# 1 Appendices

## 1.1 Appendix A – Details of unit operations

### 1.1.1 Centrifuge

The initial feedstock of raw POME that is transported to the plant is in a state that is not optimised for microwave process heating, which is primarily because of POME's high-water percentage of around 95%. Water is a highly specific heat capacity material and requires a more significant amount of energy to heat than the other components present in the mixture. It is also a polar, non-reactive material that will absorb some of the microwave radiation instead of the actual reaction materials. In conjunction with the large initial volume of water to other components, both factors result in a high energy requirement to heat the reaction mixture to the desired temperature of 150 °C.

It is, therefore, necessary to first process POME before subjecting it to the esterification reaction. The POME is passed through some form of a solid separator to remove water from the feedstock. In the case of the prior experimental work, the POME was first processed within a centrifuge. While this is still applicable on larger scales, there is the potential to use a hydrocyclone. A hydrocyclone offers separate solids using centrifugal principles, but the produced separation is generally coarse (Wilson and Poole, 2009). As the initial solids, separation is a significant critical step in POME to biodiesel; the potential to reduce this separation's required energy demands could impart substantial operational cost savings. Alternatively, a system could be set up first to remove the bulk of water with a hydrocyclone and then subsequently process the remainder in a centrifuge, thereby reducing the flow rate through the centrifuge and consequently lowering its costs.

This separation step is significant in taking a green approach to biodiesel production because it simultaneously purifies one of the reactant streams whilst removing the polluting components from the outputted water. Therefore, during the actual design of this unit operation, the reactant stream should not be optimised at the determent of the produced water quality. Additionally, it will be necessary to identify whether further water treatment is required and how this 'waste' water will be used, be it human consumption, cultivation, or discharged.

### 1.1.2 Mixer

After the plant matter and contained oils have been separated from the POME solution, the other necessary materials must be combined. Some mixing equipment will blend the two reactant streams, catalyst, solvent, and any proposed recycle streams into a single flow fed to the microwave reactor section. While it is possible to have reaction materials introduced directly into the reactor and different heights or lengths, a mixer's inclusion has been made to simplify the design. Determining these different feed points would require a more detailed individual reactor design process.

### 1.1.3 Microwave reactor

Once all of the required materials have been sufficiently mixed into a single stream and enter the reaction vessel, the contents must be brought to the conditions present during the experimental work to provide a good chance of reproducing the rapid reaction and high conversion. There is the issue of transferring the reaction method from the batch experimental work to continuous industrial processing. The reactor will be heated by a microwave producing unit and likely fitted with a back-pressure regulator or control valve to ensure that the pressure is sufficiently high and mimics a pressurised sealed situation vessel.

If a plug flow reactor is used, the potential to have a system where only a small section of the reactor length is subject to heating with the rest of the vessel is sufficiently insulated to retain the necessary temperature for the reaction (Doraiswamy, 2001). This design can overcome penetration depth issues. The microwaves can rapidly and uniformly heat the fluid passing through the microwave section. The reactors radial direction is usually significantly smaller than the total length, reducing the power required for heating. However, this would need confirmation that the reaction is not dependent on direct microwave interaction instead of quickly achieving high temperatures and pressures.

PFRs are also preferred to reduce the possibility of side reactions due to the assumption of no axial mixing or backflow (Lipták, 2006). Once the reaction occurs, products do not contact fresh reactants and potentially further react to unwanted compounds. This method is preferred as minimising impurities' potential in the final biodiesel product is vital to reduce the likelihood of undesirable emissions. The projects aim for a green approach. In the case of photobioreactors, which are dependent on light penetration, tubular designs are seen to have an enhanced performance to that of CSTR's (Pandey et al., 2011). The light issues are similar to microwaves. It would be likely that tubular designs offer a similar advantage in microwave reactors.

For this paper's work, including the Aspen HYSYS software simulations, a plug flow reactor (PFR) was chosen. The initially retrieved reaction data was from a batch reactor setup, which effectively behaves the same as a PFR (if perfectly mixed), with material moving through time instead of space (Towler and Sinnott, 2013). Another minor reason is that a PFR unit better represents the lab-scale experiments with a single input and output with no vapour stream due to being batch reactions.

Single tube reactors can have substantial lengths, with more than 1000 m being used in the industry. To compensate for the significant size, they are often coiled or trombone-shaped to safe crucial site ground area (Couper et al., 2012).

### 1.1.4 Decanter (Gravity settler)

After the reaction mixture has remained in the reactor for the desired residence time, it exits the reactor section comprised of two liquid phases:

- light liquid phase – containing primarily the heptane solvent and the methyl palmitate product
- heavy liquid phase – containing mainly water, methanol, and the sulphuric acid catalyst

There are several ways that the methyl palmitate product could be extracted from the collective material stream using different separator units. However, due to these two phases that naturally settle into distinct layers, a gravity settling tank or decanter will be used. Additionally, this separation method replicates how the experimental method extracts the biodiesel from the rest of the materials present. It is the key reason why heptane is added to the reaction mixture. The heptane provides good organic-aqueous phase separation and is widely used across several solvent extraction chemical processes (Ash and Ash, 2018).

As heptane is not directly used in the reaction mechanism, there is the potential for modification to the design by introducing the heptane after the reactor unit to reduce the reactor's required size and the energy necessary to heat it by minimising the volumetric flow of material in the reactor. However, as heptane is quite a costly material concerning the other feedstocks, it will be best to recycle it during the process. Furthermore, this heptane will not be pure and will likely contain valuable unreacted reactants. Thus it would make the most sense to feed the heptane before the reactor so that these reactants can be converted whilst minimising the required quantity of heptane.

### 1.1.5 Separator

During the lab-scale experiments, the final stage was the gravity settling process, with the top layer being analysed for its biodiesel content. Finishing the process is appropriate for research purposes to examine the technical feasibility of the reaction process. However, it is not an acceptable state to leave a final biodiesel product, as it contains significant quantities of other substances resulting in below standard commercial biodiesel. Therefore, an additional separation step must be implemented after the gravity settler to purify the product.

As the light liquid layer contains heptane largely as its unwanted 'impurity', it is possible to use some form of separation based on differing volatilities. Inspecting the relative volatilities in **Error! Reference source not found.** shows that a split to separate heptane and methyl palmitate is achievable as the volatilities are significantly different. Furthermore, the same split can separate two of the other potential impurities, water and methanol, from the final biodiesel product. Additionally, while this separation would appear to leave sulphuric acid and palmitic acid in the final mixture; however, nearly all of the sulphuric acid exits the earlier gravity settler in the heavy liquid reaction is around 100% conversion. Hence, the quantity of palmitic acid present will be small.

K-Value is said to be the measure of a components tendency to vaporise, with values above 1, resulting in a vapour tendency and values below 1, resulting in a liquid tendency (Coker, 2007). Although this definition would suggest that the split would occur between n-heptane and methanol, K-Value is considered a composition and temperature function. Therefore, the temperature of the separator can be adjusted to modify the splitting point as desired.

*Table A1 – Light Liquid volatility data (values obtained from Aspen HYSYS stream worksheet and databank)*

| Component | K-Value | Normal boiling point |
|---|---|---|
| Methanol | 3.764 | 64.65 |
| n-Heptane | 0.9848 | 98.43 |
| Water | 0.8292 | 100.0 |
| Methyl palmitate | $1.712 \times 10^{-6}$ | 326.1 |
| Sulphuric acid | $9.269 \times 10^{-7}$ | 326.9 |
| Palmitic acid | $2.149 \times 10^{-7}$ | 351.0 |

In this work, it was found that a simple flash separation unit was sufficient to provide an adequate purification step and produce biodiesel of commercial standard. In actuality, it may be discovered that a distillation column is a preferable unit operation, as a much more specific design can be utilised with the possibility of multiple vapour outlets for different components. However, a flash separator was chosen for two main reasons: firstly, it allowed for a more straightforward simulation setup without the necessity to optimise and establish a working distillation unit; Secondly, distillation columns usually incur a higher cost than that of flash separators due to the inclusion of vessel internal sieve trays, and minimising the cost of significant unit operations leads to a greater likelihood of the process's feasibility.

## 1.2 Appendix B – Details of simulated unit operations

### 1.2.1 Centrifuge – Component splitter

A component splitter was implemented to model the first unit operation, the centrifuge. Aspen HYSYS's help function indicates that a component splitter is to be used to approximate non-standard separation processes that are not handled elsewhere in the software. Although a centrifuge is a typical separation process, there was difficulty translating the physical process into the simulation environment. A hydrocylone was unable to handle a stream containing multiple liquids. A simple solids separator failed to specify a split that reflected how the palmitic acid primarily remains with or is contained within the plant matter solids.

### 1.2.2 Microwave reactor – Plug flow reactor

In the experimental studies, the reaction was a batch process undertaken within a sealed vessel. The pressure is not directly set but is a function of the specified temperature, determined using the Clausius Clapeyron relation (Fink, 2015). However, for the scale-up process simulation using a continuous configuration, the temperature and pressure can be adjusted. Therefore, the vessel temperature was set at 150°C for the initial simulations, reflecting the optimum conditions determined experimentally, using a constant heat distribution along the length of the PFR. Whereas the pressure was determined using an iterative testing approach in the Aspen HYSYS simulation environment, using the experimental pressure values as a starting basis. A pressure of 15 bar was found to result in sufficient conversion for the given reactor size and other process parameters during the primary simulation phase. While conducting this pressure determination, both reaction pressure and reactor volume (via residence time) affected the reactor's conversion. Therefore, to determine the most optimum design in terms of the total cost, a study would need to be conducted to identify the best combination of pressure and reactor volume.

The diameter of the tubular/plug flow reactor was set at an arbitrary value of 0.25 m. It was assumed that a pipe section could be made to more or less any dimensions because pipes and tubes are known to be available to an extensive number of different specifications (Nesbitt, 2007). During primary simulations, before optimisation attempts, the remaining reactor dimensions were as follows:

| | |
|---|---|
| Total Volume | 1.000 $m^3$ |
| Number of Tubes: | 1 |
| Wall Thickness: | 0.005 m |
| Void Fraction: | 1.000 |

### 1.2.3 Decanter (Gravity settler) – 3 Phase separator

A 3-phase separator was used for the simulation of the decanter unit operation. Although there was no vapour in the inlet stream, a vapour outlet stream was included to allow the simulation to converge. In reality, this would allow any build-up of entrained gases to merge at the top of the separator tank and be safely discharged. No specifications were made for this vessel, as the separation was based upon the inlet stream composition and the property package used. The decanter's equilibrium was significantly affected by the ratio of heptane in the feed stream. An increase in heptane leads to a better separation of the two phases. However, using an excessive quantity of heptane led to several issues. One is that of significantly increased costs, as heptane is relatively expensive to the other primary feedstocks; another point is the difficulty in removing this heptane during the subsequent product purification step.

A stream cutter was used before the decanter inlet to transform the property package from the NTRL basis to the UNIQUAC basis. It was found from testing that both property packages appeared to the same effect on the simulation of the succeeding flash separator unit operation. Therefore, no stream cutter was used to transform the stream back to the NTRL basis.

This 3-phase separator is the first unit operation that produces a stream that does not directly follow on to make the final biodiesel product, the bottom-heavy liquid stream. For the initial simulation phase, this stream was left as a 'waste' stream to minimise the overall simulation process's complexity. Nevertheless, it should be mentioned that in reality, this stream which comprises both the catalyst and some of the unreacted raw materials, would almost surely be reused in one fashion or another.

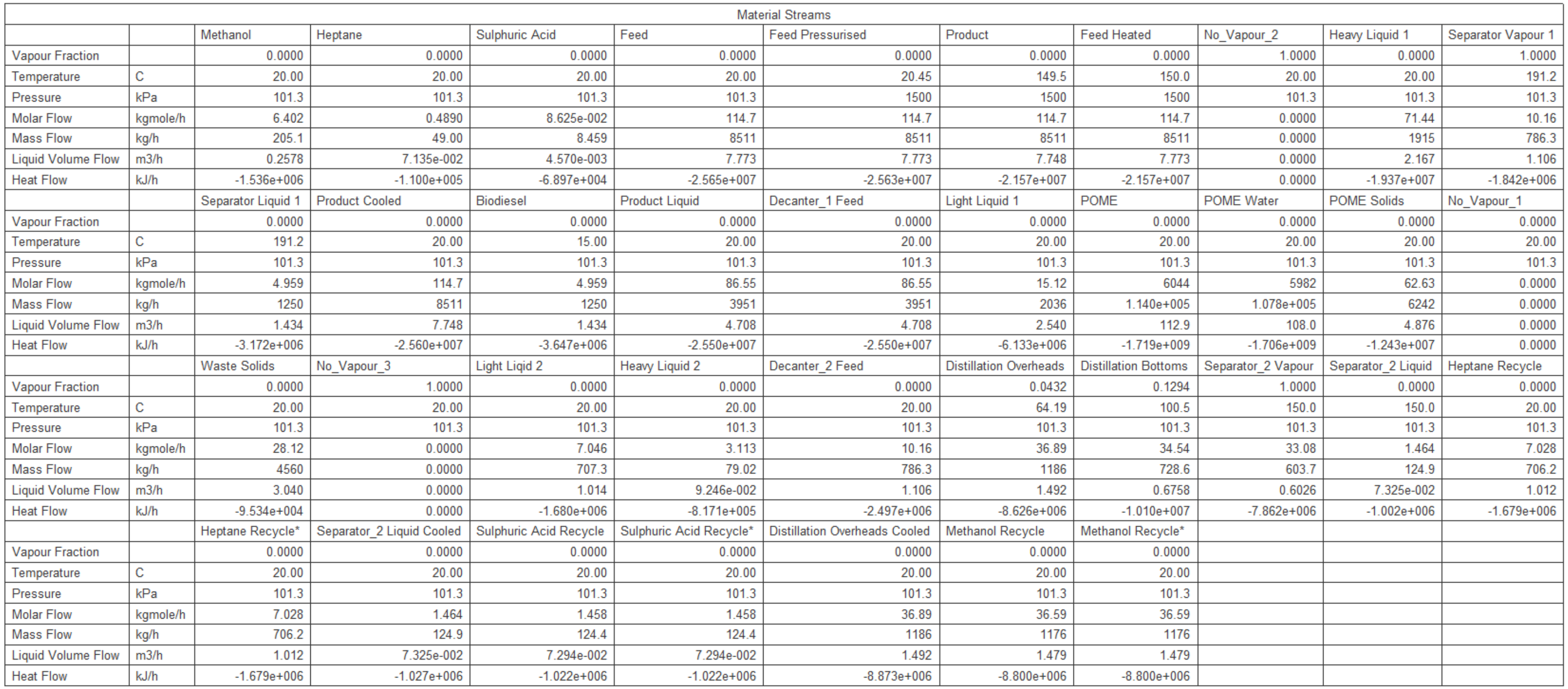
### 1.2.4 Separator – Flash separator

Like the previous 3-phase separator, the flash separator was not specified through vessel design and instead set up using the default HYSYS setting. This operation simulated the separation of the vapour and liquid phases of the inlet stream. The degree of separation was adjusted by implementing an energy stream to increase the vessel temperature and derive more volatile components into the vapour phase.

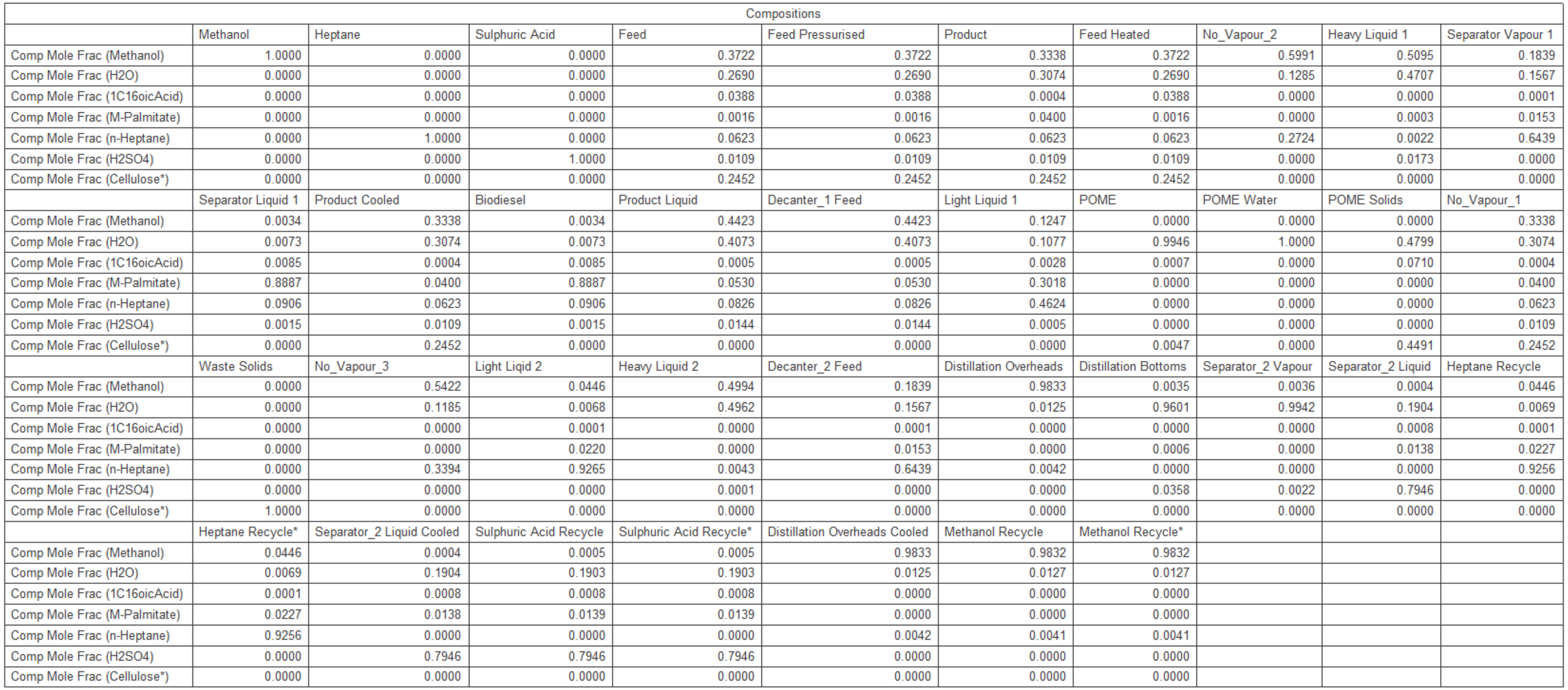
Another parallel to the previous unit operation was that this separator produced a 'waste' stream that contained valuable material components, importantly a significant quantity of the expensive heptane solvent. Therefore, this stream would also likely be recycled to a previous unit operation to reduce the purchased amount of fresh heptane.

Initially, the heptane quantity in the feed stream was based on the experimental work ratio to give a good preliminary estimate for the heptane ratio. Once the overall simulation produced the biodiesel product, tweaks were made to this quantity using a combination of iterative trials and the Aspen HYSYS 'adjust' logic operation to improve the final product to commercial standards. It was found that a reduced quantity of heptane could be used, which resulted in an easier final separation and, therefore, an improved biodiesel quality. The two main parameters for verifying its quality were ester content mass percentage of a minimum of 96.5% and a density range at 15°C of 860-900 kg/m$^3$. These values were based upon those outlined by the European Standards, EN 14214:2008 – "Automotive fuels — Fatty acid methyl esters (FAME) for diesel engines — Requirements and test methods" (BSI, 2010).

## 1.3 Appendix C – Simulation stream and compositions



| Material Streams | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Methanol | Heptane | Sulphuric Acid | Feed | Feed Pressurised | Product | Feed Heated | No_Vapour_2 | Heavy Liquid 1 | Separator Vapour 1 |
| Vapour Fraction | | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 1.0000 | 0.0000 | 1.0000 |
| Temperature | C | 20.00 | 20.00 | 20.00 | 20.00 | 20.45 | 149.5 | 150.0 | 20.00 | 20.00 | 191.2 |
| Pressure | kPa | 101.3 | 101.3 | 101.3 | 101.3 | 1500 | 1500 | 1500 | 101.3 | 101.3 | 101.3 |
| Molar Flow | kgmole/h | 6.402 | 0.4890 | 8.625e-002 | 114.7 | 114.7 | 114.7 | 114.7 | 0.0000 | 71.44 | 10.16 |
| Mass Flow | kg/h | 205.1 | 49.00 | 8.459 | 8511 | 8511 | 8511 | 8511 | 0.0000 | 1915 | 786.3 |
| Liquid Volume Flow | m3/h | 0.2578 | 7.135e-002 | 4.570e-003 | 7.773 | 7.773 | 7.748 | 7.773 | 0.0000 | 2.167 | 1.106 |
| Heat Flow | kJ/h | -1.536e+006 | -1.100e+005 | -6.897e+004 | -2.565e+007 | -2.563e+007 | -2.157e+007 | -2.157e+007 | 0.0000 | -1.937e+007 | -1.842e+006 |
| | | Separator Liquid 1 | Product Cooled | Biodiesel | Product Liquid | Decanter_1 Feed | Light Liquid 1 | POME | POME Water | POME Solids | No_Vapour_1 |
| Vapour Fraction | | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| Temperature | C | 191.2 | 20.00 | 15.00 | 20.00 | 20.00 | 20.00 | 20.00 | 20.00 | 20.00 | 20.00 |
| Pressure | kPa | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 |
| Molar Flow | kgmole/h | 4.959 | 114.7 | 4.959 | 86.55 | 86.55 | 15.12 | 6044 | 5982 | 62.63 | 0.0000 |
| Mass Flow | kg/h | 1250 | 8511 | 1250 | 3951 | 3951 | 2036 | 1.140e+005 | 1.078e+005 | 6242 | 0.0000 |
| Liquid Volume Flow | m3/h | 1.434 | 7.748 | 1.434 | 4.708 | 4.708 | 2.540 | 112.9 | 108.0 | 4.876 | 0.0000 |
| Heat Flow | kJ/h | -3.172e+006 | -2.560e+007 | -3.647e+006 | -2.550e+007 | -2.550e+007 | -6.133e+006 | -1.719e+009 | -1.706e+009 | -1.243e+007 | 0.0000 |
| | | Waste Solids | No_Vapour_3 | Light Liqid 2 | Heavy Liquid 2 | Decanter_2 Feed | Distillation Overheads | Distillation Bottoms | Separator_2 Vapour | Separator_2 Liquid | Heptane Recycle |
| Vapour Fraction | | 0.0000 | 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0432 | 0.1294 | 1.0000 | 0.0000 | 0.0000 |
| Temperature | C | 20.00 | 20.00 | 20.00 | 20.00 | 20.00 | 64.19 | 100.5 | 150.0 | 150.0 | 20.00 |
| Pressure | kPa | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 |
| Molar Flow | kgmole/h | 28.12 | 0.0000 | 7.046 | 3.113 | 10.16 | 36.89 | 34.54 | 33.08 | 1.464 | 7.028 |
| Mass Flow | kg/h | 4560 | 0.0000 | 707.3 | 79.02 | 786.3 | 1186 | 728.6 | 603.7 | 124.9 | 706.2 |
| Liquid Volume Flow | m3/h | 3.040 | 0.0000 | 1.014 | 9.246e-002 | 1.106 | 1.492 | 0.6758 | 0.6026 | 7.325e-002 | 1.012 |
| Heat Flow | kJ/h | -9.534e+004 | 0.0000 | -1.680e+006 | -8.171e+005 | -2.497e+006 | -8.626e+006 | -1.010e+007 | -7.862e+006 | -1.002e+006 | -1.679e+006 |
| | | Heptane Recycle* | Separator_2 Liquid Cooled | Sulphuric Acid Recycle | Sulphuric Acid Recycle* | Distillation Overheads Cooled | Methanol Recycle | Methanol Recycle* | | | |
| Vapour Fraction | | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | | | |
| Temperature | C | 20.00 | 20.00 | 20.00 | 20.00 | 20.00 | 20.00 | 20.00 | | | |
| Pressure | kPa | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 | 101.3 | | | |
| Molar Flow | kgmole/h | 7.028 | 1.464 | 1.458 | 1.458 | 36.89 | 36.59 | 36.59 | | | |
| Mass Flow | kg/h | 706.2 | 124.9 | 124.4 | 124.4 | 1186 | 1176 | 1176 | | | |
| Liquid Volume Flow | m3/h | 1.012 | 7.325e-002 | 7.294e-002 | 7.294e-002 | 1.492 | 1.479 | 1.479 | | | |
| Heat Flow | kJ/h | -1.679e+006 | -1.027e+006 | -1.022e+006 | -1.022e+006 | -8.873e+006 | -8.800e+006 | -8.800e+006 | | | |



| | Compositions | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Methanol | Heptane | Sulphuric Acid | Feed | Feed Pressurised | Product | Feed Heated | No_Vapour_2 | Heavy Liquid 1 | Separator Vapour 1 |
| Comp Mole Frac (Methanol) | 1.0000 | 0.0000 | 0.0000 | 0.3722 | 0.3722 | 0.3338 | 0.3722 | 0.5991 | 0.5095 | 0.1839 |
| Comp Mole Frac (H2O) | 0.0000 | 0.0000 | 0.0000 | 0.2690 | 0.2690 | 0.3074 | 0.2690 | 0.1285 | 0.4707 | 0.1567 |
| Comp Mole Frac (1C16oicAcid) | 0.0000 | 0.0000 | 0.0000 | 0.0388 | 0.0388 | 0.0004 | 0.0388 | 0.0000 | 0.0000 | 0.0001 |
| Comp Mole Frac (M-Palmitate) | 0.0000 | 0.0000 | 0.0000 | 0.0016 | 0.0016 | 0.0400 | 0.0016 | 0.0000 | 0.0003 | 0.0153 |
| Comp Mole Frac (n-Heptane) | 0.0000 | 1.0000 | 0.0000 | 0.0623 | 0.0623 | 0.0623 | 0.0623 | 0.2724 | 0.0022 | 0.6439 |
| Comp Mole Frac (H2SO4) | 0.0000 | 0.0000 | 1.0000 | 0.0109 | 0.0109 | 0.0109 | 0.0109 | 0.0000 | 0.0173 | 0.0000 |
| Comp Mole Frac (Cellulose*) | 0.0000 | 0.0000 | 0.0000 | 0.2452 | 0.2452 | 0.2452 | 0.2452 | 0.0000 | 0.0000 | 0.0000 |
| | Separator Liquid 1 | Product Cooled | Biodiesel | Product Liquid | Decanter_1 Feed | Light Liquid 1 | POME | POME Water | POME Solids | No_Vapour_1 |
| Comp Mole Frac (Methanol) | 0.0034 | 0.3338 | 0.0034 | 0.4423 | 0.4423 | 0.1247 | 0.0000 | 0.0000 | 0.0000 | 0.3338 |
| Comp Mole Frac (H2O) | 0.0073 | 0.3074 | 0.0073 | 0.4073 | 0.4073 | 0.1077 | 0.9946 | 1.0000 | 0.4799 | 0.3074 |
| Comp Mole Frac (1C16oicAcid) | 0.0085 | 0.0004 | 0.0085 | 0.0005 | 0.0005 | 0.0028 | 0.0007 | 0.0000 | 0.0710 | 0.0004 |
| Comp Mole Frac (M-Palmitate) | 0.8887 | 0.0400 | 0.8887 | 0.0530 | 0.0530 | 0.3018 | 0.0000 | 0.0000 | 0.0000 | 0.0400 |
| Comp Mole Frac (n-Heptane) | 0.0906 | 0.0623 | 0.0906 | 0.0826 | 0.0826 | 0.4624 | 0.0000 | 0.0000 | 0.0000 | 0.0623 |
| Comp Mole Frac (H2SO4) | 0.0015 | 0.0109 | 0.0015 | 0.0144 | 0.0144 | 0.0005 | 0.0000 | 0.0000 | 0.0000 | 0.0109 |
| Comp Mole Frac (Cellulose*) | 0.0000 | 0.2452 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0047 | 0.0000 | 0.4491 | 0.2452 |
| | Waste Solids | No_Vapour_3 | Light Liqid 2 | Heavy Liquid 2 | Decanter_2 Feed | Distillation Overheads | Distillation Bottoms | Separator_2 Vapour | Separator_2 Liquid | Heptane Recycle |
| Comp Mole Frac (Methanol) | 0.0000 | 0.5422 | 0.0446 | 0.4994 | 0.1839 | 0.9833 | 0.0035 | 0.0036 | 0.0004 | 0.0446 |
| Comp Mole Frac (H2O) | 0.0000 | 0.1185 | 0.0068 | 0.4962 | 0.1567 | 0.0125 | 0.9601 | 0.9942 | 0.1904 | 0.0069 |
| Comp Mole Frac (1C16oicAcid) | 0.0000 | 0.0000 | 0.0001 | 0.0000 | 0.0001 | 0.0000 | 0.0000 | 0.0000 | 0.0008 | 0.0001 |
| Comp Mole Frac (M-Palmitate) | 0.0000 | 0.0000 | 0.0220 | 0.0000 | 0.0153 | 0.0000 | 0.0006 | 0.0000 | 0.0138 | 0.0227 |
| Comp Mole Frac (n-Heptane) | 0.0000 | 0.3394 | 0.9265 | 0.0043 | 0.6439 | 0.0042 | 0.0000 | 0.0000 | 0.0000 | 0.9256 |
| Comp Mole Frac (H2SO4) | 0.0000 | 0.0000 | 0.0000 | 0.0001 | 0.0000 | 0.0000 | 0.0358 | 0.0022 | 0.7946 | 0.0000 |
| Comp Mole Frac (Cellulose*) | 1.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| | Heptane Recycle* | Separator_2 Liquid Cooled | Sulphuric Acid Recycle | Sulphuric Acid Recycle* | Distillation Overheads Cooled | Methanol Recycle | Methanol Recycle* | | | |
| Comp Mole Frac (Methanol) | 0.0446 | 0.0004 | 0.0005 | 0.0005 | 0.9833 | 0.9832 | 0.9832 | | | |
| Comp Mole Frac (H2O) | 0.0069 | 0.1904 | 0.1903 | 0.1903 | 0.0125 | 0.0127 | 0.0127 | | | |
| Comp Mole Frac (1C16oicAcid) | 0.0001 | 0.0008 | 0.0008 | 0.0008 | 0.0000 | 0.0000 | 0.0000 | | | |
| Comp Mole Frac (M-Palmitate) | 0.0227 | 0.0138 | 0.0139 | 0.0139 | 0.0000 | 0.0000 | 0.0000 | | | |
| Comp Mole Frac (n-Heptane) | 0.9256 | 0.0000 | 0.0000 | 0.0000 | 0.0042 | 0.0041 | 0.0041 | | | |
| Comp Mole Frac (H2SO4) | 0.0000 | 0.7946 | 0.7946 | 0.7946 | 0.0000 | 0.0000 | 0.0000 | | | |
| Comp Mole Frac (Cellulose*) | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | | | |

## 1.4 Appendix D – Details of economic analysis using cost estimating techniques

### 1.4.1 Fixed capital investment

The fixed capital investment of a chemical plant is comprised of four key components:

- Inside battery limits (ISBL) – process equipment, piping, building etc.
- Outside battery limits (OSBL) – power generation, water treatment, offices etc.
- Engineering Costs – design, procurement, construction etc.
- Contingency – a safety net to account for errors in budgeting and unexpected issues.

These components have been estimated and totalled to estimate the fixed capital investment required for this biodiesel production route.

### 1.4.2 ISBL Costs

Process III of Zhang et al. (2003) was used as an initial basis for the order of magnitude estimate of the microwave-assisted process, as it provides the capital cost estimate of biodiesel from acid catalysed waste material, which was found to be a suitable comparison to the process of this project.

The estimate was made using the cost curve relationship detailed by Towler and Sinnott (2013) for ISBL capital costs and then calculating other expenses as a factor of the ISBL costs. Although Towler and Sinnott (2013) describe an alternate method using cost correlation data that does not require a similar plant's details, the chosen capacity fell outside the biodiesel plant's bounds.

$$C_2 = C_1 \left(\frac{S_2}{S_1}\right)^n \qquad (1)$$

| | |
|---|---|
| Process exponent: | $n = 0.6$ |
| Zhang et al. (2003): | $S_1 = 8000$ tonne/year |
| | $C_1 = \$0.81\times10^6$ |
| This work: | $S_2 = 10000$ tonne/year, |
| | $C_2 = \$0.93\times10^6$ |

### 1.4.3 OSBL costs

OSBL costs will be taken as 40% of the ISBL expenses as recommended by Towler and Sinnott (2013) as specific site details are not known due to the project's theoretical nature.

### 1.4.4 Engineering costs

Engineering costs will be taken as 30% of the ISBL plus OSBL costs as suggested as a thumb rule for smaller projects (Towler and Sinnott, 2013).

### 1.4.5 Contingency charges

Contingency charges will also be assumed as 50% of ISBL plus OSBL (Towler and Sinnott, 2013), considering that while the technology performs well on the lab scale, there may potentially be unforeseen issues at industrial scales that will require modification through investment.

## 1.5 Working capital

The plant's working capital will be taken as a factor of the fixed capital for this class 5 estimate but will be estimated in more detail in future cost evaluations. A suggested typical figure for working capital is 15% of fixed capital costs for a general chemical plant (Towler and Sinnott, 2013). It is what has been used for this early stage of cost estimation.

## 1.6 Appendix E – Details of Aspen HYSYS economic assessment

### 1.6.1 Economic scenario

As outlined previously, a plant capacity of 10,000 tonnes was used based on other biodiesel production plants' economic assessment in literature. It is a value that is realistic based on the relatively available amount of POME waste in the top producing palm oil countries.

A chemical plant's operating life suggests roughly 10 to 20 years (Sinnott and Towler, 2009). These simulations have been taken like 20 years to reflect the project's 'green' ideals, which a long-lasting plant would better accomplish. Because the initial construction resources would be used more efficiently, the plant would be less wasteful. It is also recommended that a plant takes approximately 1-3 years to reach a full production rate (Sinnott and Towler, 2009). Therefore the plant start-up duration has been set to 3 years to provide a more conservative estimate. Many construction projects can easily overrun their initially planned periods, especially in a novel technological process. Many plant cost estimates use a value for operational hours of 8000. Similarly, the default HYSYS economic settings share this value. Consequently, 8000 operational hours per year has been used for this simulation process.

Although the plant location has a reasonably significant effect on the plants, economic performance, the available settings for location in Aspen HYSYS are limited by the selected cost template. The default and only cost template provided with a basic installation of HYSYS it that of North America and is the template that has been used for these estimates. Additionally, the plant location will not affect comparisons as each economic assessment has been conducted with the same template. Furthermore, the costing currency has been taken on a US dollar basis because of the location. Many standards, feedstock prices, and other literature sources used this basis for comparison.

### 1.6.2 Stream costs

Most feedstock prices can fluctuate considerably over time, with accurate records of material price data considered extremely valuable to engineering, procurement, and construction companies (Towler and Sinnott, 2013). As reliable up to date cost information from such companies is difficult to source, online chemical market services have been used to obtain the bulk of the feedstock cost information, presented in Table E1.

*Table E1– Stream economic cost data*

| Stream | Cost (US$/Tonne) | Source |
|---|---|---|
| POME | 0 | Assumed due to its consideration as a waste material |
| Methanol | 370 | Methanex Express (2019) |
| Heptane | 2000 | Alibaba (2019a), PharmaCompass (2019) |
| Sulphuric acid | 200 | Alibaba (2019b), Hatfield (2018) |
| Biodiesel | 900 | U. S. Department of Energy (2019) |

### 1.6.3 Utility costs

The utility type of individual energy streams was based upon previous engineering experience of similar unit operations to the units' conditions, such as temperature and pressure. Any errors in initially designated utility types were identified and corrected through Aspen Process Economic Analyser.

### 1.6.4 Equipment costing

Here is a breakdown of the equipment costs for the modified simulation design (Table E2), where the component type was selected as the default recommended by Aspen HYSYS, except in the case of a few specific units. These were the Solids Removal and Centrifuge, which were selected as disk centrifuges, as they are commonly used for process streams with 1-15% solid matter (Towler and Sinnott, 2013). Additionally, it should be noted that the mixer unit's cost was not included as a selection of a component type requires the determination of the mixers dimensions. Therefore, instead, it was assumed that a static mixer was used and incurred negligible cost. Static mixers have achieved widespread use for low viscosity fluid mixing for blending, liquid-liquid, and even gas-liquid dispersions (Chhabra and Shankar, 2018). Their main advantage is the lack of moving parts, keeping operating and capital costs relatively low (Reay, Ramshaw and Harvey, 2008).

*Table E2 – Modified flowsheet equipment cost summary*

| Flowsheet Name | Component Type | Equipment Cost (USD) | Installed Cost (USD) |
|---|---|---|---|
| Separator_1 | DVT CYLINDER | 15700 | 118400 |
| Cooler_2 | DHE TEMA EXCH | 11100 | 108900 |
| Cooler_1 | DHE TEMA EXCH | 30800 | 195900 |
| Pump | DCP CENTRIF | 16700 | 43700 |
| Cooler_5 | DHE TEMA EXCH | 10900 | 84500 |
| Cooler_3 | DHE TEMA EXCH | 11000 | 89200 |
| Centrifuge | ECT DISK | 840800 | $1.05 \times 10^6$ |
| Heater | DHE TEMA EXCH | 40200 | 136800 |
| Cooler_4 | DHE TEMA EXCH | 8000 | 57500 |
| Separator_2 | DVT CYLINDER | 15700 | 117000 |
| Decanter_1 | DVT CYLINDER | 15700 | 108500 |
| Decanter_2 | DVT CYLINDER | 15700 | 108500 |
| Solids Removal | ECT DISK | 210200 | 262100 |
| Microwave Reactor | DHT JACKETED | 109100 | 214300 |
| Condenser | DHE TEMA EXCH | 12800 | 69100 |
| Reboiler | DHE TEMA EXCH | 64500 | 178600 |
| Main Tower | DTW TOWER | 58900 | 202700 |

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