms are depicted in the following figure.



(a)



(b)

Figure A 1.1 Polymerisation mechanisms: (a) step growth polymerisation (PET synthesis), (b) chain-growth polymerisation (Polymethacrylate synthesis) [37]

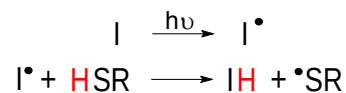
The two mechanisms have their advantages and disadvantages which are outlined in the following table.

Table A 1.1 Advantages and disadvantages of step growth and chain growth polymerisation

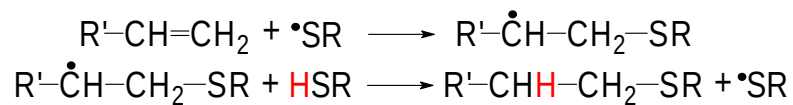
Step growth polymerisation	Chain growth polymerisation
• High strength and toughness	• Fast polymerisation
• Low molecular weight	• Exothermic • High molecular weight • Lower mechanical properties
• Energy intensive • Slow polymerisation • Stoichiometric	

The challenge lies in the combination of the advantages of the two mechanisms, i.e. we should find a molecule which can be polymerised in a combined mechanism. One of the molecules which can be polymerised in a combined mechanism is the unsaturated thioic acid. The molecule has two active groups and can therefore be polymerised in a radical step polymerisation which is presented in the figure below.

Initiation



Propagation



Termination: radical termination (no oxygen termination)

Figure A 1.2 Radical step polymerisation of unsaturated thioic acid [37]

Reference: [37], [20]

Appendix 2 The overall yield in fermentation process

This appendix is written to calculate the overall yield of the fermentation process, which has been discussed in 2.5.

In order to calculate the yield in the fermentation process, the following assumptions are made:

1. Glucose is the raw material used in the fermentation process.
2. All the reactions in the fermentation pathway, which include glucose respiratory metabolism pathway and fatty acid metabolism pathway, are assumed to be complete reactions.
3. In the glucose respiratory metabolism pathway Co-enzyme A is supplied from the outside.
4. In fatty acid metabolism pathway we assume that energy is solely consumed by the formation of C-C bond.

Glucose respiratory metabolism produces *Acetyl-CoA* and also 6 ATP as shown in the figure below:

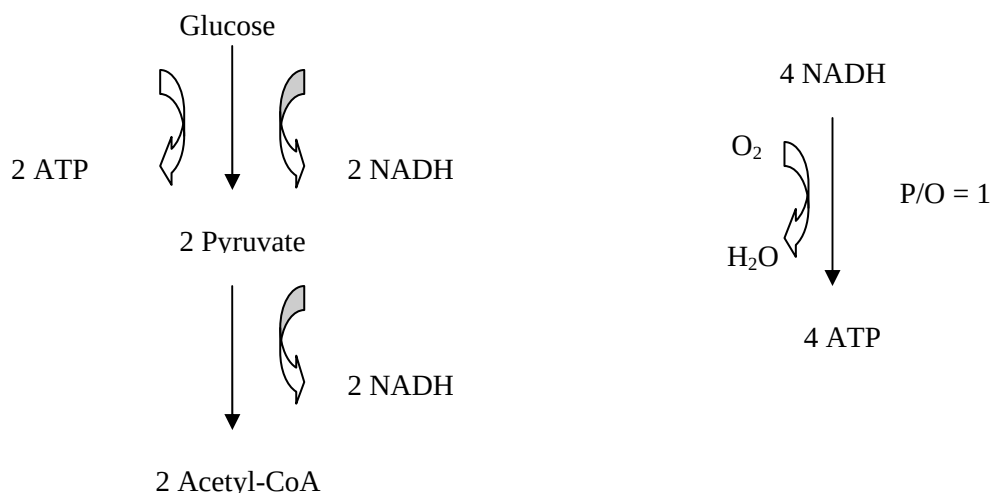


Table A 2.1 Respiratory glucose metabolism in *S. cerevisiae*

A mole of ATP is equivalent 50kJ energy. From the picture above the energy produced from the pathway is 150kJ/mole *Acetyl-CoA*.

The expected product of the fermentation process is unsaturated long chain thioic acid (C18:1). As described in 2.5 the fermentation part can be separated into four steps.

Step one:

Acetyl-[acyl-carrier protein] is produced from *Acetyl-CoA*. The stoichiometric ratio is 1:1. The yield for this step is 100% mole product/mole A-CoA.

Step two:

Acetoacetyl-[acyl-carrier protein] is produced from *Acetyl-[acyl-carrier protein]* and *Malonyl-[acyl-carrier protein]*. The stoichiometric ratio is still 1:1. A C-C bond is formed in this reaction.

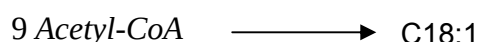
The *Malonyl-[acyl-carrier protein]* is also produced from *Acetyl-CoA* with stoichiometric ratio 1:1. Therefore yield is 50% mole product/mole A-CoA.

Step three and four are oxidizing steps. The stoichiometric ratio are also 1:1.

After four steps, the product is *Butyryl-[acyl-carrier protein]* (C₄H₇ORS).

The expected product is unsaturated long chain thioic acid (C18:1), therefore, more *Malonyl-[acyl-carrier protein]* is required to increase the length of carbon chain to desired product. In this case steps two to four will be repeated six times. The intermediate product after all those repeated is saturated long chain thioic acid (C16:0). During process other six C-C bonds are built up.

One more *Malonyl-[acyl-carrier protein]* is needed to join the reaction in order to increase the size of carbon chain to C₁₈, and with this, a new C-C bond produced. This time the reaction will stop at step two for obtaining the required one unsaturated carbon bond. The overall chemical reaction is:



yield : 1/9 mole product / mole A-CoA

There are nine moles *Acetyl-CoA* consumed to produce one mole long chain acid in the process. In total, 8 moles C-C bonds are built up. Because every mole C-C bond consumes 30kJ energy, the energy consumed to produce one mole product is 240kJ. As calculated before, nine moles *Acetyl-CoA* requires 4.5 mole glucose and produces 1350kJ energy. The overall process is carbon limited process and the yield is:

$$11.1\% \text{ mole product/mole } A\text{-CoA}$$

which is equivalent to

$$22.2\% \text{ mole product/mole } \textit{glucose}$$

and

$$66.7\% \text{ kg product/kg glucose}$$

References: [40][45][58]

Appendix 3 Emissions and Legislations

Emissions

After performing a thorough analysis of the datasheets of all the raw materials, products and by-products, for the production route chosen it was found that hydrogen sulphide represents the higher risk of causing an environmental impact.

Hydrogen Sulphide

- Emission regulation applicable for facilities, wells and pipelines

The policy of the EPA recommends that facilities and pipelines that deal with H₂S should have their emissions (if any) below **0.1 ppm**. This regulation accounts for facilities working near any populated location -- homes, public buildings, businesses, parks, prisons, schools, churches, etc. The next table resumes the exposure limits

The exposure limits are:

Table A 3.1 Exposure Limits

Agency	Exposure Limits [ppm]
EPA	<0.1
OSHA	10
ACGIH	15*

* Short term exposure limit.

Within the Netherlands legislation states that the emission of hydrogen sulphide from any trade or industrial process should not exceed **7.6 mg/Nm³** (*Environmental Pollution Control (Air Impurities) Regulations 2000 New Air Emission Standards Report. Last update January 2001.*)

Therefore our production site has to keep a tight control on handling this raw material. It will be considered of great importance due to the strict regulation already presented.

Oleic acid (Raw material)

Oleic acid is expected to be a low hazard compound for usual industrial handling. There are no exposure limits reported by any agency (ACGIH,NIOSH or OSHA), but it should be remembered that any storage facility or usage site of this material should be equipped with

an eyewash facility and a safety shower, and keep an adequate ventilation to keep airborne concentrations low.

Appendix 4 Prices and compositions of raw materials

Table A 4.1 Composition of vegetable oils [19]

Oil	%w triacylglycerols	%w C16:0	%w C18:0	%w C18:1	%w C18:2	%w C18:3
Palm oil	99.6	44	4.5	39.2	10.1	0.4
Soybean	95	11	4	23.4	53.2	8
Soybean	95			23.4	53.2	8
Soybean	95			23.4	53.2	8
Olive	95.7	11	2	68.8	4.6	1
canola oil, extracted	94.4	3.6	1.5	62	20	9
safflower oil, hi oleic				74	16	
canola oil	94.4			62	20	9
Canola	94.4			62	20	9
Canola	94.4			62	20	9
Olive oil, mild	95.7			68.8	4.6	1
corn oil	96.8	11	2	23.9	56.5	1.4
Soybean	95			23.4	53.2	8

Table A 4.2 Prices of vegetable oils [23][28]

Oil	Price min	Price max	Unit	Price per ton	Price per ton (C18:1) ester	Price per ton (C18:1+C1 8:2+C18:3) ester
Palm oil	285	458	ton	285	730	576
Soybean	354	585	ton	354	1592	440
soybean		550	MT	550	2474	684
Soybean		700	MT	700	3149	871
Olive		2.15	kg	2150	3265	3020
canola oil, extracted		10.75	gal	3373	5762	3926
safflower oil, hi oleic		13.35	gal	4188		
canola oil		14.25	gal	4471	7638	5204
Canola		3.7	32 oz	4596	7852	5350
Canola	27.94		gal	8765	14977	10204
Olive oil, mild	4.7		17 oz	10988	16689	15433
corn oil	0.27		lb	594	2568	750
Soybean	0.214		lb	470.8	2118	586

Table A 4.3 Prices of raw materials ([26][6][18])

Compound	Price (US\$)	Unit	Price per ton (US\$)
Corn oil	0.285	lb	628
Oleic acid	0.46	lb	1013
Olive oil	4.5	lb	9912
Palm oil	0.3175	lb	699
Rapeseed oil	0.8	lb	1762
Safflower oil	0.7	lb	1542
Sunflowerseed oil	0.24	lb	529
Soybean oil	0.22	lb	485
H ₂ S	0.73	lb	1600
Water	0.45	kg	450

Table A 4.4 Physical and chemical specifications of bulk oleic acid [27]

Name	Physical & Chemical Specifications						
	Appearance	Acid Number	Saponification Number	Iodine Number	Titre, Value °C	Colour in 51/4" Cell, max.	Fatty Acid Composition, %
OLEIC-70	Pale Yellow to Colourless liquid	195 Min.	196 Min.	85-100	10 Max.	Y=12; R=1.5	Upto Lauric
							Myristic (C14)
							Palmitic (C16)
							Stearic (C18:0)
							Oleic (C18:1)
							Linoleic (C18:2)
							Arachidic & others (C20:0)
							5.0 Max.
							3.0 Max.
							7.0 Max.
							4.0 Max.
							70 Min.
							19 Max.
							2.0 Max.

Appendix 5 Physical and chemical properties

Table A 5.1 Pure component properties-technological data

PURE COMPONENT PROPERTIES									
Component Name		Technological Data							
Design	Systematic	Formula	Mol. Weight g/mol	Phase	Boiling Point [1] °C	Melting Point [1] °C	Flash Point [1] °C	Liquid Density [2] g/cm³	Vapour Density [3] kg/m³
Lauric acid	Dodecanoic Acid	C ₁₂ H ₂₄ O ₂	200.32	S	298.9	44-46	180	0.87	N/A
Myristic acid	Tetradecanoic Acid	C ₁₄ H ₂₈ O ₂	228.38	S	250	55.1	>230	0.86	N/A
Palmitic acid	Hexadecylic acid	C ₁₆ H ₃₂ O ₂	256.43	S	352	61-64		0.84	N/A
Stearic acid	Octadecanoic Acid	C ₁₈ H ₃₆ O ₂	284.48	S	383	67-69	196	0.87	N/A
Oleic acid	9-octadecanoic acid	CH ₃ (CH ₂) ₇ CHCH(CH ₂) ₇ COOH	282.47	L	360	14 - 16	189	0.89	N/A
Linoleic acid	9c, 12c-Octadecadienoic Acid	C ₁₈ H ₃₂ O ₂	280.46	L	229-230	-5		0.90	N/A
Arachidic acid	n-Eicosanoic Acid	C ₂₀ H ₄₀ O ₂	312.54	S	214-215	74-76		0.82	N/A

Table A 5.1 Pure component properties-technological data

PURE COMPONENT PROPERTIES									
Component Name		Technological Data							
Design	Systematic	Formula	Mol. Weight	Phase	Boiling Point [1]	Melting Point [1]	Flash Point [1]	Liquid Density [2]	Vapour Density [3]
			g/mol		°C	°C	°C	g/cm³	kg/m³
Water	Water	H2O	18	L	100	0		1	N/A
Hydrogen sulfide	Hydrogen sulfide	H2S	34.08	G	-85.5	-60.7	Flammable	1.53	1.2

Table A 5.2 Pure component properties-Health and Safety data, Thermodynamic data

Component Name		Health &Safety data									Thermodynamic data		
Design	Systematic	Auto-ignition	Flammable	Lower	Upper	LC ₅₀	MAC	LD ₅₀	Chemical Reactivity	Notes	ΔH _f	Cp	ΔS _{stand}
		Temp.	Limits	Explosion	Explosion	In air/	Value	Oral			[KJ/mol]	[J / mol K]	[J/mol.K]
		[1] °C	% by vol in air	Limit (LEL) %	Limit (LEL) %	water mg/m ³	[4] mg/m ³	mg/kg					
Lauric acid	Dodecanoic Acid	N/A	N/A	N/A	N/A		N/A	131	Eye, skin and respiratory irritant	(5),	-774.6	404.3	452.4
Myristic acid	Tetradecanoic Acid	N/A	N/A	N/A	N/A	118	N/A	432.6	Skin, eye and respiratory irritant.	(7), (6)	-833.5	432	
Palmitic acid	Hexadecylic acid	N/A	N/A	N/A	N/A	150	N/A	57	Skin, eye and respiratory irritant.		-891.5	460.7	
	<i>Octadecanoic Acid</i>												
Stearic acid		N/A	N/A	N/A	N/A	N/A	N/A	21,5-23			-947.7	501.5	
	<i>9-octadecanoic acid</i>												
Oleic acid		N/A	N/A	N/A	N/A	N/A	N/A	230	May act as an irritant. May be harmful if ingested in quantity.		815.21		
Linoleic acid	9c, 12c-Octadecadienoic Acid	363	N/A	N/A	N/A	N/A	N/A	N/A		- (8),	640.2		
Arachidic acid									May be harmful or act as an irritant. Toxicology not fully investigated.	(9),	-1012.6	545.14	
	n-Eicosanoic Acid	N/A	N/A	N/A	N/A	N/A	N/A	N/A		(10),	-13.77	73.53	-152
Water	Water	N/A	N/A	N/A	N/A	N/A	N/A	N/A					
Hydrogen sulfide	Hydrogen sulfide	260		4.3	46	24	15	444	TOXIC; Extremely Hazardous; very flammable gas		-20.6		

Appendix 6 Mass Balance of Alternative Processes

Table A 6.1 The input/output flow mass balance of Alternative process A

Alternative A (tons/year)

Stream Description Pure Components	S-101 (IN)	S-103 (OUT)	S-201 (IN)	S-202 (IN)	S-203 (IN)	S-207 (OUT)	S-302 (OUT)	S-303 (OUT)
C18:1 OH	5082	51					2	49
C18:2 OH	1379	14					0	13
Impurities	799	791					0	0
H ₂ S				771				
Lipase					43 [Munits]			
C18:1 SH							5000	263
C18:2 SH							1386	43
Water							12	393
Total	7260	855	0	771	0	0	6400	761
Assumptions: <i>The product includes 5000 tons C18:1 SH per year</i> <i>Pretreatment 99% [wt]</i> <i>Sulphurylation 99% [mol/mol]</i> <i>Sep. & Pur. 97% [mol/mol]</i> <i>No recycle was considered</i> <i>Water was not taken into account</i> <i>All the impurities are equal to C:12</i> <i>Purge H₂S was not taken into account</i> <i>Total In:</i> 8031 tons <i>Total Out:</i> 8016 tons <i>Purity of Final Product</i> 99.8% <i>% Error [(In-Out)/In]</i> 0.2 %								

Table A 6.2 The input/output mass balance of alternative process B

Alternative B (tons/year)

Stream Description Pure Components	S-101 (IN)	S-102 (IN)	S-201 (OUT)	S-202 (OUT)	S-203 (OUT)	S-204 (OUT)
C12	356					
C14	213					
C16	498					
C18	285					
C18:1	4981					
C18:2	782					
C12 SH			383		1	
C14 SH			228		1	
C16 SH			527		2	
C18 SH				299	1	
C18:1 SH				263	5000	
C18:2 SH				41	786	
H ₂ S		887				
H ₂ O						469
Total	7115	887	1137	604	5791	469
Assumptions: <i>Sulphurylation 100% [mol/mol]</i> <i>Sep. & Pur. 95% [mol/mol]</i> <i>Recycle was considered</i> <i>The worst condition on H₂S requirement is considered, and the composition of input is given in Table A 6.6.</i> <i>Water was not taken into account</i> <i>Lipase was not taken into account</i> <i>Purge H₂S was not taken into account</i>						
Purity of Final Product 99.9%						
Total In: 8002 tons						
Total Out: 8002 tons						
% Error [(In-Out)/In] 0.0 %						

Table A 6.3 The input/output mass balance of Alternative process C

Alternative C (tons/year)

Stream Description Pure Components	S-101 (IN)	S-102 (OUT)	S-201 (IN)	S-206 (OUT)	S-301 (OUT)	S-302 (OUT)	S-303 (OUT)	S-305 (OUT)
C18:1	5031	50			19			230
C18:2	1366	14				5		63
Saturated acid	791	783					0.4	
H ₂ S			774					
Product mixture				48				
C18:1 SH					5000			
C18:2 SH						1357		
Saturated acid-SH					6	2		
H ₂ O							384	
Total	7188	847	774	48	5025	1364	384	293

Assumptions:

Product Purity is 99.5% with 5000 tons C18:1 SH per year

Purity of Final Product

Sulphurylation 95% [mol/mol]

C18:1 SH 99.5%

Sep. & Pur. 99% [mass]

C18:2 SH 99.5%

Feed Pretreatment 99% (mass)

Impurities (C12) also react with the H₂S with the same yield 95%

No recycle was considered

Water was not taken into account

Lipase was not taken into account

No reacted H₂S was purge out

Total In: 7962 tons

Total Out: 7961 tons

Error [(In-Out)/In] 0.01 %

Table A 6.4 The input/output mass balance of Alternative process D

Alternative D (tons/year)

Stream Description Pure Components	S-101 (IN)	S-103 (OUT)	S-302 (IN)	S-306 (OUT)	S-401 (OUT)	S-403 (OUT)	S-603 (OUT)
C18:1	4082	41			3	249	10
C18:2	1108	11			0	1	54
Saturated acid	641	635			0	0	38
H ₂ S			608				
Product mixture							
C18:1 SH					5000	51	
C18:2 SH					11	0	
Saturated acid-SH					0		
H ₂ O					305		
H ₂							
Total	5831	687	608	0	5319	301	103
Assumptions: <i>Product includes 5000 tons C18:1 SH per year</i> <i>Sulphurylation 95% [mol/mol]</i> <i>Sep. & Pur. 99% [mass]</i> <i>Feed Pretreatment 99% [mass]</i> <i>Hydrogenation treatment 95% [mol/mol]</i> <i>No recycle was considered</i> <i>The process water was not taken into account</i> <i>The lipase was not taken into account</i> <i>No H₂S was purged out</i> <i>Total In:</i> 6440 tons <i>Total Out:</i> 6416 tons <i>Purity of Final Product</i> C18: 1 SH 99.95% Error 0.36%							

Table A 6.5 The input/output mass balance of the Alternative process E

Alternative E (tons/year)

Stream Description Pure Components	S-101 (IN)	S-103 (OUT)	S-301 (IN)	S-401 (OUT)	S-402 (OUT)	S-501 (IN)	S-601 (OUT)	S-602 (OUT)
Impurity	751	722						
C18:1	4780	48						
C18:2	1297	13						
C18:1 HS				5000			1357	
C18:2 HS								
H ₂ S			574			157		
H ₂ O					304			82
Lipase								
Impurity SH				25			7	
Total	6828	782	574	5025	304	157	1364	82
Assumptions: <i>Product Purity is 99.5% with 5000 tons C18:1 SH per year</i> <i>Sulphurylation 100% [mol/mol]</i> <i>Sep. & Pur. 100% [mass]</i> <i>Feed Pretreatment 99% (mass)</i> <i>Impurities (C12) also react with the H₂S with the same yield 100%</i> <i>Recycle was considered</i> <i>Water was not taken into account</i> <i>Lipase was not taken into account</i> <i>No purge was taken into account</i> Purity of Final Product C18:1 SH 99.5% C18:2 SH 99.5% Total In: 7558 tons Total Out: 7558 tons % Error [(In-Out)/In] 0.00 %								

Table A 6.6 The assumed composition of the inlet stream and the H₂S requirement of the Alternative process B

The productivity of the plant is 5000 tons C18:1/year
 By assuming that the yield of A&P section is 95% Therefore, the total raw material is 7595
 By using the worst condition that the low M.W. fatty acids (C12 - C18) all have the Max. composition
 The amount of H₂S, which is required from the process has been calculated out as

Chemicals	M.W. for chemicals (g/mol)	Composition in the oleic oil (%)	Fatty Acid Amount In (ton/year)	Fatty Acid Amount (mol/year)	H ₂ S Amount (mol/year)	H ₂ S Amount In (ton/year)
C12	200.32	5%	356	1776158	1776158	60.39
C14	228.38	3%	213	934758	934758	31.78
C16	256.43	7%	498	1942518	1942518	66.05
C18:0	284.48	4%	285	1000562	1000562	34.02
C18:1	282.47	70%	4981	17633792	17633792	599.55
C18:2	280.46	11%	782	2789812	2789812	94.85
SUM		100%	7116	26077601	26077601	886.64

The amount of H₂S input is 886.64 tons/year

Appendix 7 Block diagrams

Project: CPD - Thioic Acid
Drawing Name: BFD - Alternative A
Last Update: 04/15/03
Responsible: ESTEBAN

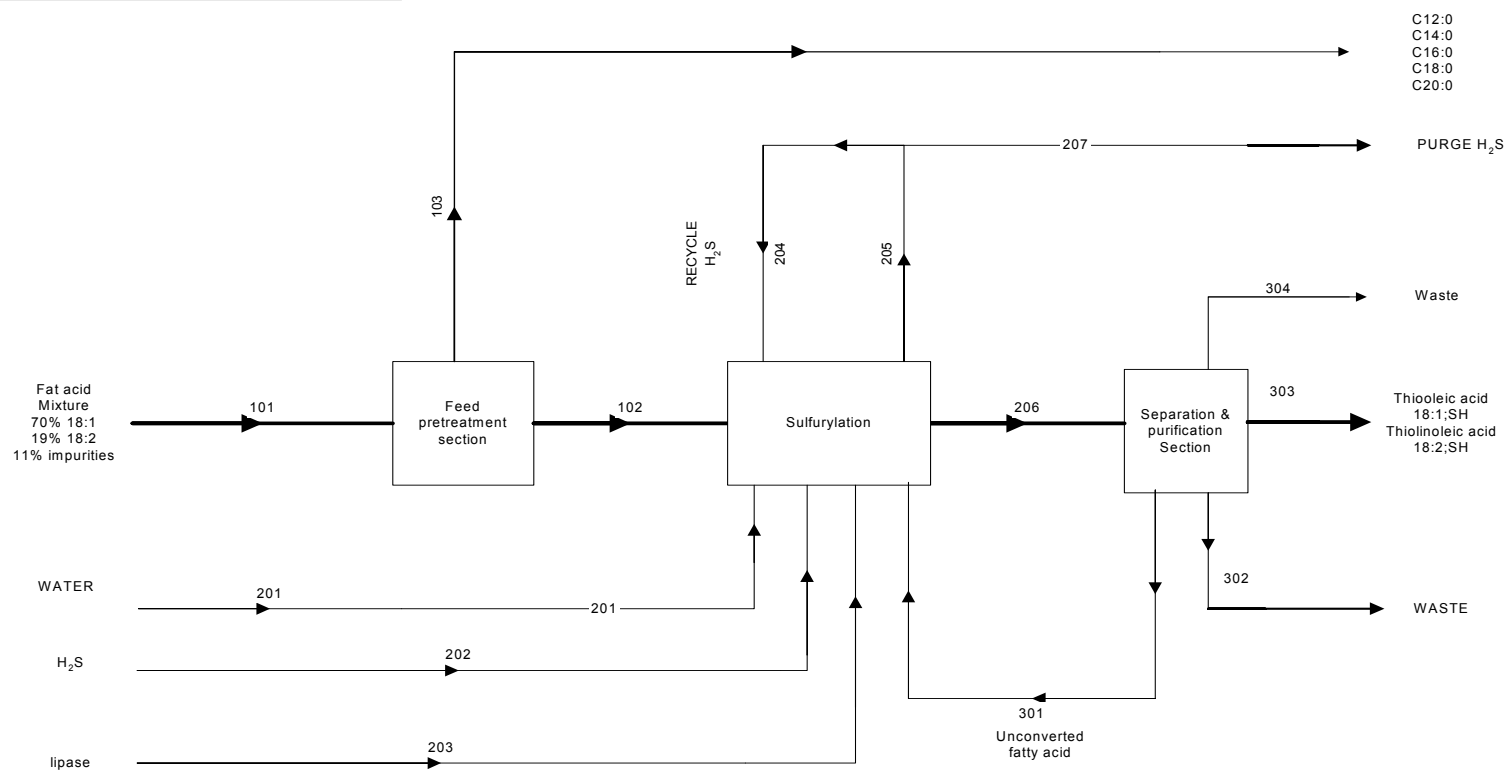


Figure A 7.1 Alternative A

Project : CPD - Thioic Acid
Drawing Name: BFD - Alternative B
Last Update : 04/15/03
Responsible : ESTEBAN

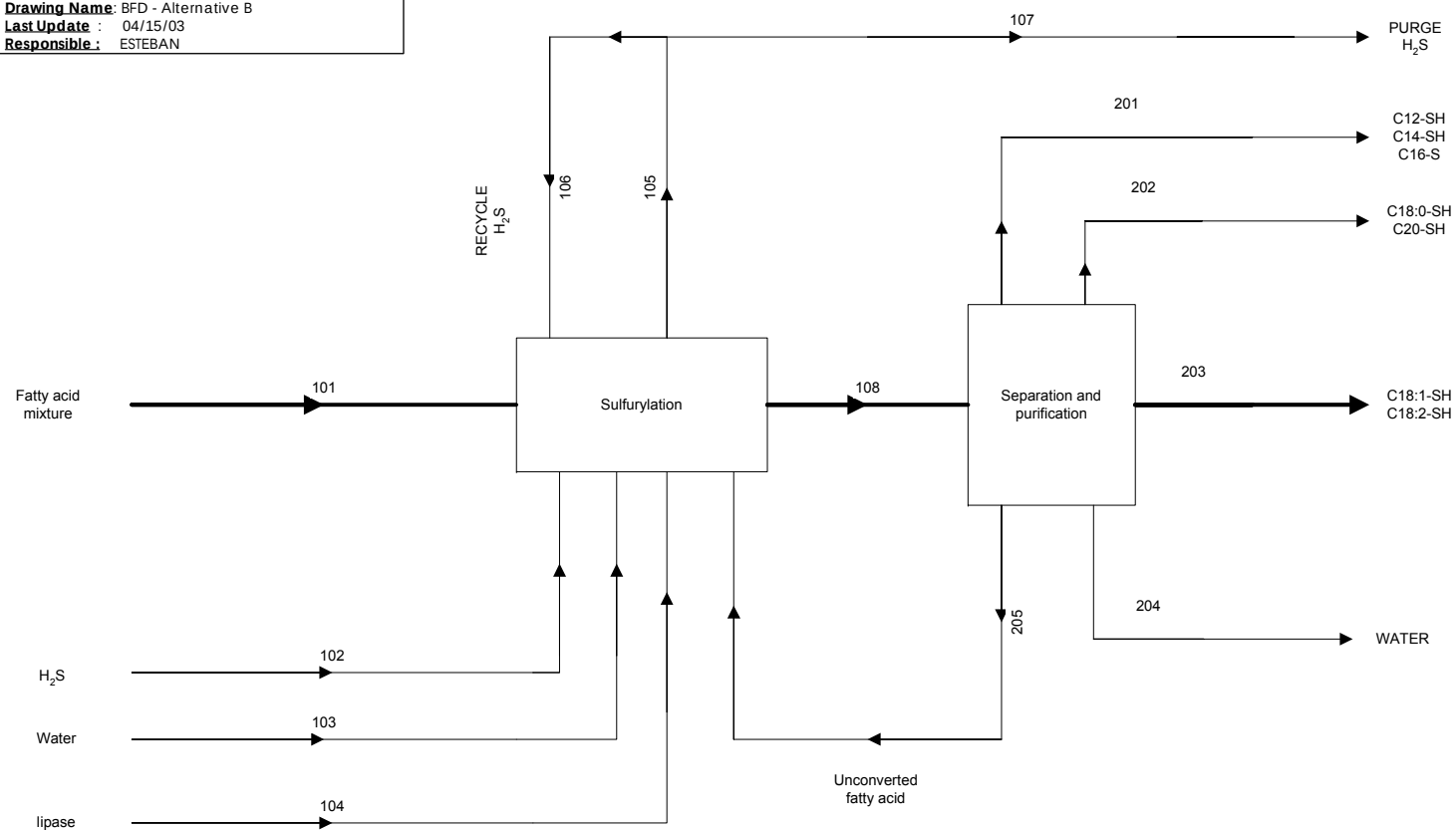


Figure A 7.2 Alternative B

Project: CPD - Thioic Acid
Drawing Name: BFD - Alternative C
Last Update: 04/15/03
Responsible: ESTEBAN

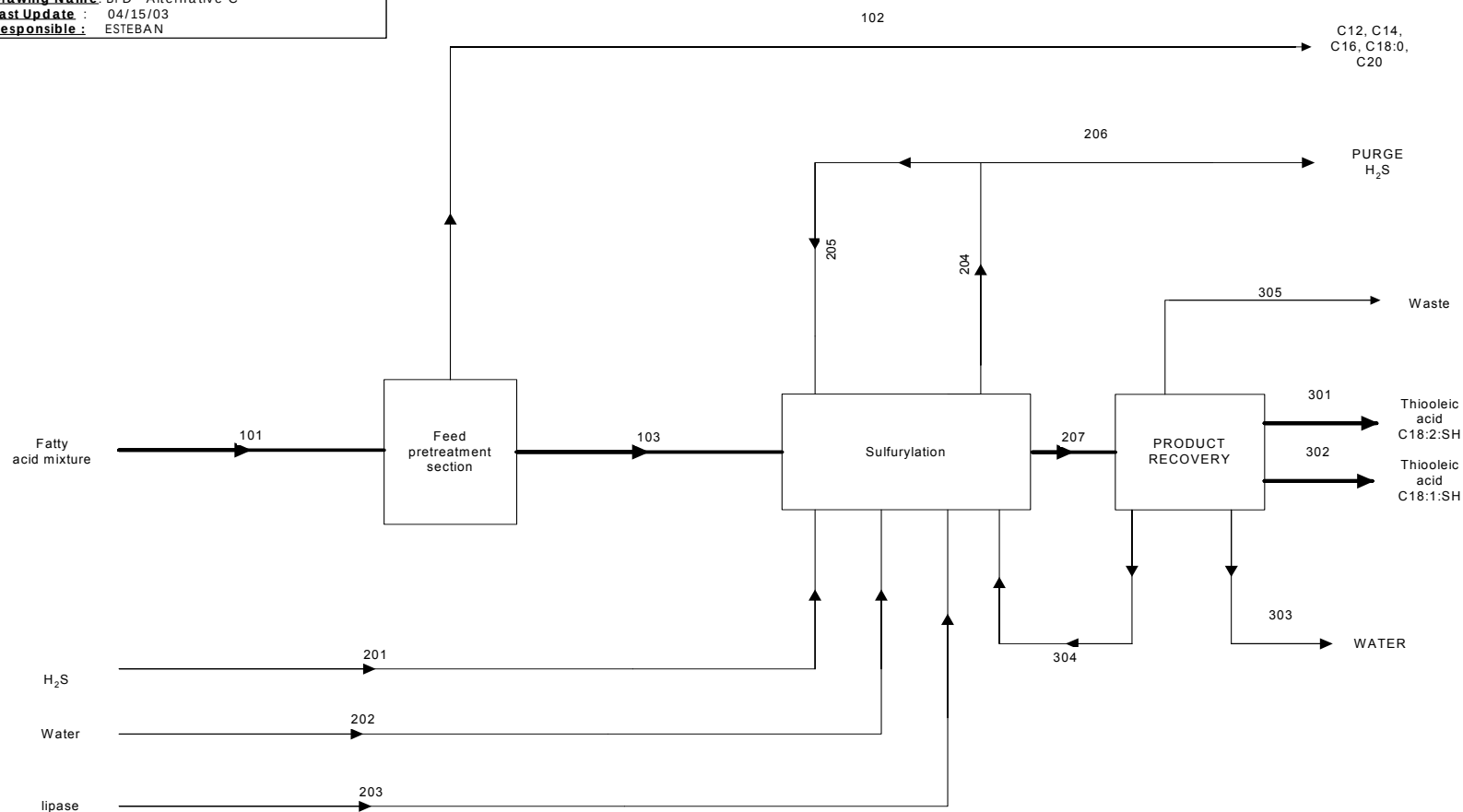


Figure A 7.3 Alternative C

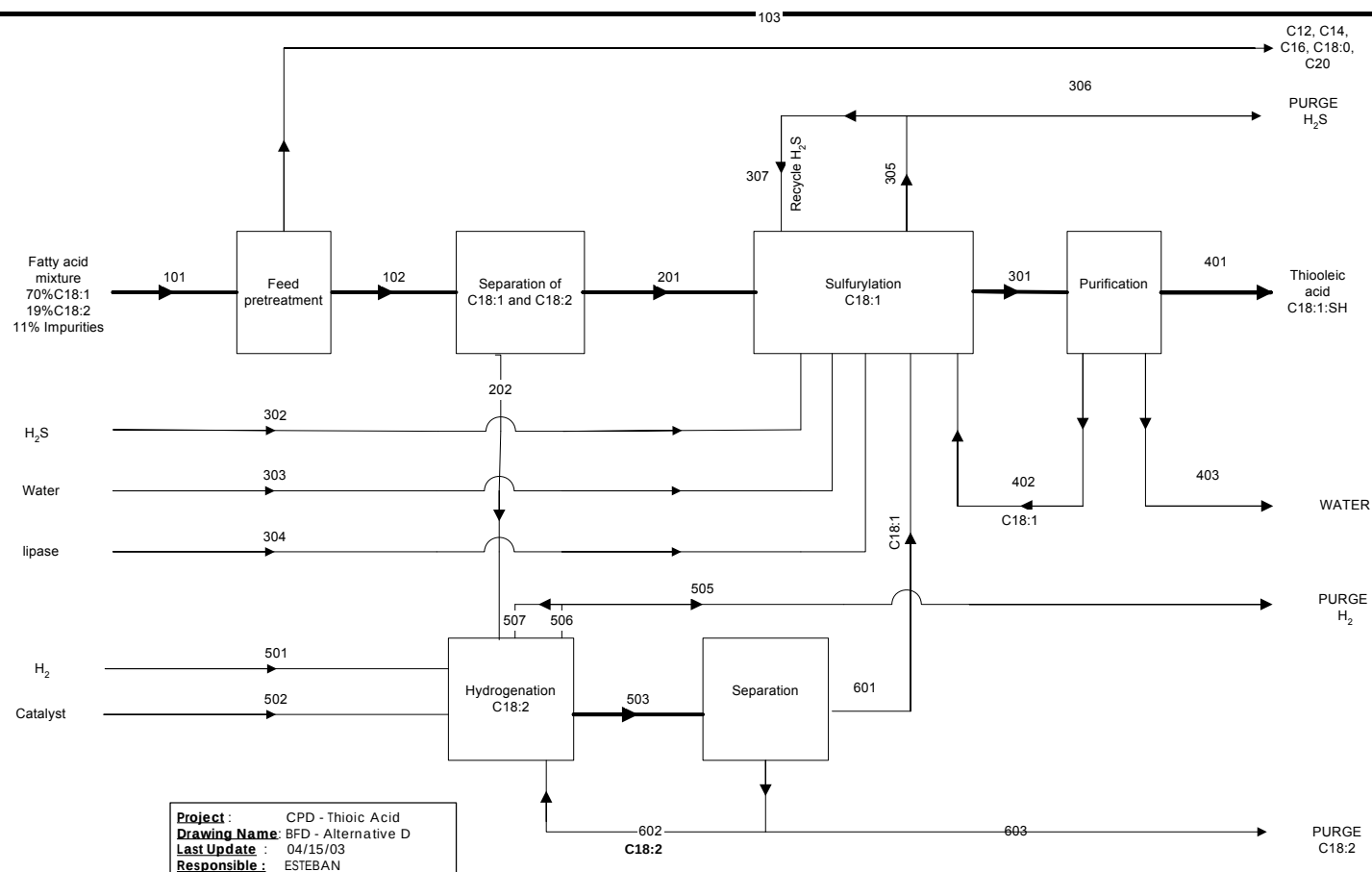
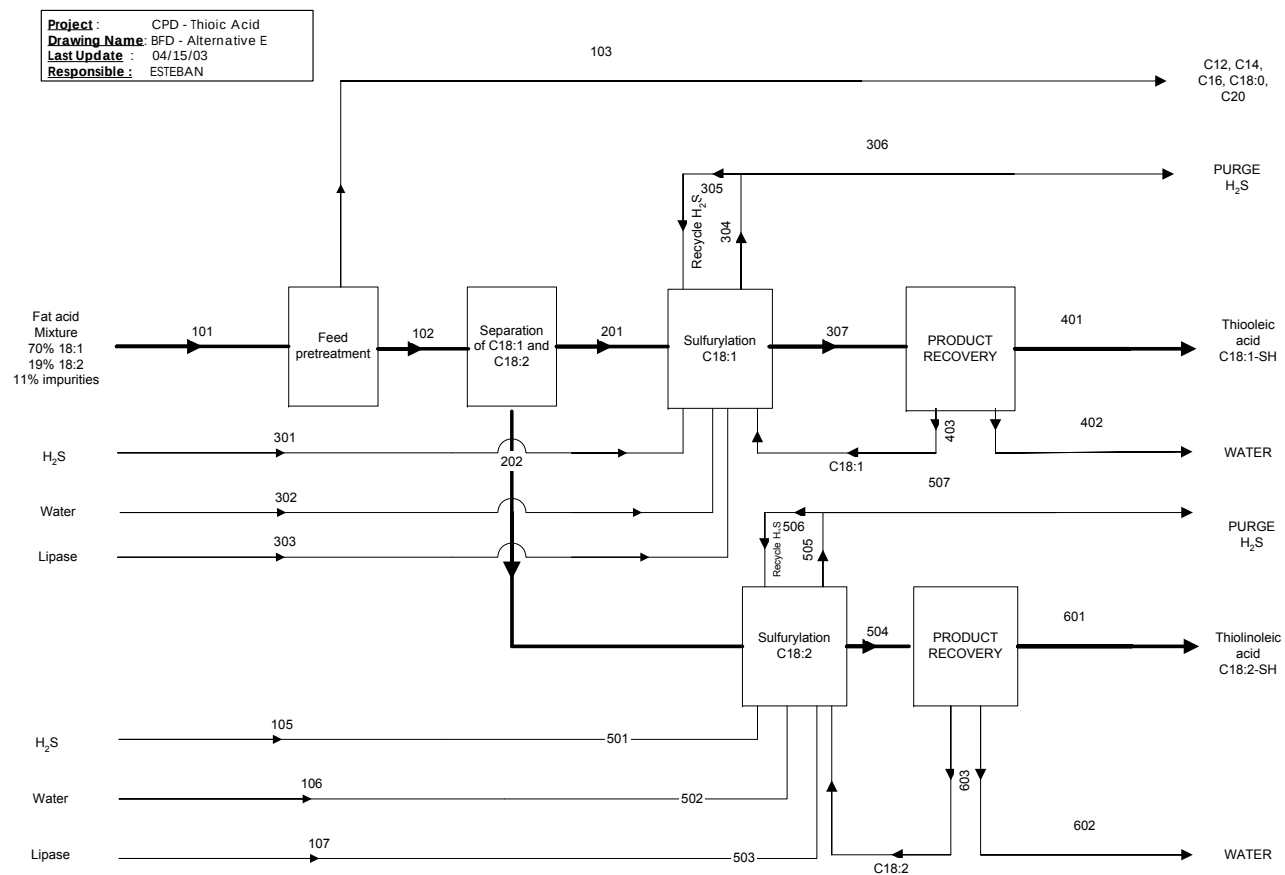


Figure A 7.4 Alternative D



Appendix 8 PIQUAR analysis of alternatives

A 8.01 Alternative A

Table A 8.1 PIQUAR analysis of alternative A

Criteria	Weighting factor	Average Ranking	$W_f \cdot AvR$
Product quality and quantity	0.22	3	0.66
Plant makes money	0.193	4	0.772
Low risk	0.138	4	0.552
Goal of the process must be clear in advance	0.138	4	0.587
Sustainability	0.083	4	0.291
As few equipment as possible	0.083	4	0.332
Space, water and energy saving	0.028	3	0.091
Controllability	0.083	4	0.291
Design decisions are explicit and can be repeated	0.028	4	0.098
Safe startup and shutdown	0.009	4	0.032
RESULT			3.70

A 8.02 Alternative B

Table A 8.2 PIQUAR analysis of alternative B

Criteria	Weighting factor	Average Ranking	$W_f \cdot AvR$
Product quality and quantity	0.22	2	0.33
Plant makes money	0.193	4	0.772
Low risk	0.138	5	0.621
Goal of the process must be clear in advance	0.138	4	0.5865
Sustainability	0.083	2	0.166
As few equipment as possible	0.083	4	0.332
Space, water and energy saving	0.028	4	0.098
Controllability	0.083	3	0.249
Design decisions are explicit and can be repeated	0.028	4	0.105
Safe start-up and shutdown	0.009	4	0.0315
			3.29

A 8.03 Alternative C

Table A 8.3 PIQUAR analysis of alternative C

Criteria	Weighting factor	Average Ranking	$W_f \cdot AvR$
Product quality and quantity	0.22	4	0.88
Plant makes money	0.193	3	0.62725
Low risk	0.138	4	0.552
Goal of the process must be clear in advance	0.138	4	0.5865
Sustainability	0.083	4	0.2905
As few equipment as possible	0.083	3	0.26975
Space, water and energy saving	0.028	3	0.091
Controllability	0.083	3	0.26975
Design decisions are explicit and can be repeated	0.028	4	0.098
Safe start-up and shutdown	0.009	4	0.0315
			3.70

A 8.04 Alternative D

Table A 8.4 PIQUAR analysis for process D

Criteria	Weighting factor	Average Ranking	$W_f \cdot AvR$
Product quality and quantity	0.22	5	1.045
Plant makes money	0.193	2	0.386
Low risk	0.138	2	0.276
Goal of the process must be clear in advance	0.138	4	0.587
Sustainability	0.083	2	0.166
As few equipment as possible	0.083	2	0.125
Space, water and energy saving	0.028	2	0.049
Controllability	0.083	2	0.125
Design decisions are explicit and can be repeated	0.028	3	0.07
Safe start-up and shutdown	0.009	1	0.011
RESULT			2.84

A 8.05 Alternative E

Table A 8.5 PIQUAR analysis for alternative E

CRITERIA	Weighting factor	Average Ranking	$W_f \cdot AvR$
Product quality and quantity	0.22	5	1.045
Plant makes money	0.193	4	0.6755
Low risk	0.138	3	0.3795
Goal of the process must be clear in advance	0.138	4	0.5865
Sustainability	0.083	3	0.249
As few equipment as possible	0.083	2	0.1245
Space, water and energy saving	0.028	2	0.056
Controllability	0.083	3	0.2075
Design decisions are explicit and can be repeated	0.028	3	0.077
Safe start-up and shutdown	0.009	2	0.018
RESULT			3.42

Appendix 9 Analysis of scenarios

A 9.01 Scenario 1 “The Client requires only the C18:1 monomer (>5% of C: 18:2 on the product stream)”

Table A 9.1 Analysis of the first scenario

Factor	A		C		E	
Product quality and quantity	1	0.22	3	0.66	5	1.1
Plant makes money	1	0.193	5	0.965	4	0.772
Low risk	4	0.552	4	0.552	3	0.414
Goal of the process must be clear in advance	5	0.69	5	0.69	5	0.69
Sustainability	4	0.332	4	0.332	4	0.332
As few equipment as possible	4	0.332	3	0.249	2	0.166
Space, water and energy saving	3	0.084	3	0.084	2	0.056
Controllability	4	0.332	3	0.249	2	0.166
Design decisions are explicit and can be repeated	4	0.112	4	0.112	3	0.084
Safe start-up and shutdown	4	0.036	4	0.036	2	0.018
RESULT		2.88		3.93		3.8

The criteria, which have more relevance upon this scenario are “Product quality and quantity” and related to this “Plant makes money”. After testing the three alternatives the best one turned out to be alternative C.

After consulting with the client, we realized that this scenario emulates quite well the real situation; hence we will work at first with Alternative C.

A 9.02 Scenario 2 ““The construction site is limited. The client suggested that the plant must be built on an existing site.”

Table A 9.2 Analysis of the second scenario

Criteria	A		C		E	
Product quality and quantity	3	0.66	4	0.88	5	1.1
Plant makes money	4	0.772	4	0.772	3	0.579
Low risk	4	0.552	4	0.552	3	0.414
Goal of the process must be clear in advance	5	0.69	5	0.69	5	0.69
Sustainability	4	0.332	4	0.332	3	0.249
As few equipment as possible	5	0.415	3	0.249	1	0.083
Space, water and energy saving	3	0.084	3	0.084	2	0.056
Controllability	4	0.332	3	0.249	2	0.166
Design decisions are explicit and can be repeated	4	0.112	4	0.112	4	0.112
Safe startup and shutdown	4	0.036	4	0.036	2	0.018
RESULT		3.99		3.96		3.47

The outcome of the evaluation shows that all alternatives will perform quite similarly under this situation. The small difference between A and C is related to the expectation that alternative C will have a more complex separation section, thus require more space, energy and water

A 9.03 Scenario 3: “The presence of side reactions in the sulphuration step”

Table A 9.3 Analysis of the third scenario

Factor	A		C		E	
Product quality and quantity	3	0.66	3	0.66	5	1.1
Plant makes money	4	0.772	4	0.772	4	0.772
Low risk	4	0.552	4	0.552	3	0.414
Goal of the process must be clear in advance	5	0.69	5	0.69	5	0.69
Sustainability	4	0.332	4	0.332	3	0.249

Table A 9.3 Analysis of the third scenario

Factor	A		C		E	
As few equipment as possible	4	0.332	3	0.249	2	0.166
Space, water and energy saving	3	0.084	3	0.084	2	0.056
Controllability	2	0.166	2	0.166	4	0.332
Design decisions are explicit and can be repeated	4	0.112	4	0.112	3	0.084
Safe start-up and shutdown	4	0.036	4	0.036	2	0.018
RESULT		3.74		3.65		3.88

As side reactions we consider a lack of selectivity on behalf of the catalyst, this will result on the presence of undesired species on the reactors outflow. Therefore, it makes it more attractive to consider an alternative such as E, which offers a final step for product polishing, which, in our belief, will allow the product quality and quantity to fulfil the specifications.

Appendix 10 Task Block Diagrams

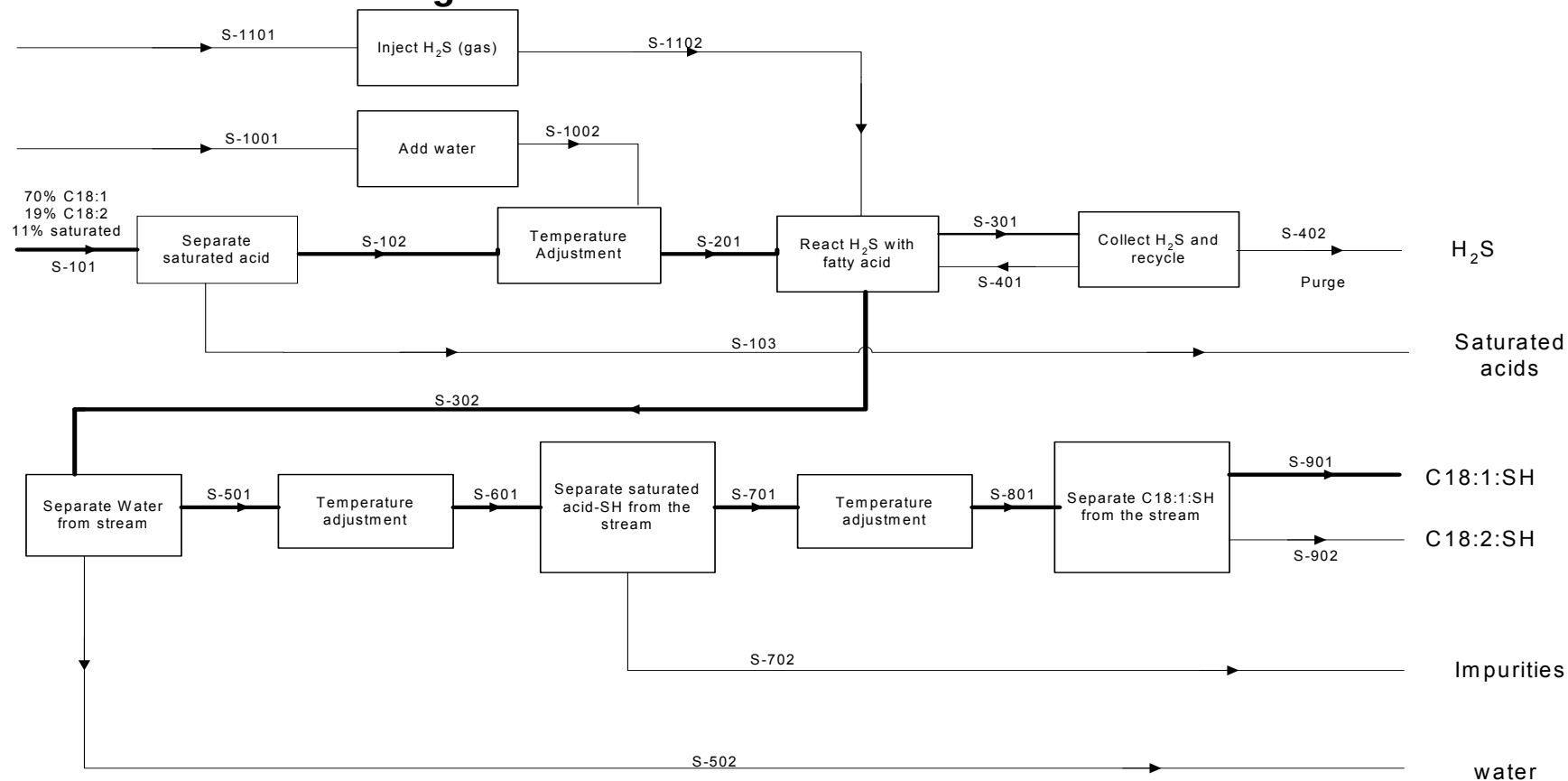


Figure A 10.1 Alternative A

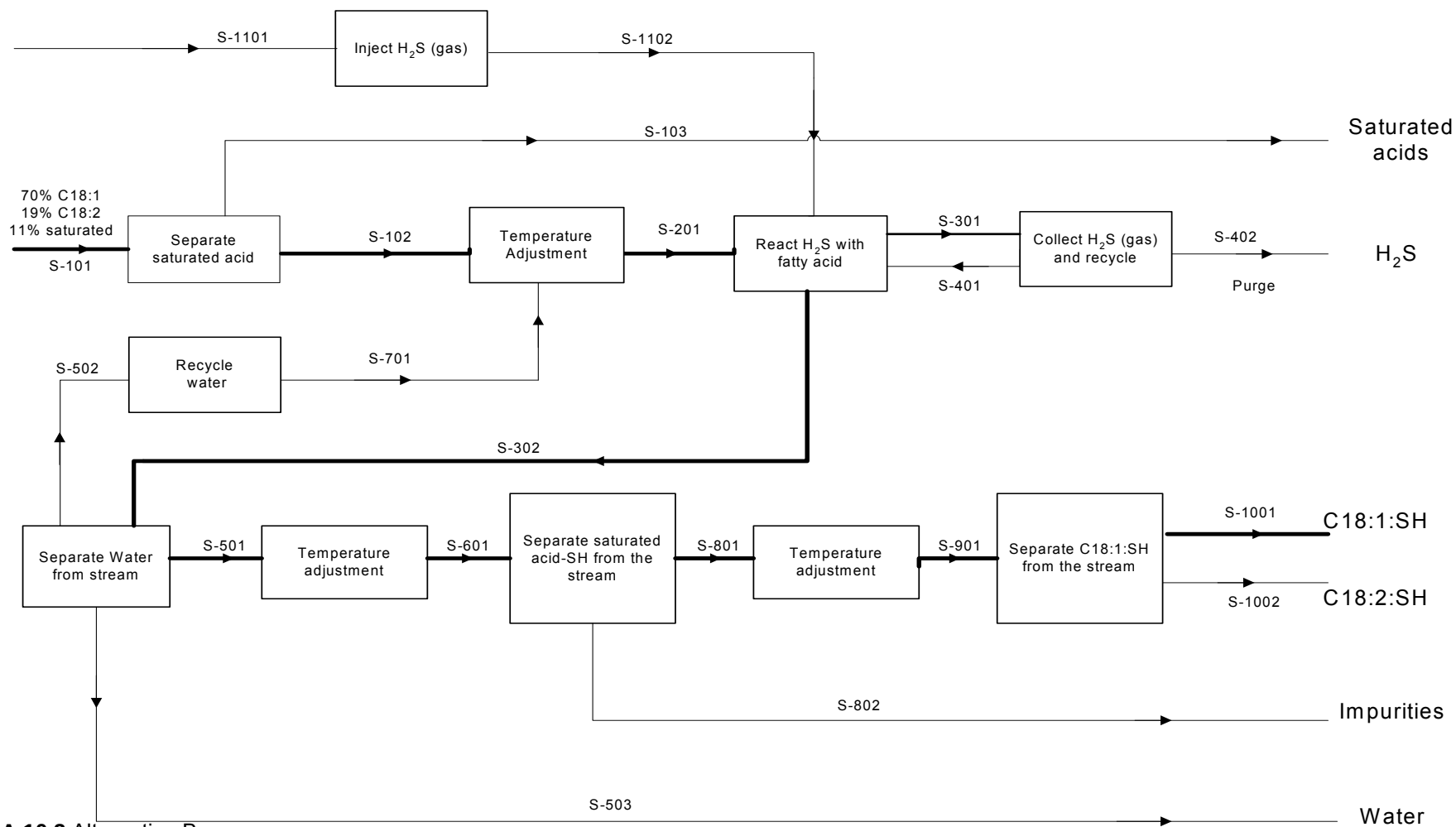


Figure A 10.2 Alternative B

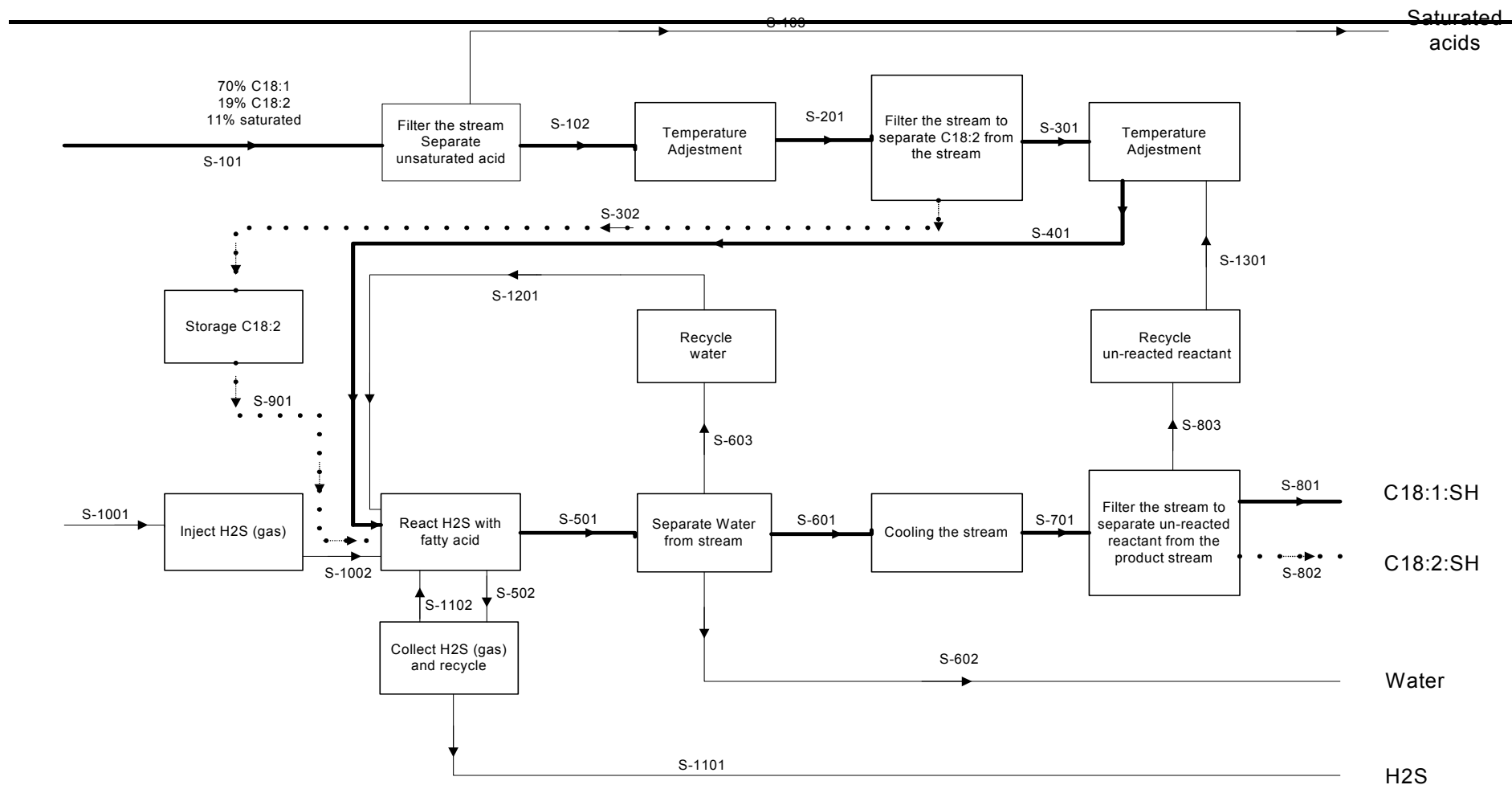


Figure A 10.3 Alternative C

Appendix 11 PIQUAR analysis of task sequence

Description			Reference
This document states the procedure of selection for outline alternatives.			None
Version	Author	Date	Delft Matrix
1.0	CPD TEAM, E.	Start : 23/04/2003 End : 23/04/2003	Design space 3.

A 11.01 Evaluation of alternatives

Four alternatives were proposed by the team and submitted to an evaluation based on the criteria stated on the PIQUAR matrix. The procedure followed was similar to that used in design space two. The best alternatives found were A, and C. The results of the evaluations are presented on the following set of tables.

A 11.02 Results

Alternative A: with water recycling

Table A 11.1 PIQUAR analysis of alternative A

Criteria	Weighting factor	Average Ranking	$W_f \cdot AvR$
Product quality and quantity	0.22	4	0.95
Plant makes money	0.193	5	0.97
Low risk	0.138	4	0.51
Goal of the process must be clear in advance	0.138	4	0.55
Sustainability	0.083	5	0.42
As few equipment as possible	0.083	3	0.28
Space, water and energy saving	0.028	4	0.12
Controllability	0.083	3	0.28
Design decisions are explicit and can be repeated	0.028	3	0.09
Safe start-up and shutdown	0.009	4	0.03
RESULT			4.19

Alternative B: without water recycling

Table A 11.2 PIQUAR analysis of alternative B

Criteria	Weighting factor	Average Ranking	$W_f \cdot AvR$
Product quality and quantity	0.22	5	1.03
Plant makes money	0.193	4	0.77
Low risk	0.138	4	0.51
Goal of the process must be clear in advance	0.138	4	0.55
Sustainability	0.083	4	0.33
As few equipment as possible	0.083	5	0.39
Space, water and energy saving	0.028	3	0.08
Controllability	0.083	4	0.36
Design decisions are explicit and can be repeated	0.028	4	0.10
Safe start-up and shutdown	0.009	4	0.04
			4.16

Alternative C: separation of the product using crystallisation

Table A 11.3 PIQUAR analysis of alternative C

Criteria	Weighting factor	Average Ranking	$W_f \cdot AvR$
Product quality and quantity	0.22	4	0.88
Plant makes money	0.193	5	0.90
Low risk	0.138	4	0.51
Goal of the process must be clear in advance	0.138	4	0.55
Sustainability	0.083	5	0.39
As few equipment as possible	0.083	4	0.33
Space, water and energy saving	0.028	4	0.11
Controllability	0.083	4	0.30
Design decisions are explicit and can be repeated	0.028	4	0.10
Safe start-up and shutdown	0.009	4	0.04
			4.11

Alternative D: separation of the product using vacuum distillation

Table A 11.4 PIQUAR analysis of alternative D

Criteria	Weighting factor	Average Ranking	$W_f \cdot AvR$
Product quality and quantity	0.22	5	1.1
Plant makes money	0.193	3	0.579
Low risk	0.138	4	0.552
Goal of the process must be clear in advance	0.138	4	0.552
Sustainability	0.083	4	0.332
As few equipment as possible	0.083	4	0.332
Space, water and energy saving	0.028	3	0.084
Controllability	0.083	3	0.276667
Design decisions are explicit and can be repeated	0.028	4	0.102667
Safe start-up and shutdown	0.009	3	0.027
RESULT			3.94

A 11.03 Summary

Table A 11.5 PIQUAR scores

Alternative	Final Score
A	4.19
B	4.16
C	4.11
D	3.94

The scale to assess this final result was set from 5 to 1, which stands for BEST and WORST option respectively. The evaluation of the alternatives should be comparing alternative A versus B; and alternative C versus D. From the table it can be seen that alternatives A, and B scored equal values, therefore a further evaluation is required, for this. The criteria selected is the environmental impact. Considering that the waste water for this process should have high amount of H_2S dissolved, the alternative B results better than A.

Appendix 12 Process stream summary-A

STREAM Nr. :		S-101		S-102		S-103		S201		S-301	
Name :		Feed flow									
COMP	MW	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y
Lauric acid	200.32	791.00	3.9487	8.00	0.0399	783.00	3.9087	8.00	0.0399		
Myristic acid	228.38										
Palmitic acid	256.43										
Stearic acid	284.48										
Oleic acid	282.47	5031.00	17.8107	4981.00	17.6337	50.00	0.1770	4981.00	17.6337		
Linoleic acid	280.46	1366.00	4.8706	1352.00	4.8207	14.00	0.0499	1352.00	4.8207		
Arachidic acid	312.54										
Water	18.00							12682.00	704.5556		
Hydrogen sulfide	34.08										
Thiolauric acid	216.32										
Thiomyristic acid	244.38										
Thiopalmatic acid	272.43										
Thiostearic acid	300.48										
Thiooleic acid	298.47										
Thiolinoleic acid	296.46										
Thioarachidic acid	328.54										
Total		7188.00	26.6300	6341.00	22.4943	847.00	4.1357	19023.00	727.0499		
Enthalpy	kW										
Phase	L/V/S	L+S		L		S		L		G	
Press.	Bara	1.01		1.01		1.01		1.01		1.01	
Temp	oC	25.0		25.0		25.0		35.0		35.0	

STREAM Nr. :		S-302		S-401		S-402		S-501		S-502	
Name :											
COMP	MW	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y
Lauric acid	200.32	0.40	0.0020							0.40	0.0020
Myristic acid	228.38										
Palmitic acid	256.43										
Stearic acid	284.48										
Oleic acid	282.47	249.00	0.8815					245.00	0.8673	4.00	0.0142
Linoleic acid	280.46	68.00	0.2425					66.00	0.2353	2.00	0.0071
Arachidic acid	312.54										
Water	18.00	13066.00	725.8889							13066.00	725.8889
Hydrogen sulfide	34.08	48.00	1.4085			48.00	1.4085				
Thiolauric acid	216.32	8.00	0.0370					8.00	0.0370		
Thiomyristic acid	244.38										
Thiopalmitic acid	272.43										
Thiostearic acid	300.48										
Thiooleic acid	298.47	5000.00	16.7521					5000.00	16.7521		
Thiolinoleic acid	296.46	1357.00	4.5773					1357.00	4.5773		
Thioarachidic acid	328.54										
Total		19796.40	749.7897			48.00	1.4085	6676.00	22.4691	13072.40	725.9122
Enthalpy	kW	-33									
Phase	L/V/S	L		G		G		L		L	
Press.	Bara	1.01		1.01		1.01		1.01		1.01	
Temp	oC										

STREAM Nr. :		S-601		S-701		S-702		S-801		S-901	
Name :											
COMP	MW	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y
Lauric acid	200.32										
Myristic acid	228.38										
Palmitic acid	256.43										
Stearic acid	284.48										
Oleic acid	282.47	245.00	0.8673	18.00	0.0637	227.00	0.8036	18.00	0.0637	18.00	0.0637
Linoleic acid	280.46	66.00	0.2353	6.00	0.0214	60.00	0.2139	6.00	0.0214		
Arachidic acid	312.54										
Water	18.00										
Hydrogen sulfide	34.08										
Thiolauric acid	216.32	8.00	0.0370			8.00	0.0370				
Thiomyristic acid	244.38										
Thiopalmic acid	272.43										
Thiostearic acid	300.48										
Thiooleic acid	298.47	5000.00	16.7521	5000.00	16.7521			5000.00	16.7521	5000.00	16.7521
Thiolinoleic acid	296.46	1357.00	4.5773	1357.00	4.5773			1357.00	4.5773		
Thioarachidic acid	328.54										
Total		6676.00	22.4691	6381.00	21.4146	295.00	1.0545	6381.00	21.4146	5018.00	16.8158
Enthalpy	kW										
Phase	L/V/S	L		L		S		L		S	
Press.	Bara	1.01		1.01		1.01		1.01		1.01	
Temp	oC										

STREAM Nr. :		S-902	S-1001	S-1002	S-1101	S-1102
Name :						
COMP	MW	ton/y Mmol/y	ton/y Mmol/y	ton/y Mmol/y	ton/y Mmol/y	ton/y Mmol/y
Lauric acid	200.32	6.00 0.0214	12682.00 704.5556	12682.00 704.5556	774.00 22.7113	774.00 22.7113
Myristic acid	228.38					
Palmitic acid	256.43					
Stearic acid	284.48					
Oleic acid	282.47					
Linoleic acid	280.46					
Arachidic acid	312.54					
Water	18.00					
Hydrogen sulfide	34.08					
Thiolauric acid	216.32					
Thiomyristic acid	244.38	1357.00 4.5773	12682.00 704.5556	12682.00 704.5556	774.00 22.7113	774.00 22.7113
Thiopalmic acid	272.43					
Thiostearic acid	300.48					
Thiooleic acid	298.47					
Thiolinoleic acid	296.46					
Thioarachidic acid	328.54					
Total		1363.00 4.5987	12682.00 704.5556	12682.00 704.5556	774.00 22.7113	774.00 22.7113
Enthalpy	kW					
Phase	L/V/S	L	L	L	G	G
Press.	Bara	1.01	1.01	1.01	1.01	1.01
Temp	oC					

Appendix 13 Process stream summary-B

STREAM Nr. :		S-101		S-102		S-103		S201		S-301	
Name :		Feed flow									
COMP	MW	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y
Lauric acid	200.32	791.00	3.9487	8.00	0.0399	783.00	3.9087	8.00	0.0399		
Myristic acid	228.38										
Palmitic acid	256.43										
Stearic acid	284.48										
Oleic acid	282.47	5031.00	17.8107	4981.00	17.6337	50.00	0.1770	4981.00	17.6337		
Linoleic acid	280.46	1366.00	4.8706	1352.00	4.8207	14.00	0.0499	1352.00	4.8207		
Arachidic acid	312.54										
Water	18.00							12682	705		
Hydrogen sulfide	34.08										
Thiolauric acid	216.32										
Thiomyristic acid	244.38										
Thiopalmatic acid	272.43										
Thiostearic acid	300.48										
Thiooleic acid	298.47										
Thiolinoleic acid	296.46										
Thioarachidic acid	328.54										
Total		7188.00	26.6300	6341.00	22.4943	847.00	4.1357	19023	727		
Enthalpy	kW										
Phase	L/V/S	L+S		L		S		L		G	
Press.	Bara	1.01		1.01		1.01		1.01		1.01	
Temp	oC	25.0		25.0		25.0		35.0		35.0	

STREAM Nr. :		S-302		S-401		S-402		S-501		S-502	
Name :											
COMP	MW	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y
Lauric acid	200.32	0.40	0.0020								
Myristic acid	228.38										
Palmitic acid	256.43										
Stearic acid	284.48										
Oleic acid	282.47	249.00	0.8815					247.00	0.8744		
Linoleic acid	280.46	68.00	0.2425					67.00	0.2389		
Arachidic acid	312.54										
Water	18.00	13066	726							12682	705
Hydrogen sulfide	34.08	48.00	1.4085			48.00	1.4085				
Thiolauric acid	216.32	8.00	0.0370					8.00	0.0370		
Thiomyristic acid	244.38										
Thiopalmittic acid	272.43										
Thiostearic acid	300.48										
Thiooleic acid	298.47	5000.00	16.7521					5000.00	16.7521		
Thiolinoleic acid	296.46	1357.00	4.5773					1357.00	4.5773		
Thioarachidic acid	328.54										
Total		19796	750			48	1	6679	22	12682	705
Enthalpy	kW	-33									
Phase	L/V/S	L		G		G		L		L	
Press.	Bara	1.01		1.01		1.01		1.01		1.01	
Temp	oC										

STREAM Nr. :		S-503		S-601		S-701		S-801		S-802	
Name :											
COMP	MW	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y
Lauric acid	200.32	0.40	0.0020								
Myristic acid	228.38										
Palmitic acid	256.43										
Stearic acid	284.48										
Oleic acid	282.47	2.00	0.0071	247.00	0.8744			18.00	0.0637	229.00	0.8107
Linoleic acid	280.46	1.00	0.0036	67.00	0.2389			5.00	0.0178	62.00	0.2211
Arachidic acid	312.54										
Water	18.00	384.00	21.3333			12682	705				
Hydrogen sulfide	34.08										
Thiolauric acid	216.32			8.00	0.0370					8.00	0.0370
Thiomyristic acid	244.38										
Thiopalmatic acid	272.43										
Thiostearic acid	300.48										
Thiooleic acid	298.47			5000.00	16.7521			5000.00	16.7521		
Thiolinoleic acid	296.46			1357.00	4.5773			1357.00	4.5773		
Thioarachidic acid	328.54										
Total		387.40	21.3460	6679.00	22.4798	12682	705	6380.00	21.4110	299.00	1.0688
Enthalpy	kW										
Phase	L/V/S	L		L		L		L		S	
Press.	Bara	1.01		1.01		1.01		1.01		1.01	
Temp	oC										

STREAM Nr. :		S-901		S-1001		S-1002		S-1101		S-1102	
Name :											
COMP	MW	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y	ton/y	Mmol/y
Lauric acid	200.32										
Myristic acid	228.38										
Palmitic acid	256.43										
Stearic acid	284.48										
Oleic acid	282.47	18.00	0.0637	18.00	0.0637						
Linoleic acid	280.46	5.00	0.0178			5.00	0.0178				
Arachidic acid	312.54										
Water	18.00										
Hydrogen sulfide	34.08							774.00	22.7113	774.00	22.7113
Thiolauric acid	216.32										
Thiomyristic acid	244.38										
Thiopalmatic acid	272.43										
Thiostearic acid	300.48										
Thiooleic acid	298.47	5000.00	16.7521	5000.00	16.7521						
Thiolinoleic acid	296.46	1357.00	4.5773			1357.00	4.5773				
Thioarachidic acid	328.54										
Total		6380.00	21.4110	5018.00	16.8158	1362.00	4.5952	774.00	22.7113	774.00	22.7113
Enthalpy	kW	-2						-18		-18	
Phase	L/V/S	L		S		L		G		G	
Press.	Bara	1.01		1.01		1.01		1.01		1.01	
Temp	oC										

Appendix 14 Estimation of Melting Points

The products in the designing process are thioic acids. During the literature research no information related to the melting point of thioic acids, is found. However, from the melting points difference of the fatty acids, which are given in the Appendix 5, it is expected that the melting points of the products also have a relatively big difference. Thus, it is possible to separate the products by using such difference. In order to prove our expectation, we decided to use group contribution methods to estimate the melting points.

There are several methods can estimate the properties of pure organic compound, like, Jorge and Rafiqul's method [33], Reid's methods, Lydersen's methods etc. The method used here is the Joback's methods [42] which is also based on the group contribution of the compounds.

The general equation to estimate melting point is given as:

$$T_f = 122 + \sum \Delta_f \quad \text{Equation 5}$$

The groups involved in the compounds are $-\text{CH}_3$, $-\text{CH}_2-$, $-\text{CH}$, $-\text{C}=\text{O}$, $-\text{C}-\text{SH}$. The contribution factors of the functional groups are given in the following table.

Table A 14.1 Functional Group Contribution Factor

Function Group	No. $\text{C}_{12}-\text{SH}$	No. $\text{C}_{18:1}-\text{SH}$	No. $\text{C}_{18:2}-\text{SH}$	ΔT_f
$-\text{CH}_3$	1	1	1	-5.10
$-\text{CH}_2-$	10	14	12	11.27
$-\text{CH}$	0	2	4	8.73
$-\text{C}=\text{O}$	1	1	1	61.20
$-\text{SH}$	1	1	1	20.09

Therefore, the melting point of thioic acids are calculated out as:

$$\text{C}_{12}-\text{SH} = 310.89\text{K} = 37.89^\circ\text{C}$$

$$\text{C}_{18:1}-\text{SH} = 373.43\text{K} = 100.43^\circ\text{C}$$

$$\text{C}_{18:2}-\text{SH} = 368.35\text{K} = 95.35^\circ\text{C}$$

The results are quite different from what we are expecting. If they were the real properties of the thioic acids, our previous assumption would have to be adjusted. The separation method would also need to be changed. But from the comparison between the calculated result and the experimental results of fatty acids, which is

given in the following table, we believe that the huge difference between expected result and calculated result of products is due to the inaccuracy of the estimation model instead of the wrong expectation of the product properties.

Table A 14.2 Comparison Between Results

	Calculated Result °C	Experimental Result °C
C12	112.1	45
C14	134.6	55.1
C18	179.7	68
C18:1	174.6	15

In order to decrease the influence of the missing information, it seems better to use Alternative E in space 2 than the Alternative C.

Appendix 15 Thermodynamic data

Table A 15.1 Thermodynamic data for lauric acid (C12:0), P=14.7 psia

TEMP	PRES	LIQUID	SOLID	TEMP	PRES	LIQUID	SOLID	TEMP	PRES	LIQUID	SOLID
		G	G			H	H			S	S
		N-DOD-01	N-DOD-01			N-DOD-01	N-DOD-01			N-DOD-01	N-DOD-01
C	psi	kJ/kg	kJ/kg	C	psi	kJ/kg	kJ/kg	C	psi	kJ/kmol-K	kJ/kmol-K
0	14.69595	-1814.06	-2.09177	0	14.69595	-3679.07	-46.9386	0	14.69595	-1367.76	-32.8896
2	14.69595	-1800.42	-1.77589	2	14.69595	-3675.21	-43.5135	2	14.69595	-1364.93	-30.3869
4	14.69595	-1786.8	-1.48507	4	14.69595	-3671.34	-40.0379	4	14.69595	-1362.12	-27.8656
6	14.69595	-1773.22	-1.21953	6	14.69595	-3667.45	-36.5099	6	14.69595	-1359.32	-25.3248
8	14.69595	-1759.66	-0.97946	8	14.69595	-3663.55	-32.9276	8	14.69595	-1356.53	-22.7633
10	14.69595	-1746.13	-0.76507	10	14.69595	-3659.63	-29.2893	10	14.69595	-1353.75	-20.1801
12	14.69595	-1732.63	-0.57658	12	14.69595	-3655.7	-25.5927	12	14.69595	-1350.98	-17.5741
14	14.69595	-1719.15	-0.41423	14	14.69595	-3651.76	-21.836	14	14.69595	-1348.23	-14.9442
16	14.69595	-1705.71	-0.27826	16	14.69595	-3647.81	-18.017	16	14.69595	-1345.48	-12.2893
18	14.69595	-1692.29	-0.16893	18	14.69595	-3643.84	-14.1334	18	14.69595	-1342.74	-9.60807
20	14.69595	-1678.9	-0.0865	20	14.69595	-3639.86	-10.1832	20	14.69595	-1340.01	-6.89945
22	14.69595	-1665.53	-0.03125	22	14.69595	-3635.86	-6.16379	22	14.69595	-1337.29	-4.16222
24	14.69595	-1652.19	-0.00349	24	14.69595	-3631.86	-2.07298	24	14.69595	-1334.58	-1.39513
26	14.69595	-1638.88	-0.0035	26	14.69595	-3627.84	2.091771	26	14.69595	-1331.87	1.403066
28	14.69595	-1625.6	-0.03161	28	14.69595	-3623.8	6.332895	28	14.69595	-1329.18	4.233592
30	14.69595	-1612.34	-0.08814	30	14.69595	-3619.75	10.65154	30	14.69595	-1326.5	7.096778
32	14.69595	-1599.11	-0.17342	32	14.69595	-3615.69	15.04774	32	14.69595	-1323.82	9.992215
34	14.69595	-1585.91	-0.28777	34	14.69595	-3611.61	19.52149	34	14.69595	-1321.15	12.91948

Table A 15.1 Thermodynamic data for lauric acid (C12:0), P=14.7 psia

TEMP	PRES	LIQUID	SOLID	TEMP	PRES	LIQUID	SOLID	TEMP	PRES	LIQUID	SOLID
		G	G			H	H			S	S
		N-DOD-01	N-DOD-01			N-DOD-01	N-DOD-01			N-DOD-01	N-DOD-01
C	psi	kJ/kg	kJ/kg	C	psi	kJ/kg	kJ/kg	C	psi	kJ/kmol-K	kJ/kmol-K
36	14.69595	-1572.73	-0.4315	36	14.69595	-3607.52	24.0728	36	14.69595	-1318.49	15.87817
38	14.69595	-1559.58	-0.60493	38	14.69595	-3603.42	28.70166	38	14.69595	-1315.84	18.86787
40	14.69595	-1546.46	-0.80836	40	14.69595	-3599.3	33.40808	40	14.69595	-1313.2	21.88818
42	14.69595	-1533.36	-1.04209	42	14.69595	-3595.17	38.19205	42	14.69595	-1310.57	24.93872
44	14.69595	-1520.29	-1.30643	44	14.69595	-3591.02	43.05358	44	14.69595	-1307.94	28.0191
46	14.69595	-1507.24	-1.60167	46	14.69595	-3586.86	47.99266	46	14.69595	-1305.32	31.12895
48	14.69595	-1494.22	-1.92811	48	14.69595	-3582.69	53.00929	48	14.69595	-1302.71	34.26789
50	14.69595	-1481.23	-2.28603	50	14.69595	-3578.5	58.10348	50	14.69595	-1300.1	37.43558
52	14.69595	-1468.26	-2.67571	52	14.69595	-3574.3	63.27522	52	14.69595	-1297.51	40.63165
54	14.69595	-1455.32	-3.09745	54	14.69595	-3570.08	68.52451	54	14.69595	-1294.92	43.85575
56	14.69595	-1442.4	-3.55151	56	14.69595	-3565.85	73.85136	56	14.69595	-1292.34	47.10755
58	14.69595	-1429.51	-4.03818	58	14.69595	-3561.61	79.25577	58	14.69595	-1289.76	50.3867
60	14.69595	-1416.65	-4.55772	60	14.69595	-3557.35	84.73773	60	14.69595	-1287.19	53.69289
62	14.69595	-1403.81	-5.1104	62	14.69595	-3553.08	90.29724	62	14.69595	-1284.63	57.02578
64	14.69595	-1391	-5.6965	64	14.69595	-3548.79	95.9343	64	14.69595	-1282.08	60.38505
66	14.69595	-1378.21	-6.31626	66	14.69595	-3544.49	101.6489	66	14.69595	-1279.53	63.7704
68	14.69595	-1365.45	-6.96994	68	14.69595	-3540.18	107.4411	68	14.69595	-1276.99	67.18152
70	14.69595	-1352.71	-7.65781	70	14.69595	-3535.85	113.3108	70	14.69595	-1274.45	70.61811
72	14.69595	-1340	-8.38012	72	14.69595	-3531.51	119.2581	72	14.69595	-1271.93	74.07986
74	14.69595	-1327.31	-9.13712	74	14.69595	-3527.15	125.283	74	14.69595	-1269.41	77.5665
76	14.69595	-1314.65	-9.92905	76	14.69595	-3522.78	131.3853	76	14.69595	-1266.89	81.07773
78	14.69595	-1302.02	-10.7562	78	14.69595	-3518.39	137.5653	78	14.69595	-1264.38	84.61328

Table A 15.1 Thermodynamic data for lauric acid (C12:0), P=14.7 psia

TEMP	PRES	LIQUID	SOLID	TEMP	PRES	LIQUID	SOLID	TEMP	PRES	LIQUID	SOLID
		G	G			H	H			S	S
		N-DOD-01	N-DOD-01			N-DOD-01	N-DOD-01			N-DOD-01	N-DOD-01
C	psi	kJ/kg	kJ/kg	C	psi	kJ/kg	kJ/kg	C	psi	kJ/kmol-K	kJ/kmol-K
80	14.69595	-1289.41	-11.6187	80	14.69595	-3514	143.8228	80	14.69595	-1261.88	88.17286

Table A 15.2 Thermodynamic data for myristic acid (C14:0), P=14.7 psia

TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID
	G	G		H	H		S	S
	N-TET-01	N-TET-01		N-TET-01	N-TET-01		N-TET-01	N-TET-01
[C]	[kJ/kg]	[kJ/kg]	[C]	[kJ/kg]	[kJ/kg]	[C]	[kcal/kg-K]	[kcal/kg-K]
0	-1567.09	-1.94065	0	-3450.26	-43.7942	0	-1.646665	-0.0365973
2	-1553.32	-1.64604	2	-3446.52	-40.5454	2	-1.643409	-0.0337668
4	-1539.57	-1.37519	4	-3442.77	-37.257	4	-1.640165	-0.0309227
6	-1525.85	-1.12821	6	-3439.01	-33.9278	6	-1.636934	-0.0280639
8	-1512.15	-0.90524	8	-3435.23	-30.5566	8	-1.633716	-0.0251897
10	-1498.49	-0.7064	10	-3431.44	-27.1418	10	-1.630509	-0.0222991
12	-1484.85	-0.53184	12	-3427.64	-23.6823	12	-1.627314	-0.0193911
14	-1471.23	-0.3817	14	-3423.83	-20.1766	14	-1.624131	-0.0164649
16	-1457.65	-0.25615	16	-3420	-16.6231	16	-1.620959	-0.0135195
18	-1444.09	-0.15534	18	-3416.16	-13.0204	18	-1.617799	-0.0105538
20	-1430.55	-0.07946	20	-3412.31	-9.36683	20	-1.614648	-0.0075669
22	-1417.05	-0.02868	22	-3408.44	-5.66089	22	-1.611509	-0.0045578
24	-1403.57	-0.0032	24	-3404.56	-1.90084	24	-1.60838	-0.0015253

Table A 15.2 Thermodynamic data for myristic acid (C14:0), P=14.7 psia

TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID
	G	G		H	H		S	S
	N-TET-01	N-TET-01		N-TET-01	N-TET-01		N-TET-01	N-TET-01
[C]	[kJ/kg]	[kJ/kg]	[C]	[kJ/kg]	[kJ/kg]	[C]	[kcal/kg-K]	[kcal/kg-K]
26	-1390.11	-0.0032	26	-3400.67	1.915015	26	-1.60526	0.00153154
28	-1376.68	-0.02892	28	-3396.76	5.788458	28	-1.602151	0.00461383
30	-1363.28	-0.08055	30	-3392.84	9.721309	30	-1.599052	0.00772269
32	-1349.9	-0.15833	32	-3388.91	13.71544	32	-1.595962	0.0108592
34	-1336.55	-0.26249	34	-3384.96	17.77279	34	-1.592881	0.0140245
36	-1323.23	-0.39328	36	-3380.99	21.89534	36	-1.589809	0.0172199
38	-1309.93	-0.55096	38	-3377.02	26.08506	38	-1.586747	0.0204464
40	-1296.65	-0.73579	40	-3373.03	30.34286	40	-1.583693	0.0237043
42	-1283.4	-0.94803	42	-3369.02	34.66878	42	-1.580647	0.0269932
44	-1270.18	-1.18794	44	-3365	39.06281	44	-1.577611	0.0303128
46	-1256.98	-1.45577	46	-3360.97	43.52495	46	-1.574582	0.0336627
48	-1243.81	-1.75178	48	-3356.92	48.05521	48	-1.571562	0.0370424
50	-1230.66	-2.07621	50	-3352.86	52.65359	50	-1.56855	0.0404517
52	-1217.54	-2.42931	52	-3348.78	57.32008	52	-1.565545	0.0438901
54	-1204.45	-2.81133	54	-3344.69	62.05468	54	-1.562549	0.0473574
56	-1191.37	-3.2225	56	-3340.58	66.85739	56	-1.55956	0.050853
58	-1178.33	-3.66305	58	-3336.46	71.72822	58	-1.556578	0.0543768
60	-1165.31	-4.13323	60	-3332.32	76.66717	60	-1.553604	0.0579283
62	-1152.31	-4.63327	62	-3328.17	81.67423	62	-1.550638	0.0615073
64	-1139.34	-5.16339	64	-3324.01	86.7494	64	-1.547678	0.0651134
66	-1126.39	-5.72381	66	-3319.83	91.89269	66	-1.544726	0.0687462
68	-1113.47	-6.31477	68	-3315.63	97.10409	68	-1.54178	0.0724056

Table A 15.2 Thermodynamic data for myristic acid (C14:0), P=14.7 psia

TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID
	G	G		H	H		S	S
	N-TET-01	N-TET-01		N-TET-01	N-TET-01		N-TET-01	N-TET-01
[C]	[kJ/kg]	[kJ/kg]	[C]	[kJ/kg]	[kJ/kg]	[C]	[kcal/kg-K]	[kcal/kg-K]
70	-1100.57	-6.93648	70	-3311.42	102.3836	70	-1.538842	0.076091
72	-1087.7	-7.58915	72	-3307.2	107.7312	72	-1.53591	0.0798024
74	-1074.85	-8.27301	74	-3302.96	113.147	74	-1.532985	0.0835392
76	-1062.02	-8.98827	76	-3298.71	118.6308	76	-1.530066	0.0873014
78	-1049.22	-9.73514	78	-3294.44	124.1828	78	-1.527154	0.0910885
80	-1036.45	-10.5138	80	-3290.15	129.8029	80	-1.524249	0.0949003

Table A 15.3 Thermodynamic data for palmitic acid (C16:0), P=14.7 psia

TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID
	G	G		H	H		S	S
	N-HEX-01	N-HEX-01		N-HEX-01	N-HEX-01		N-HEX-01	N-HEX-01
[C]	[kJ/kg]	[kJ/kg]	[C]	[kJ/kg]	[kJ/kg]	[C]	[kcal/kg-K]	[kcal/kg-K]
0	-1361.456	-1.873568	0	-3258.367	-42.43693	0	-6.944577	-0.1485021
2.5	-1344.115	-1.520425	2.5	-3253.719	-38.45802	2.5	-6.927637	-0.1340018
5	-1326.817	-1.203615	5	-3249.051	-34.42424	5	-6.910782	-0.1194342
7.5	-1309.562	-0.9233129	7.5	-3244.365	-30.33414	7.5	-6.894007	-0.1047954
10	-1292.347	-0.6797007	10	-3239.658	-26.18627	10	-6.877312	-0.0900814
12.5	-1275.175	-0.4729714	12.5	-3234.932	-21.97913	12.5	-6.860692	-0.0752885
15	-1258.044	-0.3033273	15	-3230.185	-17.71121	15	-6.844148	-0.0604125

Table A 15.3 Thermodynamic data for palmitic acid (C16:0), P=14.7 psia

TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID
	G	G		H	H		S	S
	N-HEX-01	N-HEX-01		N-HEX-01	N-HEX-01		N-HEX-01	N-HEX-01
[C]	[kJ/kg]	[kJ/kg]	[C]	[kJ/kg]	[kJ/kg]	[C]	[kcal/kg-K]	[kcal/kg-K]
17.5	-1240.954	-0.170981	17.5	-3225.418	-13.38094	17.5	-6.827675	-0.0454497
20	-1223.905	-0.0761545	20	-3220.63	-8.98673	20	-6.811272	-0.0303959
22.5	-1206.898	-0.0190802	22.5	-3215.821	-4.526968	22.5	-6.794938	-0.0152473
25	-1189.931	-1.15E-13	25	-3210.991	3.10E-14	25	-6.77867	4.90E-16
27.5	-1173.004	-0.0191658	27.5	-3206.14	4.595859	27.5	-6.762466	0.0153501
30	-1156.118	-0.0768397	30	-3201.267	9.262325	30	-6.746326	0.030807
32.5	-1139.273	-0.1732935	32.5	-3196.372	14.00115	32.5	-6.730247	0.0463747
35	-1122.467	-0.3088091	35	-3191.456	18.8141	35	-6.714227	0.0620571
37.5	-1105.701	-0.4836782	37.5	-3186.518	23.703	37.5	-6.698266	0.0778583
40	-1088.976	-0.6982028	40	-3181.557	28.66969	40	-6.682361	0.0937822
42.5	-1072.29	-0.9526948	42.5	-3176.574	33.71605	42.5	-6.666512	0.1098329
45	-1055.643	-1.247476	45	-3171.569	38.84397	45	-6.650717	0.1260143
47.5	-1039.036	-1.582879	47.5	-3166.541	44.05541	47.5	-6.634975	0.1423305
50	-1022.468	-1.959243	50	-3161.49	49.35167	50	-6.619285	0.1587836
52.5	-1005.939	-2.376909	52.5	-3156.417	54.7329	52.5	-6.603646	0.1753718
55	-989.4498	-2.836213	55	-3151.321	60.1991	55	-6.588057	0.192093
57.5	-972.9991	-3.337483	57.5	-3146.201	65.75025	57.5	-6.572516	0.2089452
60	-956.5872	-3.881046	60	-3141.059	71.38638	60	-6.557022	0.2259265
62.5	-940.214	-4.467222	62.5	-3135.894	77.10747	62.5	-6.541576	0.243035
65	-923.8793	-5.096325	65	-3130.705	82.91352	65	-6.526175	0.2602686
67.5	-907.5831	-5.768668	67.5	-3125.494	88.80453	67.5	-6.510819	0.2776257
70	-891.3252	-6.484555	70	-3120.259	94.78051	70	-6.495508	0.2951044

Table A 15.3 Thermodynamic data for palmitic acid (C16:0), P=14.7 psia

TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID
	G	G		H	H		S	S
	N-HEX-01	N-HEX-01		N-HEX-01	N-HEX-01		N-HEX-01	N-HEX-01
[C]	[kJ/kg]	[kJ/kg]	[C]	[kJ/kg]	[kJ/kg]	[C]	[kcal/kg-K]	[kcal/kg-K]
72.5	-875.1055	-7.24429	72.5	-3115	100.8415	72.5	-6.48024	0.3127029
75	-858.9239	-8.048168	75	-3109.719	106.9874	75	-6.465014	0.3304195
77.5	-842.7804	-8.896484	77.5	-3104.414	113.2182	77.5	-6.449831	0.3482525
80	-826.6747	-9.789526	80	-3099.085	119.5341	80	-6.434689	0.3662002
82.5	-810.6069	-10.72758	82.5	-3093.733	125.9349	82.5	-6.419587	0.3842611
85	-794.5768	-11.71092	85	-3088.358	132.4207	85	-6.404526	0.4024336
87.5	-778.5842	-12.73984	87.5	-3082.959	138.9914	87.5	-6.389504	0.420716
90	-762.6292	-13.8146	90	-3077.536	145.6471	90	-6.374521	0.4391069
92.5	-746.7116	-14.93546	92.5	-3072.09	152.3877	92.5	-6.359576	0.4576048
95	-730.8313	-16.10271	95	-3066.621	159.2134	95	-6.344669	0.4762083
97.5	-714.9882	-17.31659	97.5	-3061.128	166.124	97.5	-6.329799	0.4949158
100	-699.1823	-18.57737	100	-3055.612	173.1195	100	-6.314966	0.5137261

Table A 15.4 Thermodynamic data for stearic acid (C18:0), P=14.7 psia

TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID
	G	G		H	H		S	S
	STEAR-01	STEAR-01		STEAR-01	STEAR-01		STEAR-01	STEAR-01
[C]	[kJ/kg]	[kJ/kg]	[C]	[kJ/kg]	[kJ/kg]	[C]	[kcal/kg-K]	[kcal/kg-K]
0	-1203.2	-1.84098	0	-3110.36	-41.7679	0	-6.98207	-0.14617
2.5	-1185.77	-1.49346	2.5	-3105.63	-37.8331	2.5	-6.96484	-0.13183
5	-1168.38	-1.18186	5	-3100.88	-33.8479	5	-6.9477	-0.11744
7.5	-1151.03	-0.90631	7.5	-3096.12	-29.8112	7.5	-6.93064	-0.10299
10	-1133.73	-0.66695	10	-3091.33	-25.7216	10	-6.91366	-0.08849
12.5	-1116.46	-0.46393	12.5	-3086.52	-21.5779	12.5	-6.89675	-0.07392
15	-1099.24	-0.29742	15	-3081.69	-17.3788	15	-6.87993	-0.05928
17.5	-1082.06	-0.16759	17.5	-3076.85	-13.1228	17.5	-6.86317	-0.04457
20	-1064.93	-0.07462	20	-3071.98	-8.80863	20	-6.84649	-0.02979
22.5	-1047.83	-0.01869	22.5	-3067.09	-4.43485	22.5	-6.82988	-0.01494
25	-1030.78	-1.10E-13	25	-3062.18	3.16E-14	25	-6.81334	4.76E-16
27.5	-1013.77	-0.01876	27.5	-3057.24	4.497383	27.5	-6.79687	0.015021
30	-996.793	-0.07518	30	-3052.29	9.058806	30	-6.78046	0.03013
32.5	-979.862	-0.16949	32.5	-3047.31	13.6858	32.5	-6.76411	0.045331
35	-962.972	-0.30191	35	-3042.32	18.37994	35	-6.74783	0.060626
37.5	-946.123	-0.4727	37.5	-3037.3	23.1428	37.5	-6.73161	0.07602
40	-929.314	-0.68209	40	-3032.26	27.97601	40	-6.71545	0.091516
42.5	-912.546	-0.93036	42.5	-3027.19	32.88122	42.5	-6.69934	0.107117
45	-895.818	-1.21777	45	-3022.11	37.86011	45	-6.68329	0.122829
47.5	-879.129	-1.5446	47.5	-3017	42.91439	47.5	-6.6673	0.138653
50	-862.481	-1.91113	50	-3011.87	48.04523	50	-6.65136	0.154592

Table A 15.4 Thermodynamic data for stearic acid (C18:0), P=14.7 psia

TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID
	G	G		H	H		S	S
	STEAR-01	STEAR-01		STEAR-01	STEAR-01		STEAR-01	STEAR-01
[C]	[kJ/kg]	[kJ/kg]	[C]	[kJ/kg]	[kJ/kg]	[C]	[kcal/kg-K]	[kcal/kg-K]
52.5	-845.872	-2.31765	52.5	-3006.72	53.25274	52.5	-6.63548	0.170645
55	-829.304	-2.76445	55	-3001.54	58.53692	55	-6.61965	0.186809
57.5	-812.774	-3.25179	57.5	-2996.34	63.89777	57.5	-6.60387	0.203084
60	-796.284	-3.77996	60	-2991.12	69.3353	60	-6.58814	0.219467
62.5	-779.833	-4.34921	62.5	-2985.88	74.8495	62.5	-6.57246	0.235956
65	-763.422	-4.95982	65	-2980.61	80.44037	65	-6.55683	0.252551
67.5	-747.049	-5.61205	67.5	-2975.33	86.10791	67.5	-6.54125	0.26925
70	-730.716	-6.30616	70	-2970.01	91.85213	70	-6.52571	0.286051
72.5	-714.421	-7.04239	72.5	-2964.68	97.67302	72.5	-6.51022	0.302952
75	-698.164	-7.821	75	-2959.32	103.5706	75	-6.49478	0.319953
77.5	-681.947	-8.64224	77.5	-2953.94	109.5448	77.5	-6.47938	0.337051
80	-665.767	-9.50634	80	-2948.54	115.5957	80	-6.46403	0.354246
82.5	-649.627	-10.4136	82.5	-2943.11	121.7233	82.5	-6.44872	0.371536
85	-633.524	-11.3641	85	-2937.67	127.9276	85	-6.43345	0.38892
87.5	-617.459	-12.3582	87.5	-2932.19	134.2085	87.5	-6.41823	0.406396
90	-601.433	-13.3962	90	-2926.7	140.5661	90	-6.40305	0.423963
92.5	-585.444	-14.4781	92.5	-2921.18	147.0004	92.5	-6.38791	0.44162
95	-569.493	-15.6043	95	-2915.64	153.5113	95	-6.37281	0.459366
97.5	-553.58	-16.775	97.5	-2910.08	160.0989	97.5	-6.35775	0.477199
100	-537.704	-17.9904	100	-2904.49	166.7632	100	-6.34273	0.495119

Table A 15.5 Thermodynamic data for oleic acid (C18:1), P=14.7 psia

TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID
	G	G		H	H		S	S
	OLEIC-01	OLEIC-01		OLEIC-01	OLEIC-01		OLEIC-01	OLEIC-01
[C]	[kJ/kg]	[kJ/kg]	[C]	[kJ/kg]	[kJ/kg]	[C]	[kcal/kg-K]	[kcal/kg-K]
0	-1148.31	-1.52528	0	-2958.66	-35.3493	0	-6.62768	-0.12383
1.75	-1136.72	-1.31649	1.75	-2955.34	-32.8748	1.75	-6.61556	-0.1148
3.5	-1125.15	-1.12345	3.5	-2952.01	-30.4004	3.5	-6.60349	-0.10583
5.25	-1113.61	-0.94606	5.25	-2948.67	-27.9259	5.25	-6.59147	-0.09691
7	-1102.08	-0.78423	7	-2945.33	-25.4515	7	-6.57948	-0.08805
8.75	-1090.58	-0.63785	8.75	-2941.97	-22.977	8.75	-6.56754	-0.07925
10.5	-1079.1	-0.50684	10.5	-2938.61	-20.5026	10.5	-6.55565	-0.07049
12.25	-1067.64	-0.39109	12.25	-2935.23	-18.0281	12.25	-6.54379	-0.0618
14	-1056.2	-0.29052	14	-2931.85	-15.5537	14	-6.53197	-0.05315
15.75	-1044.77	-0.20502	15.75	-2928.46	-13.0792	15.75	-6.52019	-0.04456
17.5	-1033.37	-0.13452	17.5	-2925.06	-10.6048	17.5	-6.50845	-0.03602
19.25	-1021.99	-0.07891	19.25	-2921.64	-8.13034	19.25	-6.49675	-0.02754
21	-1010.64	-0.03811	21	-2918.22	-5.65589	21	-6.48509	-0.0191
22.75	-999.297	-0.01203	22.75	-2914.79	-3.18144	22.75	-6.47346	-0.01071
24.5	-987.978	-0.00059	24.5	-2911.35	-0.70699	24.5	-6.46187	-0.00237
26.25	-976.68	-0.0037	26.25	-2907.9	1.767465	26.25	-6.45031	0.005916
28	-965.402	-0.02127	28	-2904.44	4.241915	28	-6.43878	0.014156
29.75	-954.144	-0.05322	29.75	-2900.97	6.716365	29.75	-6.42729	0.022349
31.5	-942.907	-0.09946	31.5	-2897.49	9.190816	31.5	-6.41584	0.030495
33.25	-931.689	-0.15992	33.25	-2894	11.66527	33.25	-6.40441	0.038594
35	-920.491	-0.23452	35	-2890.5	14.13972	35	-6.39302	0.046647

Table A 15.5 Thermodynamic data for oleic acid (C18:1), P=14.7 psia

TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID
	G	G		H	H		S	S
	OLEIC-01	OLEIC-01		OLEIC-01	OLEIC-01		OLEIC-01	OLEIC-01
[C]	[kJ/kg]	[kJ/kg]	[C]	[kJ/kg]	[kJ/kg]	[C]	[kcal/kg-K]	[kcal/kg-K]
36.75	-909.313	-0.32316	36.75	-2886.99	16.61417	36.75	-6.38166	0.054654
38.5	-898.155	-0.42578	38.5	-2883.47	19.08862	38.5	-6.37033	0.062616
40.25	-887.017	-0.54229	40.25	-2879.94	21.56307	40.25	-6.35903	0.070534
42	-875.899	-0.67262	42	-2876.4	24.03752	42	-6.34776	0.078408
43.75	-864.8	-0.81669	43.75	-2872.84	26.51197	43.75	-6.33652	0.086238
45.5	-853.721	-0.97443	45.5	-2869.28	28.98642	45.5	-6.32531	0.094024
47.25	-842.661	-1.14575	47.25	-2865.71	31.46087	47.25	-6.31413	0.101769
49	-831.621	-1.3306	49	-2862.12	33.93532	49	-6.30297	0.109471
50.75	-820.601	-1.52888	50.75	-2858.53	36.40977	50.75	-6.29184	0.117131
52.5	-809.6	-1.74053	52.5	-2854.92	38.88422	52.5	-6.28074	0.12475
54.25	-798.618	-1.96548	54.25	-2851.31	41.35867	54.25	-6.26967	0.132328
56	-787.656	-2.20365	56	-2847.68	43.83312	56	-6.25862	0.139866
57.75	-776.713	-2.45498	57.75	-2844.04	46.30757	57.75	-6.2476	0.147363
59.5	-765.789	-2.7194	59.5	-2840.4	48.78202	59.5	-6.23661	0.154822
61.25	-754.885	-2.99684	61.25	-2836.74	51.25647	61.25	-6.22564	0.162241
63	-744	-3.28722	63	-2833.07	53.73092	63	-6.21469	0.169621
64.75	-733.133	-3.59049	64.75	-2829.39	56.20537	64.75	-6.20377	0.176963
66.5	-722.286	-3.90657	66.5	-2825.7	58.67982	66.5	-6.19287	0.184267
68.25	-711.458	-4.2354	68.25	-2821.99	61.15428	68.25	-6.182	0.191534
70	-700.649	-4.57692	70	-2818.28	63.62873	70	-6.17115	0.198763

Table A 15.6 Thermodynamic properties for linoleic acid (C18:2), P=14.7 psia

TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID
G	G	G	H	H	H	S	S	S
LINOL-01	LINOL-01	LINOL-01	LINOL-01	LINOL-01	LINOL-01	LINOL-01	LINOL-01	LINOL-01
[C]	[kJ/kg]	[kJ/kg]	[C]	[kJ/kg]	[kJ/kg]	[C]	[kcal/kg-K]	[kcal/kg-K]
-10	-810.33	-3.70964	-10	-2467.2	-60.6773	-10	-6.29631	-0.21648
-8.5	-800.893	-3.39231	-8.5	-2464.46	-58.0768	-8.5	-6.28593	-0.20663
-7	-791.472	-3.08972	-7	-2461.72	-55.4764	-7	-6.27559	-0.19683
-5.5	-782.066	-2.80179	-5.5	-2458.98	-52.8759	-5.5	-6.2653	-0.18709
-4	-772.676	-2.52843	-4	-2456.22	-50.2755	-4	-6.25506	-0.1774
-2.5	-763.301	-2.26956	-2.5	-2453.47	-47.675	-2.5	-6.24485	-0.16776
-1	-753.942	-2.02511	-1	-2450.71	-45.0746	-1	-6.23468	-0.15818
0.5	-744.597	-1.79499	0.5	-2447.95	-42.4741	0.5	-6.22456	-0.14865
2	-735.268	-1.57912	2	-2445.18	-39.8737	2	-6.21447	-0.13918
3.5	-725.954	-1.37743	3.5	-2442.41	-37.2732	3.5	-6.20443	-0.12975
5	-716.655	-1.18984	5	-2439.63	-34.6727	5	-6.19442	-0.12038
6.5	-707.37	-1.01628	6.5	-2436.85	-32.0723	6.5	-6.18445	-0.11105
8	-698.101	-0.85666	8	-2434.07	-29.4718	8	-6.17451	-0.10178
9.5	-688.847	-0.71091	9.5	-2431.28	-26.8714	9.5	-6.16461	-0.09255
11	-679.607	-0.57897	11	-2428.48	-24.2709	11	-6.15475	-0.08338
12.5	-670.383	-0.46075	12.5	-2425.68	-21.6705	12.5	-6.14492	-0.07425
14	-661.173	-0.35619	14	-2422.87	-19.07	14	-6.13512	-0.06517
15.5	-651.977	-0.26522	15.5	-2420.06	-16.4696	15.5	-6.12536	-0.05614
17	-642.796	-0.18776	17	-2417.25	-13.8691	17	-6.11563	-0.04715
18.5	-633.63	-0.12374	18.5	-2414.43	-11.2686	18.5	-6.10593	-0.03821
20	-624.479	-0.07309	20	-2411.6	-8.66819	20	-6.09627	-0.02932

Table A 15.6 Thermodynamic properties for linoleic acid (C18:2), P=14.7 psia

TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID
G	G		H	H		S	S	
LINOL-01	LINOL-01		LINOL-01	LINOL-01		LINOL-01	LINOL-01	
[C]	[kJ/kg]	[kJ/kg]	[C]	[kJ/kg]	[kJ/kg]	[C]	[kcal/kg-K]	[kcal/kg-K]
21.5	-615.341	-0.03575	21.5	-2408.77	-6.06773	21.5	-6.08663	-0.02047
23	-606.219	-0.01166	23	-2405.93	-3.46727	23	-6.07702	-0.01167
24.5	-597.11	-0.00073	24.5	-2403.09	-0.86682	24.5	-6.06745	-0.00291
26	-588.016	-0.0029	26	-2400.24	1.733637	26	-6.0579	0.005805
27.5	-578.937	-0.01812	27.5	-2397.38	4.334092	27.5	-6.04838	0.014476
29	-569.871	-0.04631	29	-2394.52	6.934548	29	-6.03889	0.023104
30.5	-560.82	-0.08741	30.5	-2391.66	9.535003	30.5	-6.02943	0.031689
32	-551.783	-0.14136	32	-2388.78	12.13546	32	-6.01999	0.040232
33.5	-542.76	-0.20809	33.5	-2385.9	14.73591	33.5	-6.01058	0.048733
35	-533.751	-0.28754	35	-2383.02	17.33637	35	-6.0012	0.057193
36.5	-524.756	-0.37964	36.5	-2380.13	19.93682	36.5	-5.99184	0.065611
38	-515.776	-0.48435	38	-2377.23	22.53728	38	-5.98251	0.073989
39.5	-506.809	-0.60159	39.5	-2374.33	25.13774	39.5	-5.9732	0.082326
41	-497.856	-0.73131	41	-2371.42	27.73819	41	-5.96391	0.090624
42.5	-488.917	-0.87344	42.5	-2368.5	30.33865	42.5	-5.95465	0.098882
44	-479.992	-1.02793	44	-2365.58	32.9391	44	-5.94541	0.107101
45.5	-471.081	-1.19473	45.5	-2362.65	35.53956	45.5	-5.9362	0.115281
47	-462.183	-1.37376	47	-2359.71	38.14001	47	-5.92701	0.123423
48.5	-453.3	-1.56497	48.5	-2356.77	40.74047	48.5	-5.91784	0.131526
50	-444.43	-1.76832	50	-2353.82	43.34092	50	-5.90869	0.139592

Table A 15.7 Thermodynamic properties for arachidic acid (C20:0), P=14.7 psia

TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID	TEMP	LIQUID	SOLID
	G	G		H	H		S	S
	N-EIC-01	N-EIC-01		N-EIC-01	N-EIC-01		N-EIC-01	N-EIC-01
[C]	[kJ/kg]	[kJ/kg]	[C]	[kJ/kg]	[kJ/kg]	[C]	[kcal/kg-K]	[kcal/kg-K]
10	-1004.51	-0.66221	10	-2971.23	-25.5268	10	-6.94585	-0.08781
12.25	-988.895	-0.47924	12.25	-2966.92	-21.8328	12.25	-6.93071	-0.07482
14.5	-973.318	-0.32557	14.5	-2962.6	-18.0929	14.5	-6.91564	-0.06177
16.75	-957.775	-0.20133	16.75	-2958.26	-14.3059	16.75	-6.90062	-0.04865
19	-942.265	-0.10668	19	-2953.91	-10.4708	19	-6.88565	-0.03548
21.25	-926.789	-0.04175	21.25	-2949.54	-6.58645	21.25	-6.87075	-0.02223
23.5	-911.347	-0.00669	23.5	-2945.15	-2.65172	23.5	-6.8559	-0.00892
25.75	-895.938	-0.00168	25.75	-2940.74	1.33456	25.75	-6.8411	0.004471
28	-880.562	-0.02687	28	-2936.32	5.373573	28	-6.82636	0.017933
30.25	-865.219	-0.08243	30.25	-2931.88	9.46652	30.25	-6.81167	0.031473
32.5	-849.909	-0.16856	32.5	-2927.42	13.61463	32.5	-6.79703	0.045095
34.75	-834.632	-0.28542	34.75	-2922.94	17.81914	34.75	-6.78243	0.0588
37	-819.388	-0.43322	37	-2918.45	22.08133	37	-6.76789	0.072592
39.25	-804.177	-0.61215	39.25	-2913.94	26.40247	39.25	-6.75339	0.086474
41.5	-788.998	-0.82243	41.5	-2909.41	30.78388	41.5	-6.73894	0.100449
43.75	-773.852	-1.06425	43.75	-2904.86	35.22689	43.75	-6.72454	0.114519
46	-758.737	-1.33784	46	-2900.29	39.73285	46	-6.71018	0.128688
48.25	-743.656	-1.64342	48.25	-2895.71	44.30313	48.25	-6.69586	0.142958
50.5	-728.606	-1.98122	50.5	-2891.1	48.93913	50.5	-6.68159	0.157332
52.75	-713.588	-2.35149	52.75	-2886.48	53.64225	52.75	-6.66736	0.171813
55	-698.603	-2.75446	55	-2881.84	58.41394	55	-6.65317	0.186404

Table A 15.7 Thermodynamic properties for arachidic acid (C20:0), P=14.7 psia

TEMP [C]	LIQUID G N-EIC-01 [kJ/kg]	SOLID G N-EIC-01 [kJ/kg]	TEMP [C]	LIQUID H N-EIC-01 [kJ/kg]	SOLID H N-EIC-01 [kJ/kg]	TEMP [C]	LIQUID S N-EIC-01 [kcal/kg-K]	SOLID S N-EIC-01 [kcal/kg-K]
57.25	-683.649	-3.19039	57.25	-2877.18	63.25564	57.25	-6.63903	0.201108
59.5	-668.727	-3.65953	59.5	-2872.51	68.16844	59.5	-6.62492	0.215927
61.75	-653.837	-4.16215	61.75	-2867.81	73.15247	61.75	-6.61085	0.230859
64	-638.978	-4.69848	64	-2863.1	78.20773	64	-6.59682	0.245903
66.25	-624.151	-5.26879	66.25	-2858.36	83.33423	66.25	-6.58283	0.261058
68.5	-609.356	-5.87332	68.5	-2853.61	88.53195	68.5	-6.56888	0.276322
70.75	-594.591	-6.51232	70.75	-2848.84	93.8009	70.75	-6.55496	0.291693
73	-579.858	-7.18602	73	-2844.05	99.14109	73	-6.54108	0.307171
75.25	-565.156	-7.89467	75.25	-2839.25	104.5525	75.25	-6.52724	0.322753
77.5	-550.486	-8.63849	77.5	-2834.42	110.0352	77.5	-6.51343	0.338439
79.75	-535.846	-9.41772	79.75	-2829.58	115.589	79.75	-6.49966	0.354227
82	-521.237	-10.2326	82	-2824.71	121.2141	82	-6.48592	0.370116
84.25	-506.659	-11.0833	84.25	-2819.83	126.9105	84.25	-6.47222	0.386105
86.5	-492.112	-11.9701	86.5	-2814.93	132.6781	86.5	-6.45855	0.402192
88.75	-477.596	-12.8933	88.75	-2810.01	138.5169	88.75	-6.44491	0.418376
91	-463.11	-13.8529	91	-2805.07	144.4269	91	-6.43131	0.434656
93.25	-448.655	-14.8493	93.25	-2800.12	150.4082	93.25	-6.41774	0.45103
95.5	-434.23	-15.8826	95.5	-2795.14	156.4607	95.5	-6.4042	0.467498
97.75	-419.836	-16.9531	97.75	-2790.15	162.5844	97.75	-6.3907	0.484059
100	-405.472	-18.0609	100	-2785.13	168.7793	100	-6.37722	0.500711

Table A 15.8 Thermodynamic data for hydrogen sulphide

TEMP [C]	VAPOR G HYDRO-01 [kJ/kg]	TEMP [C]	VAPOR H HYDRO-01 [kJ/kg]	TEMP [C]	VAPOR S HYDRO-01 [kJ/kg-K]
-10	-939.888	-10	-642.04	-10	1.131856
-8.6076	-941.468	-8.6076	-640.645	-8.6076	1.137143
-7.21519	-943.055	-7.21519	-639.25	-7.21519	1.142404
-5.82279	-944.649	-5.82279	-637.854	-5.82279	1.147639
-4.43038	-946.251	-4.43038	-636.458	-4.43038	1.152848
-3.03798	-947.86	-3.03798	-635.061	-3.03798	1.158032
-1.64557	-949.476	-1.64557	-633.664	-1.64557	1.163191
-0.25316	-951.099	-0.25316	-632.267	-0.25316	1.168325
1.139241	-952.729	1.139241	-630.869	1.139241	1.173435
2.531646	-954.367	2.531646	-629.47	2.531646	1.17852
3.924051	-956.011	3.924051	-628.072	3.924051	1.183581
5.316456	-957.663	5.316456	-626.672	5.316456	1.188619
6.708861	-959.321	6.708861	-625.273	6.708861	1.193633
8.101266	-960.987	8.101266	-623.872	8.101266	1.198623
9.493671	-962.659	9.493671	-622.472	9.493671	1.203591
10.88608	-964.339	10.88608	-621.071	10.88608	1.208537
12.27848	-966.025	12.27848	-619.669	12.27848	1.213459
13.67089	-967.718	13.67089	-618.267	13.67089	1.21836
15.06329	-969.418	15.06329	-616.864	15.06329	1.223239
16.4557	-971.124	16.4557	-615.461	16.4557	1.228095
17.8481	-972.838	17.8481	-614.057	17.8481	1.232931

Table A 15.8 Thermodynamic data for hydrogen sulphide

TEMP [C]	VAPOR G HYDRO-01 [kJ/kg]	TEMP [C]	VAPOR H HYDRO-01 [kJ/kg]	TEMP [C]	VAPOR S HYDRO-01 [kJ/kg-K]
19.24051	-974.558	19.24051	-612.653	19.24051	1.237745
20.63291	-976.284	20.63291	-611.248	20.63291	1.242538
22.02532	-978.018	22.02532	-609.843	22.02532	1.247311
23.41772	-979.758	23.41772	-608.437	23.41772	1.252062
24.81013	-981.505	24.81013	-607.03	24.81013	1.256794
26.20253	-983.258	26.20253	-605.623	26.20253	1.261505
27.59494	-985.018	27.59494	-604.216	27.59494	1.266196
28.98734	-986.784	28.98734	-602.808	28.98734	1.270867
30.37975	-988.557	30.37975	-601.399	30.37975	1.275519
31.77215	-990.336	31.77215	-599.989	31.77215	1.280152
33.16456	-992.122	33.16456	-598.58	33.16456	1.284765
34.55696	-993.914	34.55696	-597.169	34.55696	1.28936
35.94937	-995.712	35.94937	-595.758	35.94937	1.293935
37.34177	-997.517	37.34177	-594.346	37.34177	1.298492
38.73418	-999.328	38.73418	-592.934	38.73418	1.303031
40.12658	-1001.15	40.12658	-591.521	40.12658	1.307551
41.51899	-1002.97	41.51899	-590.107	41.51899	1.312054
42.91139	-1004.8	42.91139	-588.693	42.91139	1.316538
44.3038	-1006.64	44.3038	-587.278	44.3038	1.321005
45.6962	-1008.48	45.6962	-585.862	45.6962	1.325454
47.08861	-1010.33	47.08861	-584.446	47.08861	1.329886
48.48101	-1012.18	48.48101	-583.03	48.48101	1.334301

Table A 15.8 Thermodynamic data for hydrogen sulphide

TEMP G HYDRO-01 [C]	VAPOR [kJ/kg]	TEMP H HYDRO-01 [C]	VAPOR [kJ/kg]	TEMP S HYDRO-01 [C]	VAPOR [kJ/kg-K]
49.87342	-1014.04	49.87342	-581.612	49.87342	1.338698
51.26582	-1015.91	51.26582	-580.194	51.26582	1.343079
52.65823	-1017.78	52.65823	-578.775	52.65823	1.347443
54.05063	-1019.66	54.05063	-577.356	54.05063	1.351791
55.44304	-1021.55	55.44304	-575.935	55.44304	1.356122
56.83544	-1023.44	56.83544	-574.515	56.83544	1.360437
58.22785	-1025.34	58.22785	-573.093	58.22785	1.364735
59.62025	-1027.24	59.62025	-571.671	59.62025	1.369018
61.01266	-1029.15	61.01266	-570.248	61.01266	1.373285
62.40506	-1031.06	62.40506	-568.824	62.40506	1.377536
63.79747	-1032.99	63.79747	-567.4	63.79747	1.381772
65.18987	-1034.91	65.18987	-565.975	65.18987	1.385993
66.58228	-1036.84	66.58228	-564.549	66.58228	1.390198
67.97468	-1038.78	67.97468	-563.123	67.97468	1.394388
69.36709	-1040.73	69.36709	-561.696	69.36709	1.398563
70.75949	-1042.68	70.75949	-560.268	70.75949	1.402723
72.1519	-1044.63	72.1519	-558.839	72.1519	1.406869
73.5443	-1046.6	73.5443	-557.41	73.5443	1.411
74.93671	-1048.56	74.93671	-555.98	74.93671	1.415116
76.32911	-1050.54	76.32911	-554.549	76.32911	1.419219
77.72152	-1052.52	77.72152	-553.118	77.72152	1.423307
79.11392	-1054.5	79.11392	-551.686	79.11392	1.427381

Table A 15.8 Thermodynamic data for hydrogen sulphide

TEMP [C]	VAPOR G HYDRO-01 [kJ/kg]	TEMP [C]	VAPOR H HYDRO-01 [kJ/kg]	TEMP [C]	VAPOR S HYDRO-01 [kJ/kg-K]
80.50633	-1056.49	80.50633	-550.253	80.50633	1.43144
81.89873	-1058.49	81.89873	-548.819	81.89873	1.435487
83.29114	-1060.49	83.29114	-547.384	83.29114	1.439519
84.68354	-1062.5	84.68354	-545.949	84.68354	1.443538
86.07595	-1064.51	86.07595	-544.513	86.07595	1.447543
87.46835	-1066.53	87.46835	-543.076	87.46835	1.451535
88.86076	-1068.55	88.86076	-541.639	88.86076	1.455514
90.25316	-1070.58	90.25316	-540.2	90.25316	1.459479
91.64557	-1072.62	91.64557	-538.761	91.64557	1.463432
93.03797	-1074.66	93.03797	-537.321	93.03797	1.467371
94.43038	-1076.7	94.43038	-535.881	94.43038	1.471298
95.82278	-1078.75	95.82278	-534.439	95.82278	1.475212
97.21519	-1080.81	97.21519	-532.997	97.21519	1.479113
98.60759	-1082.87	98.60759	-531.554	98.60759	1.483002
100	-1084.94	100	-530.11	100	1.486878

Table A 15.9 Thermodynamic data of water, P=14.7 psia

TEMP [C]	VAPOR G WATER [kJ/kg]	LIQUID G WATER [kJ/kg]	SOLID G WATER [kJ/kg]	TEMP [C]	VAPOR H WATER [kcal/mol]	LIQUID H WATER [kcal/mol]	SOLID H WATER [kcal/mol]	TEMP [C]	VAPOR S WATER [kJ/kg-K]	LIQUID S WATER [kJ/kg-K]	SOLID S WATER [kJ/kg-K]
-17.7778	-12802.3	-13565.6	-13596.5	-17.7778	-58.124	-68.9238	-70.3574	-17.7778	-2.76425	-9.60345	-10.7871
-16.3861	-12798.4	-13552.3	-13581.5	-16.3861	-58.1127	-68.9017	-70.3455	-16.3861	-2.75396	-9.58317	-10.7763
-14.9944	-12794.6	-13539	-13566.5	-14.9944	-58.1013	-68.8795	-70.3336	-14.9944	-2.74373	-9.56306	-10.7655
-13.6027	-12790.8	-13525.7	-13551.6	-13.6027	-58.09	-68.8573	-70.3216	-13.6027	-2.73356	-9.5431	-10.7547
-12.211	-12787	-13512.5	-13536.6	-12.211	-58.0787	-68.8352	-70.3095	-12.211	-2.72344	-9.52331	-10.744
-10.8193	-12783.2	-13499.2	-13521.7	-10.8193	-58.0674	-68.813	-70.2974	-10.8193	-2.71338	-9.50367	-10.7332
-9.42761	-12779.4	-13486	-13506.7	-9.42761	-58.056	-68.7908	-70.2852	-9.42761	-2.70337	-9.48419	-10.7224
-8.03592	-12775.7	-13472.8	-13491.8	-8.03592	-58.0447	-68.7686	-70.2729	-8.03592	-2.69342	-9.46485	-10.7116
-6.64422	-12771.9	-13459.5	-13476.9	-6.64422	-58.0334	-68.7464	-70.2606	-6.64422	-2.68352	-9.44567	-10.7009
-5.25253	-12768.2	-13446.3	-13462	-5.25253	-58.0221	-68.7243	-70.2482	-5.25253	-2.67368	-9.42664	-10.6901
-3.86083	-12764.5	-13433.2	-13447.2	-3.86083	-58.0107	-68.7021	-70.2358	-3.86083	-2.66388	-9.40775	-10.6793
-2.46914	-12760.8	-13420	-13432.3	-2.46914	-57.9994	-68.6799	-70.2232	-2.46914	-2.65414	-9.38901	-10.6685
-1.07744	-12757.1	-13406.8	-13417.5	-1.07744	-57.9881	-68.6577	-70.2106	-1.07744	-2.64445	-9.37041	-10.6577
0.314252	-12753.4	-13393.7	-13402.6	0.314252	-57.9768	-68.6356	-70.198	0.314252	-2.63481	-9.35195	-10.647
1.705946	-12749.8	-13380.5	-13387.8	1.705946	-57.9655	-68.6133	-70.1853	1.705946	-2.62522	-9.33355	-10.6362
3.097641	-12746.1	-13367.5	-13373	3.097641	-57.9542	-68.5911	-70.1725	3.097641	-2.61568	-9.31519	-10.6254
4.489336	-12742.5	-13354.4	-13358.3	4.489336	-57.9429	-68.5688	-70.1596	4.489336	-2.60618	-9.29687	-10.6146
5.881031	-12738.9	-13341.4	-13343.5	5.881031	-57.9315	-68.5464	-70.1467	5.881031	-2.59674	-9.27858	-10.6038
7.272725	-12735.3	-13328.4	-13328.8	7.272725	-57.9202	-68.524	-70.1338	7.272725	-2.58734	-9.26033	-10.593
8.66442	-12731.7	-13315.4	-13314	8.66442	-57.9089	-68.5016	-70.1207	8.66442	-2.57799	-9.24211	-10.5823
10.05611	-12728.1	-13302.5	-13299.3	10.05611	-57.8976	-68.4791	-70.1076	10.05611	-2.56869	-9.22393	-10.5715

Table A 15.9 Thermodynamic data of water, P=14.7 psia

TEMP [C]	VAPOR G WATER [kJ/kg]	LIQUID G WATER [kJ/kg]	SOLID G WATER [kJ/kg]	TEMP [C]	VAPOR H WATER [kcal/mol]	LIQUID H WATER [kcal/mol]	SOLID H WATER [kcal/mol]	TEMP [C]	VAPOR S WATER [kJ/kg-K]	LIQUID S WATER [kJ/kg-K]	SOLID S WATER [kJ/kg-K]
11.44781	-12724.5	-13289.6	-13284.6	11.44781	-57.8863	-68.4566	-70.0944	11.44781	-2.55943	-9.20578	-10.5607
12.8395	-12721	-13276.7	-13269.9	12.8395	-57.875	-68.434	-70.0812	12.8395	-2.55022	-9.18767	-10.5499
14.2312	-12717.4	-13263.8	-13255.2	14.2312	-57.8637	-68.4114	-70.0679	14.2312	-2.54105	-9.16959	-10.5391
15.62289	-12713.9	-13251	-13240.6	15.62289	-57.8524	-68.3887	-70.0545	15.62289	-2.53193	-9.15155	-10.5283
17.01459	-12710.4	-13238.2	-13225.9	17.01459	-57.8411	-68.3659	-70.0411	17.01459	-2.52285	-9.13354	-10.5176
18.40628	-12706.9	-13225.4	-13211.3	18.40628	-57.8298	-68.3432	-70.0276	18.40628	-2.51381	-9.11556	-10.5068
19.79798	-12703.4	-13212.7	-13196.7	19.79798	-57.8185	-68.3203	-70.014	19.79798	-2.50482	-9.09762	-10.496
21.18967	-12699.9	-13200	-13182.1	21.18967	-57.8072	-68.2975	-70.0004	21.18967	-2.49587	-9.07971	-10.4852
22.58137	-12696.4	-13187.3	-13167.5	22.58137	-57.7958	-68.2745	-69.9867	22.58137	-2.48697	-9.06184	-10.4744
23.97306	-12693	-13174.7	-13152.9	23.97306	-57.7845	-68.2515	-69.9729	23.97306	-2.4781	-9.044	-10.4636
25.36476	-12689.5	-13162	-13138.4	25.36476	-57.7732	-68.2285	-69.9591	25.36476	-2.46928	-9.0262	-10.4528
26.75645	-12686.1	-13149.4	-13123.8	26.75645	-57.7619	-68.2054	-69.9452	26.75645	-2.46049	-9.00842	-10.442
28.14815	-12682.7	-13136.9	-13109.3	28.14815	-57.7506	-68.1823	-69.9313	28.14815	-2.45175	-8.99068	-10.4313
29.53984	-12679.3	-13124.3	-13094.8	29.53984	-57.7393	-68.1591	-69.9173	29.53984	-2.44305	-8.97298	-10.4205
30.93154	-12675.9	-13111.8	-13080.3	30.93154	-57.728	-68.1359	-69.9032	30.93154	-2.43439	-8.9553	-10.4097
32.32323	-12672.5	-13099.3	-13065.8	32.32323	-57.7167	-68.1126	-69.889	32.32323	-2.42576	-8.93766	-10.3989
33.71493	-12669.1	-13086.9	-13051.4	33.71493	-57.7054	-68.0892	-69.8748	33.71493	-2.41718	-8.92005	-10.3881
35.10662	-12665.8	-13074.4	-13036.9	35.10662	-57.6941	-68.0658	-69.8605	35.10662	-2.40863	-8.90248	-10.3773
36.49832	-12662.4	-13062	-13022.5	36.49832	-57.6828	-68.0424	-69.8462	36.49832	-2.40012	-8.88493	-10.3665
37.89001	-12659.1	-13049.7	-13008.1	37.89001	-57.6714	-68.0189	-69.8318	37.89001	-2.39165	-8.86742	-10.3557
39.2817	-12655.8	-13037.3	-12993.6	39.2817	-57.6601	-67.9953	-69.8173	39.2817	-2.38322	-8.84994	-10.3449
40.6734	-12652.5	-13025	-12979.3	40.6734	-57.6488	-67.9717	-69.8028	40.6734	-2.37482	-8.83249	-10.3342

Table A 15.9 Thermodynamic data of water, P=14.7 psia

TEMP [C]	VAPOR G WATER [kJ/kg]	LIQUID G WATER [kJ/kg]	SOLID G WATER [kJ/kg]	TEMP [C]	VAPOR H WATER [kcal/mol]	LIQUID H WATER [kcal/mol]	SOLID H WATER [kcal/mol]	TEMP [C]	VAPOR S WATER [kJ/kg-K]	LIQUID S WATER [kJ/kg-K]	SOLID S WATER [kJ/kg-K]
42.06509	-12649.2	-13012.7	-12964.9	42.06509	-57.6375	-67.948	-69.7882	42.06509	-2.36646	-8.81508	-10.3234
43.45679	-12645.9	-13000.4	-12950.5	43.45679	-57.6262	-67.9243	-69.7735	43.45679	-2.35814	-8.79769	-10.3126
44.84848	-12642.6	-12988.1	-12936.2	44.84848	-57.6149	-67.9005	-69.7588	44.84848	-2.34985	-8.78034	-10.3018
46.24018	-12639.3	-12975.9	-12921.9	46.24018	-57.6036	-67.8767	-69.744	46.24018	-2.3416	-8.76301	-10.291
47.63187	-12636.1	-12963.7	-12907.5	47.63187	-57.5922	-67.8528	-69.7291	47.63187	-2.33338	-8.74572	-10.2802
49.02357	-12632.8	-12951.5	-12893.2	49.02357	-57.5809	-67.8288	-69.7142	49.02357	-2.3252	-8.72846	-10.2694
50.41526	-12629.6	-12939.4	-12879	50.41526	-57.5696	-67.8048	-69.6992	50.41526	-2.31705	-8.71122	-10.2586
51.80696	-12626.4	-12927.2	-12864.7	51.80696	-57.5583	-67.7807	-69.6841	51.80696	-2.30894	-8.69402	-10.2478
53.19865	-12623.2	-12915.1	-12850.4	53.19865	-57.547	-67.7566	-69.669	53.19865	-2.30086	-8.67685	-10.237
54.59035	-12620	-12903.1	-12836.2	54.59035	-57.5356	-67.7324	-69.6538	54.59035	-2.29281	-8.65971	-10.2262
55.98204	-12616.8	-12891	-12822	55.98204	-57.5243	-67.7082	-69.6386	55.98204	-2.2848	-8.64259	-10.2154
57.37374	-12613.6	-12879	-12807.8	57.37374	-57.513	-67.6839	-69.6232	57.37374	-2.27681	-8.62551	-10.2046
58.76543	-12610.5	-12867	-12793.6	58.76543	-57.5017	-67.6595	-69.6078	58.76543	-2.26887	-8.60846	-10.1939
60.15713	-12607.3	-12855	-12779.4	60.15713	-57.4903	-67.6351	-69.5924	60.15713	-2.26095	-8.59143	-10.1831
61.54882	-12604.2	-12843	-12765.2	61.54882	-57.479	-67.6106	-69.5769	61.54882	-2.25307	-8.57444	-10.1723
62.94052	-12601.1	-12831.1	-12751.1	62.94052	-57.4677	-67.5861	-69.5613	62.94052	-2.24521	-8.55747	-10.1615
64.33221	-12597.9	-12819.2	-12736.9	64.33221	-57.4563	-67.5615	-69.5457	64.33221	-2.23739	-8.54053	-10.1507
65.7239	-12594.8	-12807.3	-12722.8	65.7239	-57.445	-67.5368	-69.53	65.7239	-2.2296	-8.52362	-10.1399
67.1156	-12591.7	-12795.4	-12708.7	67.1156	-57.4337	-67.5121	-69.5142	67.1156	-2.22184	-8.50674	-10.1291
68.50729	-12588.6	-12783.6	-12694.6	68.50729	-57.4223	-67.4873	-69.4983	68.50729	-2.21411	-8.48989	-10.1183
69.89899	-12585.6	-12771.8	-12680.5	69.89899	-57.411	-67.4625	-69.4824	69.89899	-2.20641	-8.47306	-10.1075
71.29068	-12582.5	-12760	-12666.5	71.29068	-57.3996	-67.4376	-69.4665	71.29068	-2.19874	-8.45626	-10.0967

Table A 15.9 Thermodynamic data of water, P=14.7 psia

TEMP [C]	VAPOR G WATER [kJ/kg]	LIQUID G WATER [kJ/kg]	SOLID G WATER [kJ/kg]	TEMP [C]	VAPOR H WATER [kcal/mol]	LIQUID H WATER [kcal/mol]	SOLID H WATER [kcal/mol]	TEMP [C]	VAPOR S WATER [kJ/kg-K]	LIQUID S WATER [kJ/kg-K]	SOLID S WATER [kJ/kg-K]
72.68238	-12579.4	-12748.2	-12652.4	72.68238	-57.3883	-67.4126	-69.4504	72.68238	-2.1911	-8.43949	-10.0859
74.07407	-12576.4	-12736.5	-12638.4	74.07407	-57.3769	-67.3876	-69.4343	74.07407	-2.18349	-8.42275	-10.0751
75.46577	-12573.4	-12724.8	-12624.4	75.46577	-57.3656	-67.3625	-69.4182	75.46577	-2.17591	-8.40603	-10.0643
76.85746	-12570.3	-12713.1	-12610.4	76.85746	-57.3542	-67.3374	-69.4019	76.85746	-2.16836	-8.38934	-10.0535
78.24916	-12567.3	-12701.4	-12596.4	78.24916	-57.3429	-67.3121	-69.3857	78.24916	-2.16084	-8.37268	-10.0427
79.64085	-12564.3	-12689.7	-12582.5	79.64085	-57.3315	-67.2869	-69.3693	79.64085	-2.15334	-8.35605	-10.0319
81.03255	-12561.3	-12678.1	-12568.5	81.03255	-57.3202	-67.2615	-69.3529	81.03255	-2.14587	-8.33944	-10.0211
82.42424	-12558.4	-12666.5	-12554.6	82.42424	-57.3088	-67.2361	-69.3364	82.42424	-2.13843	-8.32285	-10.0103
83.81594	-12555.4	-12654.9	-12540.6	83.81594	-57.2974	-67.2107	-69.3198	83.81594	-2.13102	-8.3063	-9.99951
85.20763	-12552.4	-12643.3	-12526.7	85.20763	-57.2861	-67.1851	-69.3032	85.20763	-2.12364	-8.28977	-9.98871
86.59933	-12549.5	-12631.8	-12512.8	86.59933	-57.2747	-67.1596	-69.2865	86.59933	-2.11628	-8.27326	-9.97792
87.99102	-12546.5	-12620.2	-12499	87.99102	-57.2633	-67.1339	-69.2698	87.99102	-2.10895	-8.25678	-9.96712
89.38272	-12543.6	-12608.7	-12485.1	89.38272	-57.252	-67.1082	-69.253	89.38272	-2.10164	-8.24033	-9.95632
90.77441	-12540.7	-12597.3	-12471.2	90.77441	-57.2406	-67.0824	-69.2361	90.77441	-2.09437	-8.2239	-9.94552
92.16611	-12537.8	-12585.8	-12457.4	92.16611	-57.2292	-67.0566	-69.2191	92.16611	-2.08712	-8.2075	-9.93472
93.5578	-12534.9	-12574.4	-12443.6	93.5578	-57.2178	-67.0306	-69.2021	93.5578	-2.07989	-8.19112	-9.92392
94.94949	-12532	-12562.9	-12429.8	94.94949	-57.2065	-67.0047	-69.1851	94.94949	-2.07269	-8.17476	-9.91312
96.34119	-12529.1	-12551.5	-12416	96.34119	-57.1951	-66.9786	-69.1679	96.34119	-2.06552	-8.15843	-9.90232
97.73288	-12526.2	-12540.2	-12402.2	97.73288	-57.1837	-66.9525	-69.1507	97.73288	-2.05837	-8.14213	-9.89152
99.12458	-12523.4	-12528.8	-12388.5	99.12458	-57.1723	-66.9263	-69.1334	99.12458	-2.05124	-8.12585	-9.88072
100.5163	-12520.5	-12517.5	-12374.7	100.5163	-57.1609	-66.9001	-69.1161	100.5163	-2.04414	-8.10959	-9.86992
101.908	-12517.7	-12506.2	-12361	101.908	-57.1495	-66.8738	-69.0987	101.908	-2.03707	-8.09336	-9.85911

Table A 15.9 Thermodynamic data of water, P=14.7 psia

TEMP [C]	VAPOR G WATER [kJ/kg]	LIQUID G WATER [kJ/kg]	SOLID G WATER [kJ/kg]	TEMP [C]	VAPOR H WATER [kcal/mol]	LIQUID H WATER [kcal/mol]	SOLID H WATER [kcal/mol]	TEMP [C]	VAPOR S WATER [kJ/kg-K]	LIQUID S WATER [kJ/kg-K]	SOLID S WATER [kJ/kg-K]
103.2997	-12514.9	-12494.9	-12347.3	103.2997	-57.1381	-66.8474	-69.0812	103.2997	-2.03002	-8.07715	-9.84831
104.6914	-12512	-12483.6	-12333.6	104.6914	-57.1267	-66.821	-69.0637	104.6914	-2.02299	-8.06096	-9.83751
106.0831	-12509.2	-12472.4	-12319.9	106.0831	-57.1153	-66.7945	-69.0461	106.0831	-2.01599	-8.0448	-9.82671
107.4747	-12506.4	-12461.1	-12306.2	107.4747	-57.1039	-66.7679	-69.0285	107.4747	-2.00901	-8.02866	-9.81591
108.8664	-12503.6	-12449.9	-12292.6	108.8664	-57.0925	-66.7413	-69.0107	108.8664	-2.00206	-8.01254	-9.80511
110.2581	-12500.9	-12438.8	-12278.9	110.2581	-57.0811	-66.7146	-68.993	110.2581	-1.99513	-7.99645	-9.7943
111.6498	-12498.1	-12427.6	-12265.3	111.6498	-57.0697	-66.6878	-68.9751	111.6498	-1.98822	-7.98038	-9.7835
113.0415	-12495.3	-12416.4	-12251.7	113.0415	-57.0582	-66.661	-68.9572	113.0415	-1.98134	-7.96433	-9.7727
114.4332	-12492.6	-12405.3	-12238.1	114.4332	-57.0468	-66.6341	-68.9392	114.4332	-1.97448	-7.9483	-9.7619
115.8249	-12489.8	-12394.2	-12224.5	115.8249	-57.0354	-66.6071	-68.9212	115.8249	-1.96764	-7.93229	-9.75109
117.2166	-12487.1	-12383.1	-12211	117.2166	-57.024	-66.58	-68.903	117.2166	-1.96082	-7.91631	-9.74029
118.6083	-12484.4	-12372.1	-12197.4	118.6083	-57.0125	-66.5529	-68.8849	118.6083	-1.95403	-7.90035	-9.72949
120	-12481.6	-12361	-12183.9	120	-57.0011	-66.5258	-68.8666	120	-1.94726	-7.88441	-9.71868

Appendix 16 Margin estimation assumptions

Remarks:

- (1) The price of enzyme is not counted into the raw material cost. The enzyme *Lipase B from Candida Antarctica* is assumed to be solid and immobilized. Therefore, the required amount of Lipase B does not only depend on the kinetic requirement of the reaction, but also on the size design of the reactor. It is also assumed that the enzymes can be used for quite a long time (1-3 year) since its loss in activity is very low. The cost of price is considered as part of equipment (investment) cost instead of raw material cost.
- (2) The price of oleic acid is from [6].
- (3) The price of process water is from the price list in [18]. The amount of process water is estimated based on the best Aqueous/organic (v/v) ratio, which has been discussed for the hydrolytic reaction catalyzed by lipase B [61]. By assuming that similar optimal reaction condition applies for the sulphurylation reaction, the A/O ratio is estimated as 2. The process water is to be recycled in the process as discussed in the main text, therefore, the water requirement in the process is assumed to be only 10% of the required amount in the process without recycle.
- (4) The price of H_2S is estimated based on the selling price of the analytically pure *Hydrogen sulphide gas* from [26]. The price used in the following calculation is 10% of the original price, since the purity of the H_2S gas requirement is not so high and it will be purchased as bulk chemical.
- (5) The selling price of the Thiooleic Acid is from the expectation of the principal [37].
- (6) The selling price of the Thiolinoleic Acid is estimated based on the expectation from the principal [37].
- (7) The selling price of the by-product saturated acid is assumed to be half the price of the raw material oleic acid. The by-product is expected to be sold as an industrial material to other chemical company or as raw material for biodiesel.

Appendix 17 Calculation of maximum allowable investment

First method

$$\text{Present margin} = \frac{\text{Margin}}{(1+r)^n}$$

$$\text{Cumulative of margin in working years} = \sum_{n=2}^{n=11} \frac{\text{Margin}}{(1+r)^n}$$

$$\text{DCFRROR} = \frac{\text{Cumulative net cash flow at the end of project}}{\text{Life of project} \times \text{Original investment}}$$

$$\text{DCFRROR} = \frac{\text{Cumulative of margin in working years} - \text{Original investment}}{\text{Life of project} \times \text{Original investment}}$$

As DCFRROR is 10% or 0.1:

$$\frac{\text{Cumulative of margin in working years} - \text{Original investment}}{\text{Life of project} \times \text{Original investment}} = 0.1$$

$$\rightarrow \text{Original investment} = \frac{\text{Cumulative of margin in working years}}{0.1 \times \text{Life of project} + 1}$$

Year	Present Margin Euro.
2	13,565,292
3	12,332,083
4	11,210,985
5	10,191,804
6	9,265,277
7	8,422,979
8	7,657,254
9	6,961,140
10	6,328,309
11	5,753,008
12	5,230,007
13	4,754,552
14	4,322,320
15	3,929,382

Accumulat Margin	Euro.
109,924,391	
Total investment	Euro.
43,969,756	

When DCFROR (Discount Cash Flow rate of Return) is 10% the maximum acceptable investment is 43,969,756 Euro.

Second method

In the second method, end of year zero is defined as the year when construction finishes and manufacturing begins. As construction takes two years, investment spending starts at year -2. It is assumed that 30% of the investment cost will be spend in the first year of construction and the rest in the second year of construction. Production starts at end of year 0. In the first year, the plant operates at 70% capacity and in the second year the plant operates at 90% capacity. Depreciation starts in the first production year. In this calculation, 10-year straight-line depreciation is used. Tax rate is assumed at 45%. The calculation has been carried out as follows:

$$\text{Income} = \text{financial margin} \times \text{capacity}$$

$$\text{Depreciation} = \frac{\text{investment}}{\text{years of depreciation}} = \frac{\text{investment}}{10}$$

$$\text{Taxable income} = \text{income} - \text{depreciation}$$

$$\text{Tax} = \text{tax rate} \times \text{taxable income}$$

Cash flow = taxable income + depreciation - tax

Present value_n = cash flow_n × (1+i)⁻ⁿ

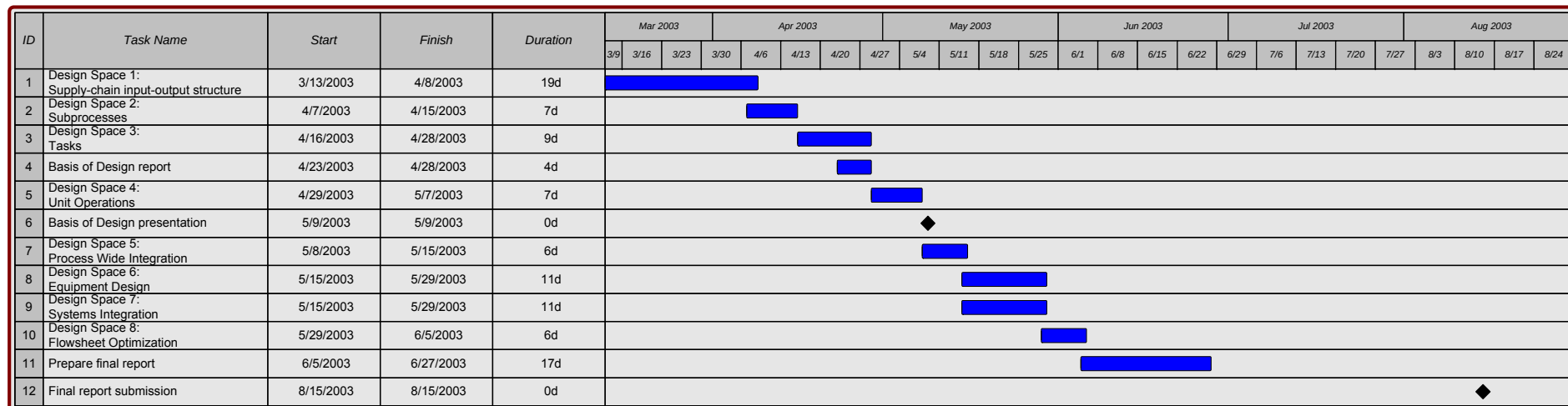
Net present value = $\sum_{i=-2}^n PV_i$

The maximum allowable investment is defined as the investment cost which will give a net present value of zero at the end of plant operation. At interest rate (i) of 10% and plant life of 15 years, the maximum allowable investment is found to be EUR 87M.

Reference: [2]

Appendix 18 Team Gantt chart

Figure A 18.1 Team Gantt chart



Appendix 19 Schedule of meetings

Table A 19.1 Schedule of meetings

Meeting Type	Week	To be present	Chairman	Secretary	Milestone	Note
IPM	15	Team, PLJS	Esteban	Xiaonan		
IPM	16	Team, PLJS	Edwin	Beatrix		
IPM	17	Team, PLJS	Xiaonan	Esteban	BOD	
IPM	18	Team, PLJS	Beatrix	Edwin		BOD Defence with PLJS
EPM	19	Team, PLJS, MvL, AN	Esteban	Xiaonan		BOD Defence
IPM	20	Team, PLJS, MvL, AN	Edwin	Beatrix		
IPM	21	Team, PLJS	Xiaonan	Esteban		
IPM	22	Team, PLJS	Beatrix	Xiaonan		
IPM	23	Team, PLJS	Esteban	Edwin		Downstream Processing AC, Beatrix & Xiaonan are not present
EPM	24	Team, PLJS, MvL, AN	Xiaonan	Beatrix		
IPM	26	Team, PLJS	Edwin	Esteban	Final report draft	Last IPM before holidays, design should be finished
IPM	30	XL, B, PLJS	Beatrix	Xiaonan	Corrected draft	
IPM	31	XL, B, PLJS	Xiaonan	Beatrix	Corrected draft	
EPM	32	Team, PLJS, MvL, AN	Edwin	Esteban	Corrected draft	
IPM	33	Team, PLJS	Beatrix	Xiaonan	Final report	

IPM: internal progress meeting, meeting of coach and team

EPM: external progress meeting, meeting of coach, client and team

BOD: basis of Design

AN: Atze Nijenhuis

PLJS: Pieter Swinkels

MvL: Mark van Loosdrecht

Appendix 20 Group rules

Description of Report

Group rules

Reference

DS 0

Version	Author	Date	Description
1.0	B	10/04/03	First draft

The members of CPD Group-3291 are committed to abide to the following rules.

Roles and responsibilities

1. The chairman and secretary roles will be taken in turn by group members.
2. The chairman and secretary are responsible for one full week.
3. The project leader role is taken by the chairman of the respective week.
4. The chairman is responsible to chair all the meetings in the respective week.
S/he will be responsible to make an agenda and distribute this internally.
5. The secretary is responsible for writing notes and minutes for all meetings in the respective week.
6. The project leader is responsible for keeping track of all actions agreed at meetings and to keep track of deadlines.

Meetings

1. External progress meetings shall be held at least once a month
2. Internal progress meetings shall be held once a week
3. Team meetings are held twice a week on Wednesday and Friday

Reports and agendas

1. Minutes of the meeting shall be internally distributed at the latest one day after the respective meeting at 17:00.
2. Agenda of the meeting shall be internally distributed at the latest two days before the respective meeting at 17:00
3. Reports, agendas and minutes are considered draft versions until they are edited by the editor.

4. Final version of the reports, agendas and minutes shall be distributed at the latest one day after the editor receives them at 17:00.
5. Reports shall be delivered to the coaches and client at the latest one day before the meeting at 17:00.
6. The members are committed to write as clearly as they can, using proper English as best as they can in order to save time in report editing.

Schedules and commitment

1. Members of the group are expected to commit at least 20 hours per week to the project.
2. The project has priority over other assignments.
3. The members are committed to finish all actions they have committed themselves to undertake.
4. The members of the group shall meet every Monday morning to check the number of hours available for each member in the respective week.
5. The group will only work in the weekend when it sees no other alternative to finish work in the working days.
6. The members agree to hold at least one social event in a month.

Description of Report

PIQUAR analysis report

Reference

PIQUAR-1

Version	Author	Date	Description
1.0	B, XL	10/04/04	First draft

Appendix 21 PIQUAR Analysis

A 21.01 The selection of PIQUAR criteria

The following table indicates the selection process of PIQUAR criteria, which will be used for the future design. At first, eighteen criteria are available as shown in the second column in Table A 21.3. The last two columns show the ten criteria which have been chosen from the original selection. The values of criteria (from 1-10) show their importance, which is based on the opinions from the group members and the supervisors, which are also shown in the table.

Two actions were done to finalize our quality criteria list. First we have to select which of the criteria to be included in the final list. It is only based on how many people select those criteria. The more people chose, the more important it is that the criteria should be included into the final range.

Second, we have to determine the position of criteria in the final list. It is shown in the last two columns of the table that the values are given by group members and P. Swinkels. If two criteria have the same estimated value, the order will be decided based on the opinion of the group, which is shown in the table as well.

The result of the selection is given in the following table with the order from the most important one to the least important.

Table A 21.1 PIQUAR Criteria

Criteria	
A	Product quality and quantity
B	Plant makes money
C	Low risk
D	Goal of the process must be clear in advance

Table A 21.1 PIQUAR Criteria

Criteria	
E	Sustainability
F	As few equipment as possible
G	Space, water and energy saving
H	Controllability
I	Design decisions are explicit and can be repeated
J	Safe startup and shutdown

A 21.02 Weighting Factor Calculation

To determine quantitatively the importance of each quality factor, we have to calculate the weighting factor for each criterion. The steps are as follows:

Step one:

The interaction factor among criteria is presented in a matrix which is presented in Table A 21.2.

Table A 21.2 Interaction factor between criteria

	A	B	C	D	E	F	G	H	I	J
A	1	1	3	5	5	6	7	7	8	9
B	1	1	4	3	5	5	7	6	7	9
C	1/3	1/4	1	1	4	4	5	5	5	5
D	1/5	1/3	1	1	3	5	5	5	5	7
E	1/5	1/5	1/4	1/3	1	1	1/3	3	3	4
F	1/6	1/5	1/4	1/5	1	1	1	2	3	7
G	1/7	1/7	1/5	1/5	3	1	1	3	1	3
H	1/7	1/6	1/5	1/5	1/3	1/2	1/3	1	3	5
I	1/8	1/7	1/5	1/5	1/3	1/3	1	1/3	1	3
J	1/9	1/9	1/5	1/7	1/4	1/7	1/3	1/5	1/3	1

The standard values are given to quantify the relative importance between two factors. The values are as follows:

- 9: C_i is extremely more important than C_j .
- 7: C_i is strongly more important than C_j .
- 5: C_i is essentially more important than C_j .
- 3: C_i is moderately more important than C_j .
- 1: C_i is equally important to C_j .

1/3: C_i is of moderate inferiority to C_j .

1/5: C_i is of essential inferiority to C_j .

1/7: C_i is of strong inferiority to C_j .

1/9: C_i is of extreme inferiority to C_j .

Step 2:

By using Matlab command $[v,d]=\text{eig}(M)$, the eigen value d is found as:

eigenvals (M) =

	0
0	11.077
1	0.174+2.924i
2	0.174-2.924i
3	-0.29+1.733i
4	-0.29-1.733i
5	-0.667
6	$8.15 \cdot 10^{-3} + 0.453i$
7	$8.15 \cdot 10^{-3} - 0.453i$
8	0.151
9	-0.345

Step three:

Column 9 is chosen as the suitable column for the weighting factor calculation. The weighting factors are calculated from the equation:

$$WF = I(i) / \text{SUM}(I) \quad i=1-10$$

Equation A 21.1

The determined weighting factor values are:

WT =

	0
0	0.22
1	0.193
2	0.138
3	0.138
4	0.083
5	0.083
6	0.028
7	0.083
8	0.028
9	$9.174 \cdot 10^{-3}$

Table A 21.3. PIQUAR selection criteria

GROUP	FACTOR	Peter's priority	Mark's priority	Li	Beatrix	Esteban	Edwin	Group's priority Value	participant	Total Value	participant
ECONOMIC	1 Plant makes money	1.00		1.00	1.00	1.00		1.00	3	1.00	5
	2 Low capital cost; high throughput						2.00		1		1
	3 Make aspects as maintainability, environmetn etc. financially quantiable						4.00		1		2
FUNCTION	4 Low risk	1.00		1.00	6.00	1.00		2.67	3	2.25	5
	5 Flexibility				3.00	2.00			2		2
	6 Product quality and quantity	1.00		1.00	1.00	1.00	1.00	1.00	4	1.00	6
	7 Sustainability	4.00		4.00		4.00	5.00	4.33	3	4.25	5
	8 Space, water and energy saving	4.00		4.00	7.00	4.00		5.00	3	4.75	5
OPERATION	9 Safe startup and shutdown	10.00		10.00	10.00	8.00	10.00	9.50	4	9.60	6
	10 Low maintenance										
	11 Short start-up period										
	12 Controllability	7.00		5.00	4.00	1.00	7.00	4.25	4	4.80	5
ORGANIZATIONAL	13 Client mast feel good	6.00			8.00		5.00		2		3
	14 Designed according to the process design methodology	7.00									1
	15 Design decisions are explicit and can be repeated	7.00		8.00		7.00	7.00	7.33	3	7.25	5
	16 Goal of the process must be clear in advance			2.00	9.00	1.00	5.00	4.25	4	4.25	5
	17 Process design should be seen as part of the entire decision making process										1
PHYSICAL	18 As few equipment as possible			7.00	5.00		2.00	4.67	3	4.67	3

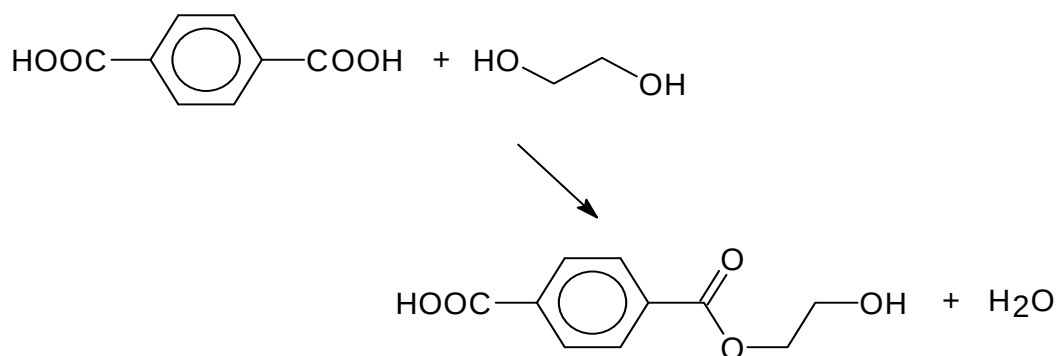
Appendix 1 - Polymerisation Mechanisms

Polymerisation reactions can be classified as either step-growth or chain growth reactions. Polymer physical properties can differ significantly depending on the polymerisation mechanism, and this is often due to the difference in molecular masses, i.e. polymers synthesised by chain growth polymerisation often have higher molecular masses.

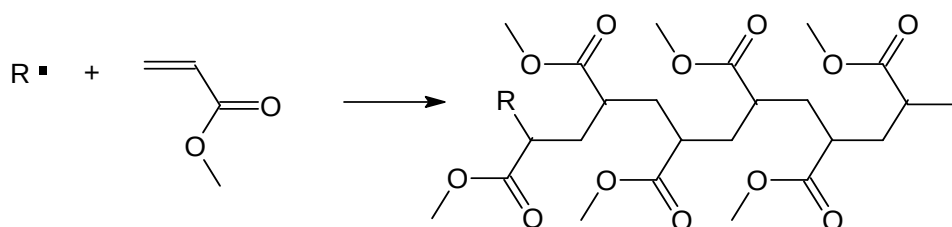
These two types of growth reaction differ basically in terms of the time scale of various reaction events, namely the size of polymer molecules increases at a relatively slow rate over a much longer period of time in step growth polymerisation. With step-growth polymerisation, the reactions that link monomers, oligomers and polymers involve the same reaction mechanism and any two molecular species (monomer, oligomer, or polymer) can be coupled. The growth of a polymer chain proceeds slowly from monomer to dimer, trimer, tetramer, and so on, until full-sized polymer molecules are formed at high monomer conversions. Polymer chains continue to grow from both ends throughout the polymerisation and, therefore, both chain lifetimes and polymerisation times are usually of the order of hours,

In chain growth polymerisation, polymer molecules generally grow to full size in a time-scale which is much smaller than the time required for high conversion of monomer to polymer. The lifetime of a growing polymer molecule may be less than a few seconds for a free-radical polymerisation, while a typical polymerisation time to obtain high monomer conversion may be several hours. Chain-growth polymerisation require an active center, which may be a free radical, cation, or anion. Once an active center is created, a polymer chain grows extremely rapidly, and when the growing chain is deactivated by a termination reaction, the polymer chain is dead and no longer takes part as a reactant. With free-radical polymerisation, however, the so-called dead polymer chain is not always truly dead, because under certain circumstances it may itself react with radicals. The active center may initiate the growth of many polymer chains.

The two mechanisms are depicted in the following figure.



(a)



(b)

Figure A1.1 Polymerisation mechanisms: (a) step growth polymerisation (PET synthesis), (b) chain-growth polymerisation (Polymethacrylate synthesis)

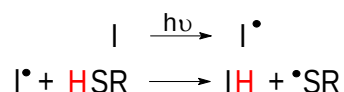
The two mechanisms have their advantages and disadvantages which are outlined in the following table.

Table 1.1 Advantages and disadvantages of step growth and chain growth polymerisation

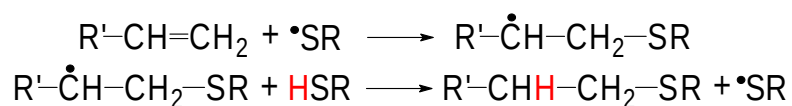
Step growth polymerisation	Chain growth polymerisation
• High strength and toughness	• Fast polymerisation
• Low molecular weight	• Exothermic • High molecular weight • Lower mechanical properties
• Energy intensive • Slow polymerisation • Stoichiometric	

The challenge lies in the combination of the advantages of the two mechanisms, i.e. we should find a molecule which can be polymerised in a combined mechanism. One of the molecules which can be polymerised in a combined mechanism is the unsaturated thioic acid. The molecule has two active groups and can therefore be polymerised in a radical step polymerisation which is presented in the figure below.

Initiation



Propagation



Termination: radical termination (no oxygen termination)

Figure A1.2 Radical step polymerisation of unsaturated thioic acid