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PROJECT TITLE:

MODELLING OF BIODIESEL PRODUCTION WITH SIMULINK
Conventional Plug Flow Reactor
Followed by Separation and Purification

By

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Abstract

A model for biodiesel production by plug flow reactor has been programmed and evaluated. The main parts of the process being modelled in this study are the reactor, the separation of glycerol and biodiesel in a centrifuge, and purification of product stream by removal of methanol. The centrifuge will for simplicity be modelled as a settling tank and split. In the reactor the kinetics are taken from publications and for now the operating conditions are taken as the optimal values given by articles. The process was reduced to these three main step in four units as a start to make sure the most important part of the process was covered first. The purification units will be assumed binary for simplicity and intermediate products are neglected.

The model has been evaluated for disturbances in the amount and composition of the feed flow for all units and complete plant model. The reactor unit by CSTRs in series follows the expected pattern from the reaction stoichiometry and kinetics literature. The settling tank for buffer effect and splitting of phases, smooth out the inlet disturbances for the downstream equipment where the product streams are purified by removal of methanol. By control of the different units, the required purification for selling the product was achieved through expected model response.

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1 Nomenclature

Symbol	Meaning
α	Relative volatility
β	Coefficient
Δu	Change in input
Δy	Change in output
γ	Activity coefficient
τ_1	Integral time [s]
τ_C	Controller time [s]
τ_{holdup}	Holdup time [sec]
τ_I	Integral time [s]
θ	Time delay [s]
A	Area [m^2]
Aa	Arrhenius constant
A_A	Antoine coefficient
B	Bottom flow [mol/s]
B_A	Antoine coefficient
C	Concentration [mol/L]
C_A	Antoine coefficient
C_i	Concentration of component i [mol/L]
D	Distillate flow [mol/s]
D_A	Antoine coefficient
D_i	Distillate flow of component i [mol/s]
e	Error in controller
E_A	Antoine coefficient
E	Activation energy [mol/s]
F	Feed flow [mol/s]
F_i	Flow of component i [mol/s]
h	Height in settling tank [mol]
k	Reaction rate constant [l/mol·s]
K_C	Controller gain

l	Length of reactor [m]
L	Liquid flow [mol/s]
m	Controller output
$\overline{m}$	Bias value in controller output
M	Molar holdup [mol]
n	Mole in flash tank [mol]
n_i	Mole of component i in flash tank [mol]
nG	Mole in gas phase [mol]
nL	Mole in liquid phase [mol]
N	Number of moles [mol]
N_i	Number of moles of component i [mol]
P	Total pressure [Pa]
P_i	Component pressure [Pa]
P_i^{sat}	Saturation pressure of component i [Pa]
r_i	Rate of reaction component i [mol/l · sec]
R	Gas constant [J/K ·mol]
t	Residence time [s]
T	Temperature [K]
T_b	Boiling temperature [K]
v	Velocity [m/s]
V	Volume [m^3]
V	Vapour flow flow [mol/s]
Vtot	Total volume [m^3]
VL	Volume in liquid phase [m^3]
VG	Volume in gas phase [m^3]
Vm	Molar volume in gas phase [m^3/mol]
x_i	Molefraction of component i in liquid
y_i	Molefraction of component i in vapour

2 Introduction

2.1 Aim

The aim of the project was to create a simplified model of a biodiesel plant operating with plug flow reactor. The model was decided to be built by Matlab and Simulink. For the author the goal with the project has been to get a better insight in the biodiesel production and extending the experience with working in Simulink. The motivation for creating a biodiesel model has been related to the increased energy demand and the development towards new energy resources as biofuel. The use of sustainable energy sources have increased focus amongst the population and the necessity will only increase over the years to come so a study of biodiesel can be related to a society interest in addition to the engineering perspective. For this project mainly the rector, settling tank and methanol removal in a distillation column and flash tank will be studied in detailed and controlled.

2.2 Biodiesel

Vegetable oil for engine gain its place as a result of the energy crises of the 1970's [1], but was already used as emergency fuel during World War II. The interest for vegetable oil as fuel has just increased since and is still increasing. Already in 1938 Walton recommended that glycerol should be removed from the oil, this is the practice in today's biodiesel (esters) production. Ester formation is an important class of reactions for adding value to oil, and some of the typical ways for doing this today is given in equation 2.1-2.3 where R, R', R" and R"' is an alkyl group [2].

Esterification

$$ROH + R'COOH \rightarrow R'COOR + H_2O \tag{2.1}$$

Transesterification

$$RCOOR' + R''COOR''' \rightarrow RCOOR''' + R''COOR' \tag{2.2}$$

Acidolysis

$$RCOOR' + R''COOH \rightarrow RCOOH + R''COOR' \tag{2.3}$$

This study will only cover the transesterification.

Several nations have long-term national goals in energy policy where the increased use of biodiesel is included in the targets [2] . Due to a closed carbon cycle biodiesel will have lower carbon emmision and will thereby not contribute to the global warming in the same extend as petrodiesel. Unfortunately the NOx emission from biodiesel is higher than conventional petrodiesel. Some of the sustainability issues related to the use of biodiesel are the required land use, water resources, air emissions and social impact related to the reduced food supply.

2.3 Industry

For large scale plants producing more than 4 million litres/year the process is operating continuous [3], while smaller plant often operate on batch basis. For home production of biodiesel smaller batch process are often used and can be bought on-line. The model has been created for continuous production since this will increase the required amount of control units and give the possibility for dynamic study related to industry. The continuous process normally use plug flow reactors or continuous stirred tanks. In production there will in addition be a step for preparation of the raw materials which may include neutralisation, washing and pre-treatment in addition to the modelled units. If the plant contains free fatty acids pretreatment will be necessary. Some part of the industry uses a two-stage process where ∼ 80% of the methanol and catalyst is added to the first reactor and remaining is added in the second with an intermediate removal of glycerol. The two-stage process will reduce the required amount of alcohol. The separation between glycerol and biodiesel phases are gravitationally, which could be speeded up by a settling tank or centrifugal. Methanol is normally removed after the phase separation to avoid the reverse reaction. Then the methyl esters passes through neutralisation, before final methanol removal and water washing. To split out any soap formed and remove the last containments of catalyst, acids is added before the process is ended by drying in vacuum flashing. The glycerol stream leaving the separation step contains excess methanol, soap and catalyst. Soap is removed by splitting into free fatty acids and salts, where the free fatty acids can be removed from the top layer. Methanol in the glycerol phase is removed by vacuum flashing or evaporation. Methanol from the product streams will be recycled after removal of water in a distillation column. A brief block diagram of the process is given in Figure 2.1 from [1], [3].

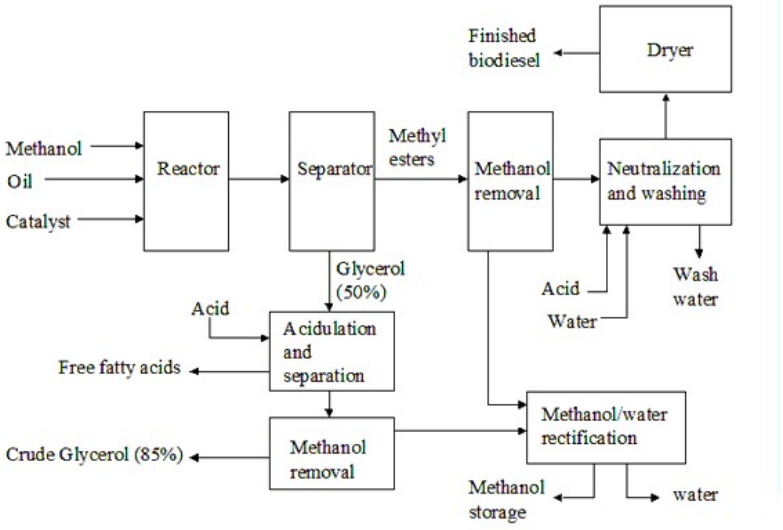
Finished biodiesel
Dryer
Methanol
Oil
Catalyst
Reactor
Separator
Methyl esters
Methanol removal
Neutralization and washing
Glycerol (50%)
Acid
Water
Wash water
Acid
Acidulation and separation
Free fatty acids
Methanol/water rectification
Crude Glycerol (85%)
Methanol removal
Methanol storage
water

Figure 2.1: Plant overview, where the model has been built for the main parts.

The separation block in Figure 2.1 is modelled by a settling tank and split, the methanol removal in methyl ester phase by a distillation column and methanol removal in the glycerol phase by a flash tank.

2.4 Feedstock

The choice of feedstock depends on the availability, price, governmental policy, and food use at the site [1]. The oil can be divided into the main parts vegetable-based, animal-based or waste oils. Some different types of vegetable-based oil are sunflower oil, soybean oil, coconut, corn, palm, peanut, tallow, lard, yellow grease and brown grease [4]. Waste oil contains more impurities than the vegetable-based and processing will be more difficult and require more pre-treatment. Impurities will have effect on the reaction conditions and side reactions will have larger significance. The model was generated for soybean oil since this is commonly used and literature are available. Soybean oil contains 49-57.1 % Linoleic acid 18:2 and the oil will for simplicity be calculated as pure Linoleic acid disregarding all impurities, see Table 2.1 [1].

Table 2.1: Composition of a typical soybean oil.

Formula	Weight percentage
C18:1	21.8
C18:2	53.1
C18:3	8
C16:0	11.8
C18:0	4.6
Other	0.7

2.5 Biodiesel in engine

Biodiesel can be used in engine in its pure form or usually mixed with traditional petrodiesel. The cetane number of the biodiesel indicates the performance and quality of the diesel fuel. Biodiesel is meant to be used in a standard diesel engine. The chemical group for biodiesel is ester, and the alkyl group attached will depend on the alcohol used for conversion while the length of the chains will be given by the original triglyceride composition. Biodiesel are by now in use in cars, buses, trains, and tried in aircrafts [1].

2.6 Biodiesel production methods

In addition to the conventional plug flow reactor plant there are several other options and even more are in the research phase. Some of the methods are given briefly below (Table 2.2). The model was generated for the conventional plug flow reactor for the possibility of comparison and connection with industry.

Table 2.2: Biodiesel production methods in use and in research phase.

Method	Advantages	Disadvantages
Supercritical methanolysis [2]	•Treats both triglyceride and free fatty acids so it will be both esterification and transesterification simultaneous. •No catalyst is required. •The reaction time is shorter than in the common used method. •The operating process is simplified due to now catalyst. •No soap formation.	•More expensive than conventional transesterifacation. •The process operates at high temperature and pressure so increased safety issues. •The necessary amount of methanol is in the molar ratio 40:1 with the oil. •Increased cost.
Batch processes [5]	•High flexibility in feedstock.	•Uses catalyst. •Low production compared to continuous.
Enzymatic processes [5]	•Low energy requirement •Ambient operating conditions.	•Reduced yield. •Increases reaction time. •Little research for industrial use.
Multi step processes [5]	•High purity of glycerol. •No need for catalyst and thereby reduction of washing and neutralisation.	
Reactive separation [5]	•Single unit. •Improved production. •Reducing energy demand. •Reactants in stoichiometry.	•Difficulties with temperature and pressure for both reaction and separation simultaneously.
Hydro-pyrolysis [5]	•Mixture of hydrocarbons.	•Complex equipment. •Requires hydrogen.
Continuous processes [5]	•Ambient operating conditions. •Widely used method in industry.	•Homogeneous catalyst.

3 Theory

The theory for the model has been divided into the main production sections necessary for modelling each of the main sections i.e. reactor, settling tank, split and purification in flash and distillation column.

3.1 Reactor

For plants producing more than 4 million litres of biodiesel per year the production is normally continuous while smaller production units are batch [3]. Conventionally the reactor has been plug flow reactor, but lately more research has been done on rotating, and oscillatory reactor for improved conversion and size reduction [6]. For the simulation the reactor is modelled as continuous-stirred tank reactors in series.

3.1.1 Reactions

The most common used alcohol is methanol, which will result in methyl ester. Other alcohol used are ethanol, isopropanol and butanol, the choice between methanol and ethanol are often related to price and availability on site. Only the main reactions given below has been accounted for in the model. The by-product of the transesterification process are glycerol which can be sold and treated further. The hydrolysis and saponification are possible side reactions neglected here, the extend of the side reactions depend on the quality of the feedstock. Reaction 3.2 - 3.4 below are the first order reversible transesterification reactions for biodiesel production. The transesterification equations are given below, where equation 3.1 is the overall reaction [2],[7].

$$Triglyceride(TG)+3\cdot Methanol(MeOH) \leftrightarrow Glycerol(GL)+3\cdot Methylester(ME) \tag{3.1}$$

$$Triglyceride(TG)+Methanol(MeOH) \Leftrightarrow Diglyceride(DG)+Methylester(ME) \tag{3.2}$$

$$Diglyceride+Methanol(MeOH) \Leftrightarrow Monoglyceride(MG)+Methylester(ME) \tag{3.3}$$

$$Monoglyceride(MG)+Methanol(MeOH) \Leftrightarrow Glycerol(GL)+Methylester(ME) \tag{3.4}$$

The rate of reaction is assumed to only be dependent of the temperature, but will also depend on the catalyst concentration. Literature values for kinetics are often given for a specific catalyst and catalyst amount, and the kinetics for an industrial comparison should be based on the correlated kinetics. The conversion in the reactor is given by how many moles of component i is reacted compared to number of moles of i in the feed [8].

3.1.2 Reactor design equations

All the reactor equations are based on the general balance given in equation 3.5.

$$In - Out + Generation = Accumulation \tag{3.5}$$

3.1.3 Plug Flow Reactor

The general design equation on differential form for a plug flow reactor (PFR) in given in equation 3.6 [8].

$$\frac{dF_i}{dV} = r_i \tag{3.6}$$

Volume is given as in equation 3.7, so that dV in equation 3.6 can be replaced with equation 3.8 when the cross sectional area is assumed given.

$$V = A \cdot l \tag{3.7}$$

$$dV = A \cdot dl \tag{3.8}$$

The molar flow F of component i can be expressed in concentrations as in equation (3.9) where A and v is assumed constant.

$$F_i = A \cdot v \cdot C_i \tag{3.9}$$

Inserting equation 3.9 and equation 3.8 into the general equation for PFR 3.6 equation 3.10 can be expressed:

$$\frac{dC_i}{dl} = \frac{r_i}{v} \tag{3.10}$$

3.1.4 Continuous-Stirred Tank Reactor

The general equation for the continuous-stirred tank reactor (CSTR) in equation 3.11 is based on the balance equation 3.5 [8].

$$\frac{dN_i}{dt} = (F_{i,in} - F_{i,out}) + V \cdot r_i \tag{3.11}$$

The number of mole of component i can be expressed as equation 3.12.

$$N_i = x_i \cdot N \tag{3.12}$$

With a given residence time in each tank, the number of moles in the tank can be expressed by the flow and residence time as given in equation 3.13.

$$N = F \cdot t \tag{3.13}$$

By combination of the three equations given above the changes in mole fraction of component i is given as 3.14.

$$\frac{dx_i}{dt} = ((x_{i,in} - x_{i,out})/t) + V \cdot r_i \tag{3.14}$$

The reaction rate r_i can be expressed by the reaction constant and the concentrations as given in equation 3.15.

$$r_i = k \cdot C_j \cdot C_k \tag{3.15}$$

transferred into mole fractions the equation becomes

$$r_i = k \cdot x_j \cdot x_k \cdot \frac{F^2 \cdot t^2}{V^2} \tag{3.16}$$

Inserting this in equation 3.14 the design equations for changes in mole fractions will be given in equation 3.17:

$$\frac{dx_i}{dt} = \frac{x_{i,0} - x_i}{t} + \frac{k \cdot F \cdot t \cdot x_i \cdot x_k}{V} \tag{3.17}$$

From the general equation given above and reaction stoichiometry in equation 3.2 - 3.4, the equations for the components are given below in equation 3.18 - 3.23 [7]:

$$\frac{dx_{TG}}{dt} = \frac{x_{TG,0} - x_{TG}}{t} + \frac{F \cdot t}{V} \cdot (-k_1 \cdot x_{TG} \cdot x_{MeOH} + k_2 \cdot x_{DG} \cdot x_{ME}) \tag{3.18}$$

$$\begin{aligned}\frac{dx_{DG}}{dt} = \frac{x_{DG,0} - x_{DG}}{t} + \frac{F \cdot t}{V} \cdot (&k_1 \cdot x_{TG} \cdot x_{MeOH} - k_2 \cdot x_{DG} \cdot x_{ME} \\ &-k_3 \cdot x_{DG} \cdot x_{MeOH} + k_4 \cdot x_{MG} \cdot x_{ME})\end{aligned} \tag{3.19}$$

$$\begin{aligned}\frac{dx_{MG}}{dt} = \frac{x_{MG,0} - x_{MG}}{t} + \frac{F \cdot t}{V} \cdot (&k_3 \cdot x_{DG} \cdot x_{MeOH} - k_4 \cdot x_{MG} \cdot x_{ME} \\ &-k_5 \cdot x_{MG} \cdot x_{MeOH} + k_6 \cdot x_{GL} \cdot x_{ME})\end{aligned} \tag{3.20}$$

$$\begin{aligned}\frac{dx_{ME}}{dt} = \frac{x_{ME,0} - x_{ME}}{t} + \frac{F \cdot t}{V} \cdot (&k_1 \cdot x_{TG} \cdot x_{MeOH} - k_2 \cdot x_{DG} \cdot x_{ME} \\ &+k_3 \cdot x_{DG} \cdot x_{MeOH} - k_4 \cdot x_{MG} \cdot x_{ME} \\ &+k_5 \cdot x_{MG} \cdot x_{MeOH} - k_6 \cdot x_{ME} \cdot x_{GL})\end{aligned} \tag{3.21}$$

$$\frac{dx_{GL}}{dt} = \frac{x_{GL,0} - x_{GL}}{t} + \frac{F \cdot t}{V} \cdot (k_5 \cdot x_{MG} \cdot x_{MeOH} - k_6 \cdot x_{ME} \cdot x_{GL}) \tag{3.22}$$

$$\begin{aligned}\frac{dx_{MeOH}}{dt} = \frac{x_{MeOH,0} - x_{MeOH}}{t} + \frac{F \cdot t}{V} \cdot (&-k_1 \cdot x_{TG} \cdot x_{MeOH} + k_2 \cdot x_{DG} \cdot x_{ME} \\ &-k_3 \cdot x_{DG} \cdot x_{MeOH} + k_4 \cdot x_{MG} \cdot x_{ME} \\ &-k_5 \cdot x_{MG} \cdot x_{MeOH} + k_6 \cdot x_{ME} \cdot x_{GL})\end{aligned} \tag{3.23}$$

Even though the industrial reactor will be a plug flow reactor it is modelled as CSTRs in series in this study to make it time dependent instead of length dependent. This will do the simulation in Simulink easier since Simulink is operating on time basis. By modelling on time basis instead of length basis, the same profiles will be created and the trends for the response to disturbances will be the same. The number of CSTRs inserted in Simulink will be based on the reactors having the same volume. A better approach might be to have smaller reactors in the beginning where the composition is changing most quickly.

3.1.5 Temperature dependence

The kinetics of the reactions will be temperature dependent and the Arrhenius equation 3.24 is often used for the temperature dependence for the reactions [8]. For the most basic model k(T) was assumed constant, and the temperature dependence could be introduced later. By inserting the temperature dependence the model will slow down due to increased stiffness of the problem. The temperature of the alcohol and the oil will often be different and it should be included a mixing device upstream of the reactor.

$$k(T) = A_a \cdot e^{-E/RT} \tag{3.24}$$

The values for A_a and the activation energy can be found in several articles [9] and [10] where data is used from [9]. The kinetics will in additon to temperature depend on the oil used, the composition of the oil, the alcohol used, the type of catalyst, concentration of catalyst and the quality of the catalyst. By finding literature for other oils under different conditions it was checked that the data found was within the expected range [11].

Table 3.1: Kinetic data for transesterification of soybean oil with NaOH catalyst.

Equation number	Average reaction rate constant [$1/mol \cdot min$]
k1	0.049
k2	0.102
k3	0.218
k4	1.28
k5	0.239
k6	0.007

The catalysts normally used for transesterification include KOH, NaOH, and H_2SO_4 [4], [2].

3.1.6 Operating conditions

The optimal operation conditions are a reaction time of one hour at 60^0C [2], [3]. Temperatures above 60^0C is avoided since this will accelerate the saponification and increase the amount of undesired bi-products [2]. The length of the reactor should be long enough to ensure the required reaction time and conversion. The pressure in the reactor will be atmospheric. Reaction data will be taken at these conditions, and later implementation of different operating conditions can be done. The optimal molar ratio is found from Figure 3.1 ([1]) being 6:1 methanol and oil, respectively. So 100 % excess methanol will be used to avoid the reverse reactions. The model was done on a basis of 100 [mol/s] of total inlet flow [1], [2], [3].

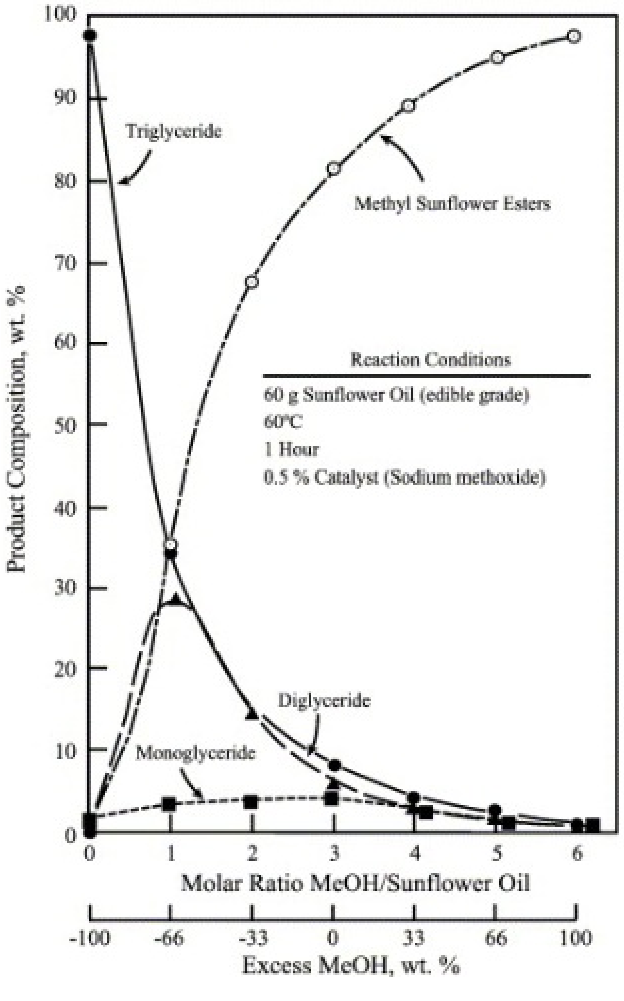

Figure 3.1: Production composition as a function of the excess methanol.

3.2 Settling tank

The settling tank will have the task of separating the methyl ester from glycerol, but also to make sure the flow downstream are changing smoothly to avoid large disturbances in sensitive equipment. The outlet is desired to be changing slowly while the inventory of the tank can change quickly. Assuming the bottom area is constant only the height in the tank is changing due to flow changes. The molar holdup will change with the variation in inlet flow compared to the outlet flow. The total volume of the tank should have a safety margin in case of emergency shut down, or problems downstream. The change in molar holdup is given by equations 3.25.

$$\frac{dM}{dt} = (F_{in} - F_{out}) \tag{3.25}$$

The changes for the different components is given in equation 3.26

$$\frac{dx_i \cdot M}{dt} = (x_{i,in} \cdot F_{in} - x_{i,out} \cdot F_{out}) \tag{3.26}$$

By having a settling tank significantly larger than the flow rate disturbances the flow composition will be smoothed out. When the hold up is significantly larger than the flow, the molar hold up for the change in component can be assumed constant. The less dense phase will be floating on top of the heavier phase and can be drained off. Most off the impurities will follow the glycerol phase, but the methanol will be distributed between the two phases.

3.3 Split

Excess methanol is usually not removed from the reaction until after the phase separation to avoid reverse transesterification reaction. Water might be added to the reaction mixture to improve the separation [2]. The ternary diagram given below with the indicated nominal composition, Table 3.2, from the outlet of the reactor [12] is used for finding the methanol distribution. The methyl ester in this case is methyl oleate and not methyl linoleate, this is due to lack of literature. The diagram for methyl oleate was used due to similar physical properties and same chain length [1].

Table 3.2: Nominal feed composition from the reactor, assumed ternary composition.

Component	Mole fraction
Methyl ester	0.37
Glycerol	0.12
Methanol	0.51

From the diagram given in Figure 3.2 the composition in the two liquid phases can be found by the feed composition and the tie line. The tie line used for the nominal composition is indicated in Figure 3.2.

From Figure 3.2 the composition in the methyl ester and glycerol phase (Table 3.3), the flow in each phase and the split of methanol between the two phases can be found. The split of methanol is assumed to be constant even though this will not be the real case. Since temperature is assumed constant it

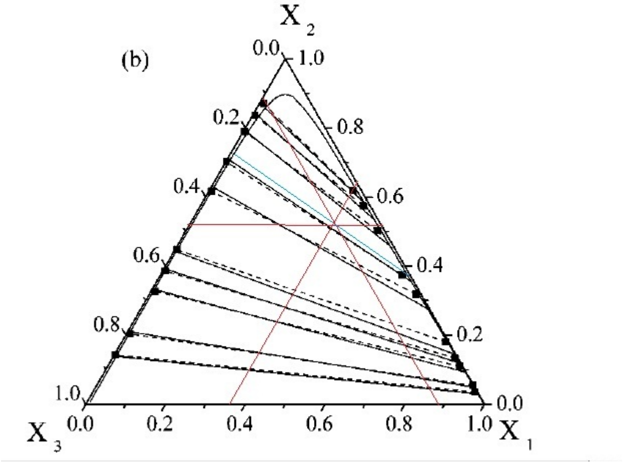

Figure 3.2: The ternary diagram for Methyl ester(oleate)(1), Methanol(2) and Glycerol(3).

Table 3.3: Nominal outlet composition from settling tank, assumed ternary composition.

Component	Mole fraction biodiesel phase	Mole fraction glycerol phase
Methyl ester	0.64	0.01
Glycerol	0	0.72
Methanol	0.36	0.27

will be within range to assume constant methanol split. The level-arm rule [13] is used to find the amount of flow in each phase and can be derived as given in equation 3.27- 3.32.

The total balance over the splitting section is given in equation 3.27.

$$L_{fattyphase} + L_{glycerolphase} = F_{inflow} \tag{3.27}$$

The component balance for component i is given in equation 3.28.

$$L_{fattyphase} \cdot x_{i,fattyphase} + L_{glycerolphase} \cdot x_{i,glycerolphase} = F_{inflow} \cdot x_{i,inflow} \tag{3.28}$$

By combination of equation 3.28 and 3.27 the level-arm rule can be derived.

$$\begin{aligned} L_{fattyphase} \cdot x_{i,fattyphase} + L_{glycerolphase} \cdot x_{i,glycerolphase} \\ = (L_{fattyphase} + L_{glycerolphase}) \cdot x_{i,inflow} \end{aligned} \tag{3.29}$$

$$L_{fattyphase}(x_{i,fattyphase} - x_{i,inflow}) = L_{glycerolphase}(x_{i,inflow} - x_{i,glycerolphase}) \tag{3.30}$$

$$\frac{L_{fattyphase}}{L_{glycerolphase}} = \frac{(x_{i,inflow} - x_{i,glycerolphase})}{(x_{i,fattyphase} - x_{i,inflow})} \tag{3.31}$$

The separation of the phases can be found from the level-arm rule in equatoin 3.32 as the distance between the inlet point and the outlet point.

$$\frac{L_{fattyphase}}{L_{glycerolphase}} = \frac{\overline{L_{glycerolphase}F_{inflow}}}{\overline{L_{fattyphase}F_{inflow}}} \tag{3.32}$$

$$L_{fattyphase} = \frac{(x_{i,inflow} - x_{i,glycerolphase})}{(x_{i,fattyphase} - x_{i,inflow})} L_{glycerolphase} \tag{3.33}$$

From the nominal composition it can be found that 40% of the methanol follows the biodiesel phase and the rest follows the glycerol phase. It is assumed that most of the intermediates and triglyceride will stay in the glycerol phase, see Table 3.4.

Table 3.4: The fraction of the inlet flow leaving in the biodiesel phase.

Component	%
Triglyceride	5
Diglyceride	5
Monoglyceride	5
Biodiesel	100
Glycerol	0
Methanol	40

3.4 Distillation

Distillation is based on difference in boiling temperatures, see Table 3.5 and the methanol will leave as the distillate for both purifications processes. The operating temperature for the column must be between the boiling temperatures for the two components separated and can therefore be higher for glycerol purification. Since the distillation is taking place at a higher temperature than the reaction this will be an energy consuming step in the production.

Table 3.5: Boiling temperatures.

Component	Boiling temperature[C]
Methyl ester	168-170 [1]
Glycerol	288 [14]
Methanol	64.7 [15]

The number of stages for methanol and biodiesel separation in the model has been set to approximately 3, due to the high relative volatility of ~ 70. For the distillation there will be assumed constant molar overflow, and equilibrium over the stages. For the total balance over the column equation 3.34 gives the conservation of mass and moles for the given system.

$$F = D + B \tag{3.34}$$

And equations 3.35 gives the component balance over the whole column.

$$x_{i,F} \cdot F = y_{i,D} \cdot D + x_{i,B} \cdot B \tag{3.35}$$

$$F_i = D_i + B_i \tag{3.36}$$

Over each stage, see figure 3.3, the flows leaving the stage will be in equilibrium.

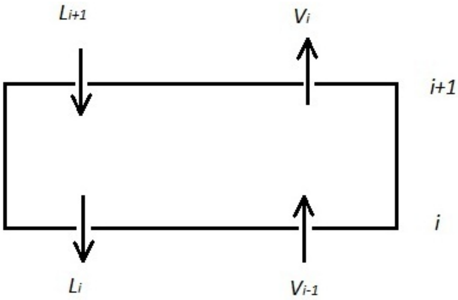

Figure 3.3: The total balance over stages in the distillation column.

And the balance over the feed stage (figure 3.4).

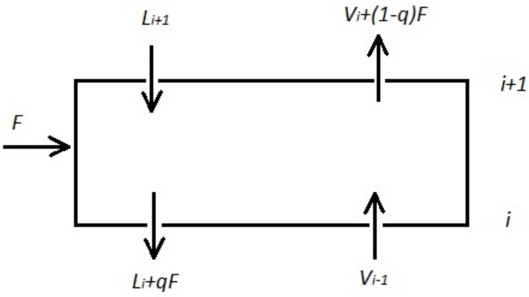

Figure 3.4: Balance over feed stage in distillation column.

The total balance equation over each stage will be given as in equation 3.37 and the component balance will be given as in equation 3.38

$$L_{i+1} + V_{i-1} = L_i + V_i \tag{3.37}$$

$$x_{i,i+1} \cdot L_{i+1} + y_{i,i-1} \cdot V_{i-1} = x_i \cdot L_i + y_i \cdot V_i \tag{3.38}$$

With a molar hold up on the stages the liquid flow from the stage will also be affected by the molar holdup compared to the nominal molar holdup equation 3.39.

$$L_i = L_{i,nominal} + \frac{M_i - M_{i,nominal}}{\tau_{holdup}} \tag{3.39}$$

3.4.1 Vapour pressure

The saturation pressure of a component is given by Antoine equation 3.40 [14]. The vapour pressure for glycerol and biodiesel will be marginally lower than methanol indicating that they will mainly stay in the liquid phase while methanol mainly will be in the vapour phase.

$$P^{sat} = e^{(A_A + B_A/T + C_A \cdot ln(T) + D_A (T)^{(E_A)}} \tag{3.40}$$

3.4.2 Raoult's law

Raoult's law defines the vapour liquid phase equilibrium. Raoult's law on ideal form is given by equation 3.41 [13].

$$P = \sum_{i=1}^{n} x_i P_i^{Sat} \tag{3.41}$$

If taken into consideration the non ideality, the activity coefficients will be introduced in equation 3.42. The activity coefficients can be found experimentally, and some articles [16] have studied the binary VLE (Vapour liquid equlibrium).

$$P = \sum_{i=1}^{n} \gamma_i x_i P_i^{Sat} \tag{3.42}$$

The fraction in the vapour phase will be given by Raoult's law for component i in ideal mixture 3.43.

$$y_i = \frac{x_i P_i^{Sat}}{P} \tag{3.43}$$

3.4.3 Relative volatility

Relative volatility is a measurement of phase separation of components, and indicates the distance from equilibrium line. The greater the distance the easier the separation and less stages and energy will be required. For a binary system the relative volatility will be given by equation 3.44 [13], [17]. The two purification units will be approximately binary due to high conversion in the reactor and excess methanol leaving little triglyceride and intermediate in the product streams for purification.

$$\alpha = \frac{y_i/x_i}{y_j/x_j} \tag{3.44}$$

For an ideal mixture and by Raoult's law α will be given by the difference in saturation pressure of the two components in equation 3.45.

$$\alpha = (P_i)^{sat}/(P_j)^{sat} \tag{3.45}$$

Dalton's law says that the total pressure is the sum of the partial pressures:

$$P = \sum_{i=1}^{N} P_i \tag{3.46}$$

A rough estimate of the relative volatility can be given by equation 3.47 [18].

$$\alpha = e^{\beta(T_{bj} - T_{bi})/T_b)} \tag{3.47}$$

Where β often can be taken as 13 in many cases and T_b is given below in equation 3.48:

$$T_b = \sqrt{T_{bj} T_{bi}} \tag{3.48}$$

3.5 Flash tank

The purity of glycerol should be 92% [2], this could be achieved in a one step flash due to the high relative volatility between methanol and glycerol. Assuming the behaviour of the component mixture is ideal then ideal gas law and Raoult's law can be used. The vapour pressure can be calculated from the Antoine parameters equation 3.40 from [14], and the system is assumed to have constant operating temperature controlled upstream. The Antoine coefficients for methanol and glycerol are given in Table 3.6.

Table 3.6: Antoine coefficients.

Coefficient	Methanol	Glycerol
A_A	$8.2718 \cdot 10$	$9.9986 \cdot 10$
B_A	$-6.9045 \cdot 10^3$	$-1.3808 \cdot 10^4$
C_A	-8.8622	-10.08
D_A	$7.4664 \cdot 10^{-6}$	$3.5712 \cdot 10^{-19}$
E_A	2	6

The differential equations necessary to solve for the flash will be equation 3.49 and 3.50 [19]. This will have the states n and $n_{glycerol}$.

$$\frac{dn}{dt} = F - V - L \tag{3.49}$$

$$\frac{dn_i}{dt} = F \cdot z_i - V \cdot y_i - L \cdot x_i \tag{3.50}$$

The algebraic equation for the changes in liquid volume in the flash tank can be removed by the given equations 3.51-3.55. This is done since Simulink can not handle algebraic equations.

$$n - nG - nL = 0 \tag{3.51}$$

$$n - \frac{P \cdot VG}{R \cdot T} - \frac{VL}{Vm} = 0 \tag{3.52}$$

$$V_{tot} = VG + VL \tag{3.53}$$

$$n - \frac{P \cdot V_{tot}}{R \cdot T} = VL(\frac{1}{Vm} - \frac{P}{R \cdot T}) \tag{3.54}$$

$$VL = \frac{n - \frac{P \cdot V_{tot}}{R \cdot T}}{\frac{1}{Vm} - \frac{P}{R \cdot T}} \tag{3.55}$$

3.5.1 Molar volume

Molar volume in liquid phase $[m^3/mol]$ indicates the liquid volume taken by one mole of a given component [14]. The molar volume will be used in the flash tank for removal of the algebraic equation, values given in Table 3.7.

Table 3.7: Molar volume $[m^3/mol]$.

Methanol	Glycerol
$4.058 \cdot 10^{-2}$	$7.3202 \cdot 10^{-2}$

3.6 Control

To achieve the necessary purity and responses for the system control structures need to be included.

3.6.1 Proportional controller

This is the simplest type of controller, and its operation can be described by equation 3.56 [20]. The advantage by a proportional controller is that K_C is the only tuning parameter. A proportional controller can often be used for level controller.

$$m(t) = \overline{m} + K_c \cdot e(t) \tag{3.56}$$

3.6.2 Proportional-Integral controller

This is the most common used controller [20], close to 85% of all controllers are of this type, equation 3.57.

$$m(t) = \overline{m} + K_C \cdot e(t) + \frac{K_C}{\tau_I} \int e(t)dt \tag{3.57}$$

3.6.3 First order process

For a first order response the tuning parameters can be calculated from the the given equations 3.58, where k can be found by making a step change in the input and observe the response in the output (Figure 3.5) [21].

$$k = \frac{\Delta y(\infty)}{\Delta u} \tag{3.58}$$

The SIMC rules for first order response is given in equation 3.59 and 3.60 [21].

$$K_C = \frac{1}{k} \cdot \frac{\tau_1}{\tau_C + \theta} \tag{3.59}$$

$$\tau_I = min(\tau_1, 4(\tau_C + \theta)) \tag{3.60}$$

When implementing PI controller in Simulink, P=K_c and $I = \frac{K_c}{\tau_I}$.

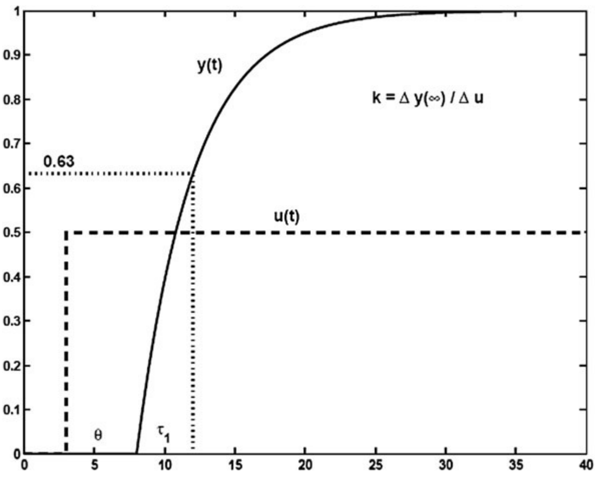

Figure 3.5: First order response.

3.6.4 Integrating process

When the response of the open loop step is integrating, see Figure 3.6, the slope can be used for finding the control parameters [21].

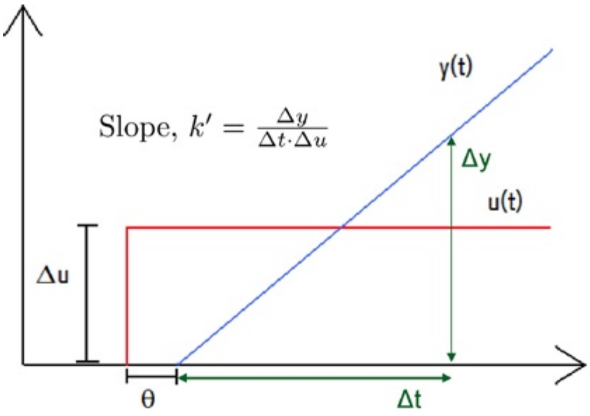

Figure 3.6: Integrating response.

The control parameters will be as given in equation 3.61 and 3.62.

$$K_C = \frac{1}{k'} \cdot \frac{1}{\tau_C + \theta} \tag{3.61}$$

$$\tau_I = 4(\tau_C + \theta) \tag{3.62}$$

3.6.5 Tight and smooth control

Within tight control the object is to keep the output to its set point and the control will be as fast as possible. Tight control is typically used for active constraints since it reduces the backoff. With tight control there is a disadvantage of input disturbances continue throughout the process. In smooth control we make the controller slower, but we still want acceptable control of the system. Even if the control is smooth it should not reject disturbances.

3.6.6 Backoff

Backoff is the necessary change in setpoint for a variable to avoid it from getting away from operating conditions. Backoff is a safety margin to keep within constraints. Like avoiding the bottom composition from getting less pure than buyer requires at any time.

$$backoff = \mid constraint - setpoint \mid \tag{3.63}$$

To reduce the backoff the squeeze and shift can be used to reduce the variance, by squeeze, and change the set point, shift.

4 Generation of model with Simulink

The Simulink model for the process contains three main part. The first level-2 Matlab S-function block is the ten CSTRs in serie. Then the settling tank and split for assuring constant flow downstream and at the end the Column A ([22]) and flash are included. The Simulink model with matlab script can be found in Appendix A being a CD with all separate units and the complete model. Due to many operation units the matlab code is not included on paper, but collected on CD in Appendix A. Figure 4.1 shows what the units will look like in Simulink, this is the reactor block, and all units and the system model can be found in Appendix A.

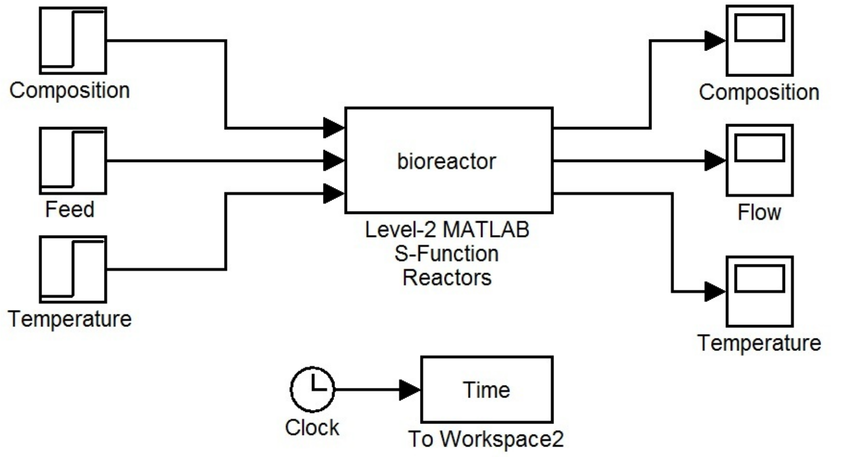

Figure 4.1: Example of a Simulink unit will look like.

The different parts of the process were modelled separately and their behaviour and response was checked for the single models. When the model is put together it slows down due to the complexity and the number of equations necessary to solve.

4.1 Solvers

By using different ordinary differential equation (ODE) solvers in Simulink the time for solving the problem was reduced. The different units seems to have different solver being the best fitted, but it was necessary for all to use a stiff solver like ode15 or ode23s. The solver used should be efficient, stable and convergent.

4.2 Reactor

The numbers of CSTRs necessary for modelling the PFR was first included as separate boxes in Simulink. This was a less elegant way to do it since a change in the number of CSTRS would lead to the model itself being modified. This was also a model which was solving very slowly. The solution to this problem was to generate one unit with the states for all the CSTRS, see Appendix A "bioreactoronly" file.

4.3 Settling tank and split

The settling tank was first modelled as one unit including the split of the components and the buffer tank behaviour. It was found that when implementing the flow controller for the outlet flow, it is better to have the settling tank and the split in separate units, see Appendix A "Settlingtanko" file . For implementing the flow controller, the outlet flow should be set as an input in the unit and the molar holdup will be one of the outputs. Related to the settling tank it was a problem with the flow downstream the split being "not a number" when starting the unit, this was solved by introduction of a transfer delay unit. The split between the two phases is assumed constant, even though in reality the split will change as the inlet composition changes.

4.4 Distillation

When implementing the distillation column " Column A" [22] into the biodiesel model (see Appendix A "colas PIBi" file), it was first converted into [mol/s] basis so that it is operating in connection with the rest of the units. The distillation unit solves the flows on each stage, three stages excluding condenser and reboiler. It is assumed that the inlet flow is at saturation, but this might not always be the case in reality and for verification towards industrial process this might be necessary to change. For control units on the distillation column, the molar holdups in the reboiler and condenser will be used for the bottom and distillate flow respectively. The composition in the flows will be controlled by the reflux and the flow from the reboiler. For the distillation of methanol from biodiesel the relative volatility was taken as 70, found from [16] when looking at the two experiments with the low mole fraction of methanol in liquid. This values is higher than the one found from the approximate method, 34 [18], this is probably due to non ideality of the mixture.

By a large relative volatility 34-70 the required number of stages will be three equilibrium stages. It can be seen from Figure 4.2 that the number of stages will not change for ideal or non-ideal system when the value of α is so high.

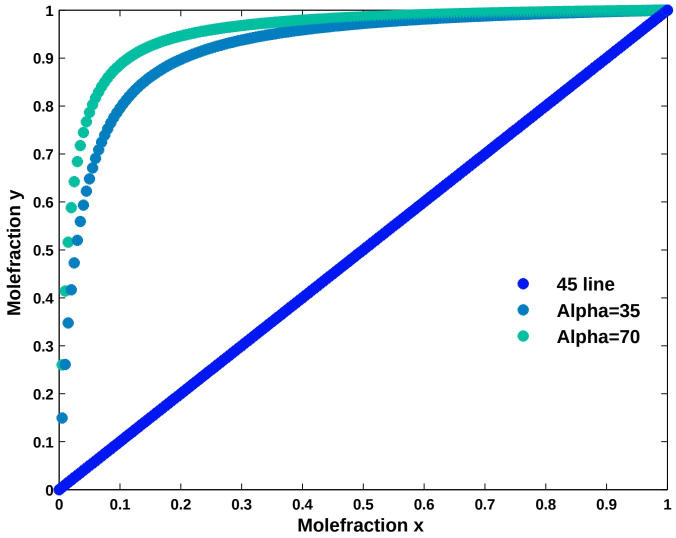

Figure 4.2: 45^0 line and equilibrium lines for given α values from approximate method and literature.

4.4.1 Control of distillation column

The most important part of the distillation column is the purity in the bottom product/the biodiesel since this is the main product for sale. The top product does not necessary need to be that pure since the this will be recycled, and processed further, purity of glycerol 92 % [2]. So when tuning the controllers in Simulink, the bottom was tuned first.

4.5 Flash

The flash unit was modelled based on a flash model given in [19], and the inlet is also here assumed saturated. When taken into Simulink (see Appendix A "Flashtank" file), all the moles of glycerol is assumed to be in the liquid phase due to the low vapour pressure of glycerol compared to methanol. The total number of moles in the tank and the number of moles of glycerol are given as the states. It is now assumed that the vapour leaves the tank quickly and the tank content is mainly given by the liquid. The relative volatility of methanol in glycerol is taken as 2440 [1] and the flash unit will provide the required purity.

5 Case study of model

The model was checked by performing different cases, observing the response and examining the results against the expected response. By doing this some mistakes in the codes were found and improved, and necessity of control structures was highlighted when unexpected responses were discovered.

5.1 Reactor

Even though the temperature dependence of the reactor is disregarded several studies of the reactor is possible. For example what happens if the feed condition changes, how will this disturbance move through the reactor? The responses should be considered based on the kinetics and stoichiometry.

Case 1: Shows the steady state response of the last reactor.

Case 2: Making a step change in the inlet flow rate without changing the composition. When pushing more into the reactor, it is expect that the reactor respond immediately by increasing the outlet flow if the reactor is full.

Case 3: Let the fraction of methanol in the inlet stream be zero and look at the responses for the last reactor. The fraction of triglyceride should reach one.

Case 4: Looking at the response in composition through the reactor when the methanol is removed. By removing methanol, the reactions can be expected to stop leaving triglyceride unconverted. It will be expected that the last reactor, being at the end of the PFR respond later than the first.

Case 5: Removing methanol in the feed stream to less than required by stoichiometry. It is expected that some reactant and intermediate will be in the outlet flow.

Case 6: What would happen if some of the intermediate products was included in the feed stream? As long as the amount of methanol is high enough one would expect the amount of products to increase. How much the amount of product increases will be dependent one the intermediate. It can be expect that the product will increase more by adding diglyceride than monoglyceride due to reaction stoichiometry.

5.2 Settling tank and split

The settling tank for separation of the phases is often a centrifuge in industry for separation of the two phases. In the model the settling tank will also have the purpose as a buffer tank to smooth out the upstream disturbances for the distillation downstream. The cases for the settling tank will be to check that it actually smooth out disturbances applied upstream.

Case 7: Changing the inlet flow into the settling tank by +10% without any other disturbances. From this disturbance it is desired that the outlet flow changes towards the inlet flow over time. The flows in the different phases should change by the same percentage as the inlet flow. The composition should stay constant.

Case 8: Reducing the fraction of glycerol and increasing the fraction of methyl linoleate in the inlet flow. The total flow from the settling tank should be constant, but the biodiesel phase flow should increase while the glycerol phase flow decrease.

5.3 Distillation

For the purification units it was performed several different scenarios: 1) what happens if the inlet feed conditions changes from units upstream 2) what happens if the requirement to the product changes. Both this scenarios are possible in the industry, as the supplier of oil might change their delivery or the customer might change their request. New product specification is required and this could introduce new operational conditions for the biodiesel plant. It is always desired that the existing unit can be used in its present form without the necessity of reconstruction or retuning of controller units.

Case 9: Making a step change in the feed composition by increasing the amount of methanol in the feed. How will this effect the amount of outlet streams?

Case 10: Increase the flow into the distillation column by 10 %. How will this effect the reflux, the vapour etc. And can the controller keep the composition at set point?

5.4 Flash

The flash will have some of the same possible industrial scenarios as the distillation column, but since biodiesel is the main product the restrictions to glycerol purity is not as strict.

Case 11: By changing the inlet flow without changing the composition it could be expected that both flows will increase by the same percentage as the inlet.

Case 12: Increasing the fraction of methanol in the feed. By increasing the amount of methanol it is expected that the vapour flow out will increase while the glycerol phase flow decreases.

Case 13: Showing the nominal fractions of methanol in the different phases. This should be a significant difference indicating the large difference in relative volatility.

5.5 Plant

Only one case has been done for the whole model due to the slow model, but since all the units has been properly tested separately case 14 only verify what was found in case 1-13.

Case 14: Step change in the inlet flow to the system of +10% and checking the response of the plant.

6 Model validation

The model has been validated for all units given in Appendix A.

6.1 Tuning of system

The controllers will be tune for the nominal flows, and for operation with large disturbances it could be necessary with re tuning.

6.1.1 Tuning of distillation column

Since the number of stages in the column is low, the interactions between the two composition controllers will be high. Due to this interactions the controller for the distillate product should be slower than the one for the bottom product so that the controllers are not working against each others actions. The distillate flow contain mainly methanol which will be recycled back to the reactor and as long as the methanol ratio is high enough in the reactor some glycerol or methyl ester in this stream should not effect the plant much. Attention should be applied to the recycle loop to avoid snowballing. If the distillate stream increases to much, leading to increased inflow in the reactor this will reduced the residence time in the reactor and can possibly reduced the over all conversion.

Tuning of holdup

P-controllers with gain of -10 was used for molar holdup in condenser and bottom. The controller gain was found from integrating process when disturbances was applied in holdup and response in distillate and bottom flow was observed.

Tuning of bottom composition

The main objective to tune for the biodiesel distillation column is the bottom product containing the biodiesel which will be sold. The biodiesel purity should be 99.6% [2]. Since x_B is of greatest importance of boilup, VB, will be tuned first. It is first done an open loop response by making a step change in VB of -10% and observe the response in x_B. The step is done in the negative direction decreasing VB since the bottom flow already is pure and future purification will require large amount of energy.

With the given step in VB the response in x_B was as given in Figure 6.1. This is a first-order process with no time delay. Since the important part of the column to control is the bottom composition τ_C is taken to be 1/3 of τ_I to ensure tight control.

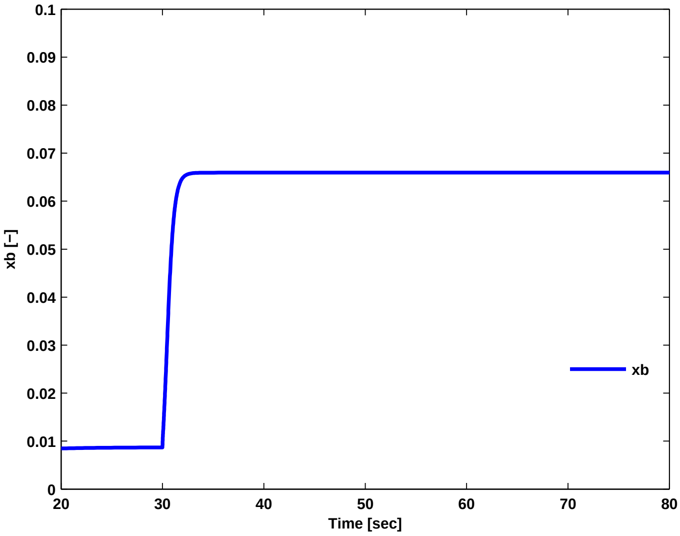

Figure 6.1: Response in bottom composition when step disturbance in VB was applied.

Tuning parameters for the bottom composition with the given disturbance and response is given in Table 6.1:

Table 6.1: Tuning parameters for bottom composition.

Parameter	Value
$\Delta y(\infty)$	0.057
Δu	-2.3
τ_1	0.57
θ	0
K_C	-116
τ_I	0.57
I	-205

After the open loop tuning it can be observed that the bottom composition moved towards the given setpoint of 0.004 mole fraction of methanol in the methyl ester phase. When applying a step in the setpoint for the bottom composition the response in the bottom composition is plotted in Figure 6.2.

To make this happen it can be observed that the amount of VB should decreases as more methanol is allowed in the bottom.

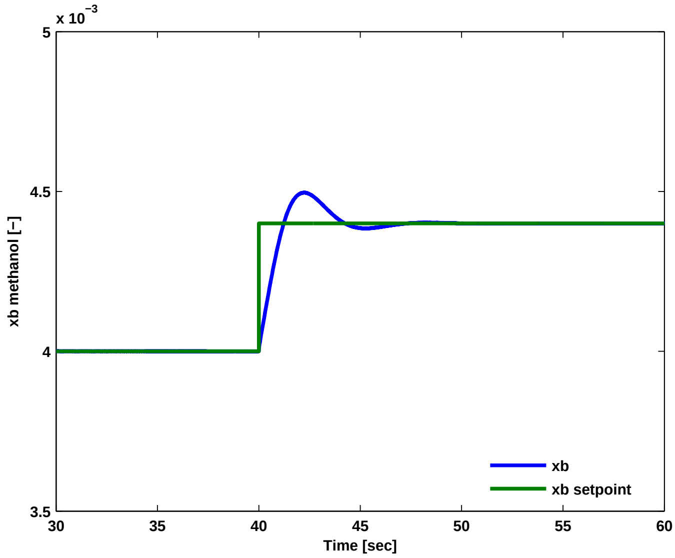

Figure 6.2: Response in bottom composition when a change in the setpoint for the bottom composition was performed.

Tuning of distillate composition

The distillate is not the important product in the production and do not need tight control. When making a step change in reflux, LT, of +10% the controller for the bottom composition will also effect the distillate composition, so the changes for *yd* was only studied in the beginning. The response in *yd* to LT is taken as integrating (Figure 6.3).

Due to the low number of stages the interactions between the top and bottom controller are large. For this reason only the response at the beginning is considered since the bottom controller is already connected and will interact. The first response is integral response and the controller is tuned for this. Since the top composition are not of that great importance the controller is used as a P controller and tuned by making τ_C large, see Table 6.2.

Table 6.2: Tuning parameters for distillate composition.

Parameter	Value
Δy	0.0001
Δu	0.25
Δt	0.38
θ	0
k'	0.001
τ_C	200
K_C	5

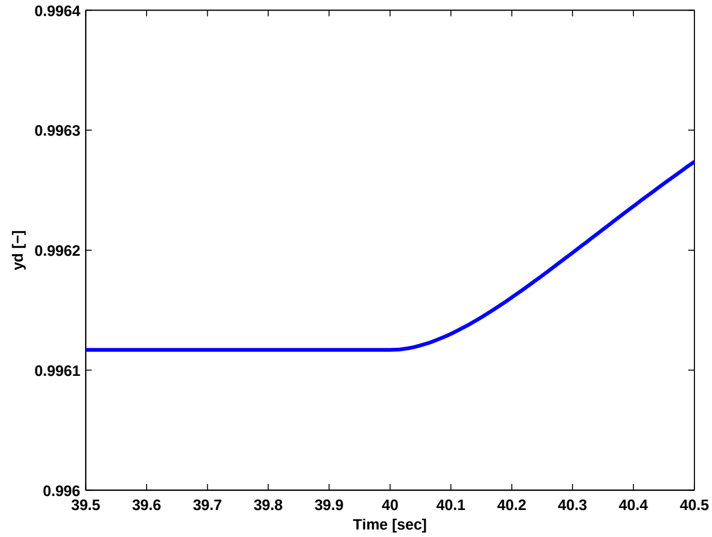

Figure 6.3: Response in distillate composition when step in reflux, LT, was applied.

When both the bottom and distillate composition have been tuned a step change was performed in the feed and the response in purity was observed.

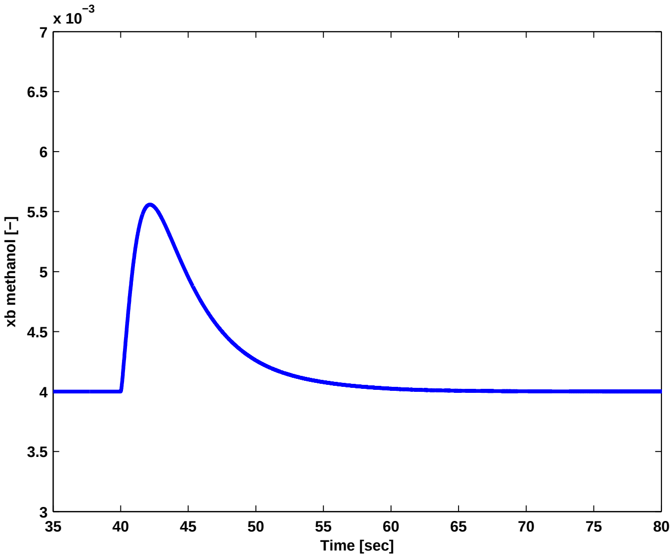

Figure 6.4: Response in bottom composition to a step in feed flow for the distillation column.

From Figure 6.4 it can be seen that a backoff should be included if the bottom composition never should contain more than 0.4 % methanol.

6.1.2 Smooth control of settling tank

For a settling tank where the output is the input to a distillation column which is being sensitive for disturbances a tight control upstream will give bad performance in the column. By using smooth control on the settling tank we can assure more constant inflow conditions to the distillation column. The importance of the settling tank is to have a large enough residence time to make sure phase separation is good enough and smooth out disturbances. The response in the holdup in the tank when making a disturbance in the inlet flow was integrating, and a P-controller with large τ_C was used to pair the holdup and outlet flow giving a K_C as -0.01.

6.2 Reactor

6.2.1 Plug Flow Reactor

For the PFR the concentration profiles will be as in Figure 6.5. The reactor was originally taken as double the length but with the given flow rate, cross sectional area and kinetics of the reactor, the reactor was unnecessary long and had a longer residence time than required for reaching steady state and desired purity. By reducing the length to half and thereby reducing the operating time to half, see Figure 6.5 the steady state condition is reached at the end of the reactor (in the last reactor).

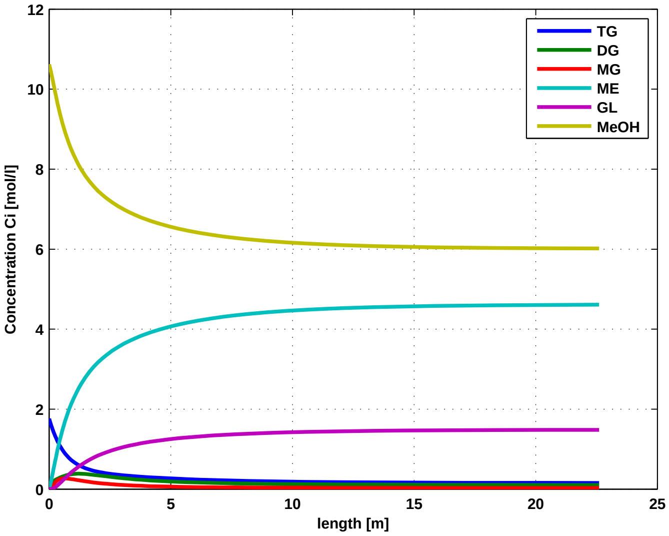

Figure 6.5: PFR concentration profiles with the length of reactor reduced to half.

Reduction of reactor size and operating time will be highly economically beneficial.

6.2.2 Approximation of PFR by CSTRs

The number of CSTRs necessary to imitate the PFR was found and then implemented into the Simulink model. After all the reactors have been included into one Simulink block their response was tested. Since the reaction is quick in the beginning it could be considered that instead of a given number of CSTR with equal size it would be better to have smaller reactors in the beginning and bigger at the end [8].

By putting CSTRS in series the behaviour of the plug flow reactor can be simulated, illustration in Figure 6.6.

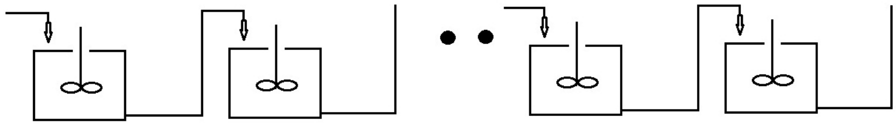

Figure 6.6: Illustration of CSTRs in serie.

By running with different numbers of CSTRs, but constant residence time and volume of the tanks the number of CSTRs to represent the PFR can be found. From Figure 6.7 it can be observed that approximation by two CSTRs are too few and 20 from Figure 6.8 can be seen to be more CSTRs than necessary. This was found for the total residence time when the length of the plug flow reactor was half of the original.

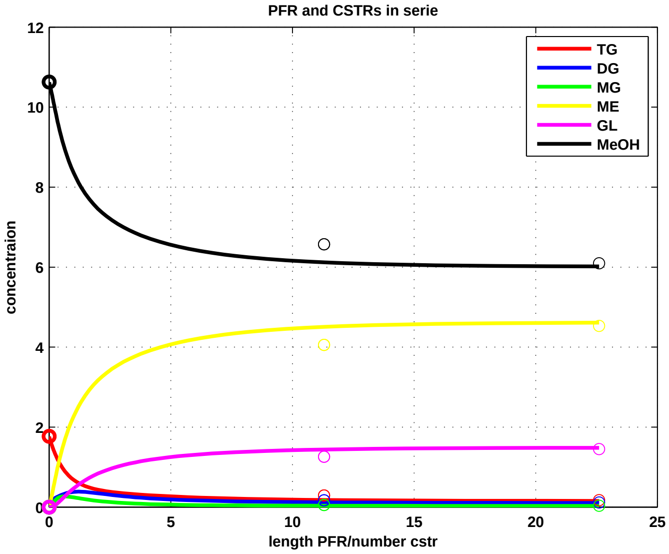

Figure 6.7: Modelling of PFR by two CSTRs of same volume in series.

The plug flow reactor ended up being approximated by ten tank reactors in series (Figure 6.9) literature uses six reactors in series [23] and ten can be taken as a good rough estimate . If the model should be used for comparison with

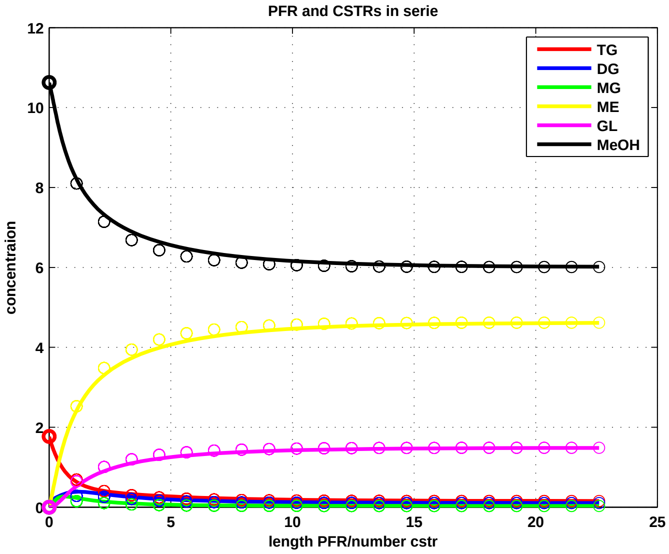

Figure 6.8: Modelling of PFR by 20 CSTRs of same volume in series.

industrial performance the model need to be redefined for the given flowrates and reactor size and the number of CSTRs approximated. Each CSTRs starts with the leaving outlet conditions from the previous reactor.

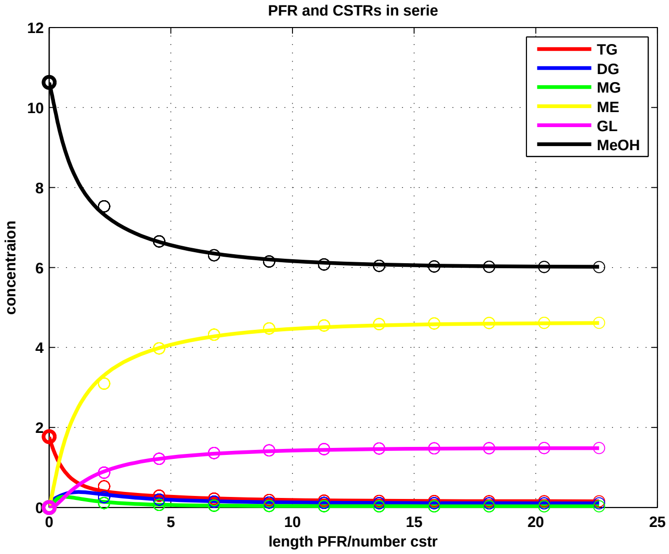

Figure 6.9: Modelling of PFR by ten CSTRs of same volume in series.

6.2.3 Result of case study of reactor

The case study on the reactor was performed to check that the behaviour of the reactor was as expected.

Case 1: This is the steady state response of the reactor. It can be seen that the flow mainly contains methanol, methyl ester and glycerol, which is the reactant in excess and product, respectively. It can also be seen that the amount of methyl ester is three times the amount of glycerol which is given by the overall reaction in equation 3.1. From Figure 6.10 it can be seen that the reaction has a high conversion as the fraction of triglyceride in the outlet is neglectable and that little triglyceride will leave the reactor compared to the amount of triglyceride in the inlet.

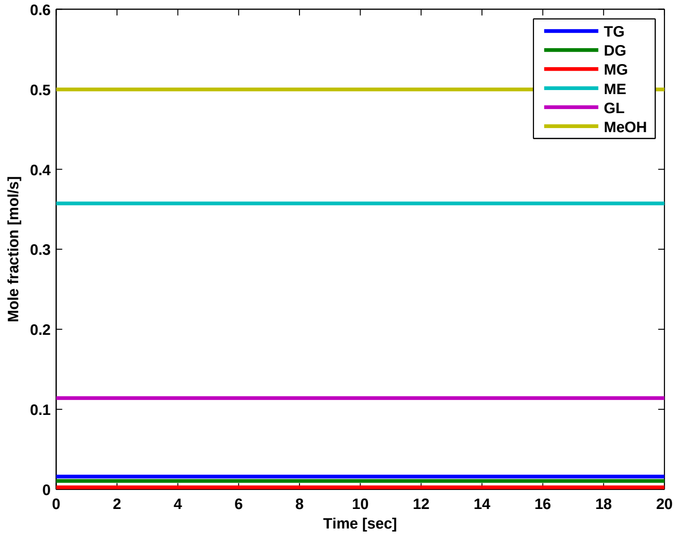

Figure 6.10: Case 1, Steady state out of the last reactor with nominal inlet composition when methanol is in 100 % excess.

Case 2: When making a step change in the inlet flow without changing the composition, it is expected that the outlet flow will increase immediately. It can be seen from Figure 6.11 that the flow responses immediately. The flow response is illustrated by the amount of triglyceride in the first and last reactor since the total in and outlet flows will be in the same range and the response will coincide with the disturbance. When the flow is increased, and the volume of the tank is constant the residence time in each tank will decrease. A too large deviation from nominal flow could lead to reduced conversion if the total residence time gets below the necessary time of reaction. The constriction with the residence time should be included in the Simulink model if the industrial production have problems with residence time.

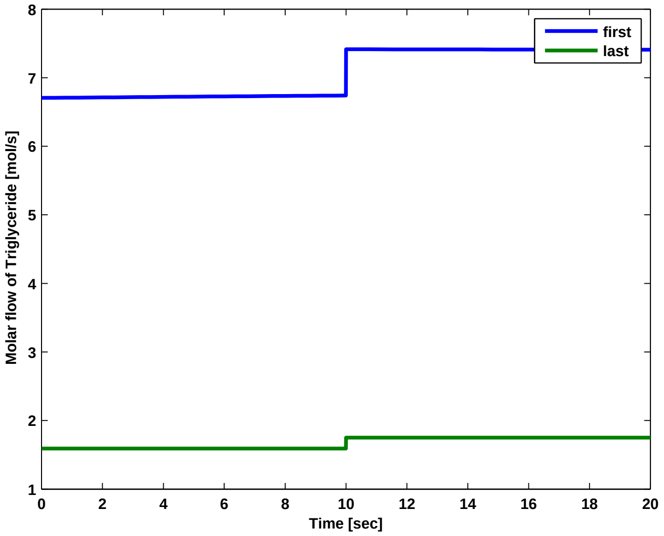

Figure 6.11: Case 2, A applied step in inlet flow and response in the outlet flow of triglyceride of the first and last reactor.

Case 3: Let the fraction of methanol in the inlet stream be zero. One would now expect the fraction of triglyceride to become 1 as no reaction will take place. The response of the reactor Figure 6.12 is as expected with no conversion at all when the methanol is removed.

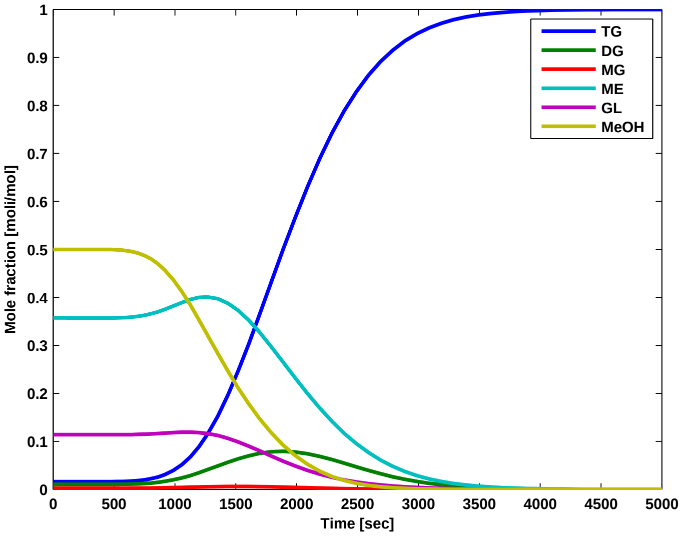

Figure 6.12: Case 3, No methanol in the feed stream leading to unreacted triglyceride in the outlet stream.

Case 4: Looking at the response in composition through the reactor when the methanol is removed in the inlet. From Figure 6.13 it can be seen that the first reactor change first and most rapidly, while the later reactors changes more smoothly and later in time. The smoothing is due to the fact that a disturbance in the inlet flow will be ”diluted” in the previous reactor before it flows downstream to the next reactor. The time delay is related to the fluid motion assumption of complete mixing in each tank.

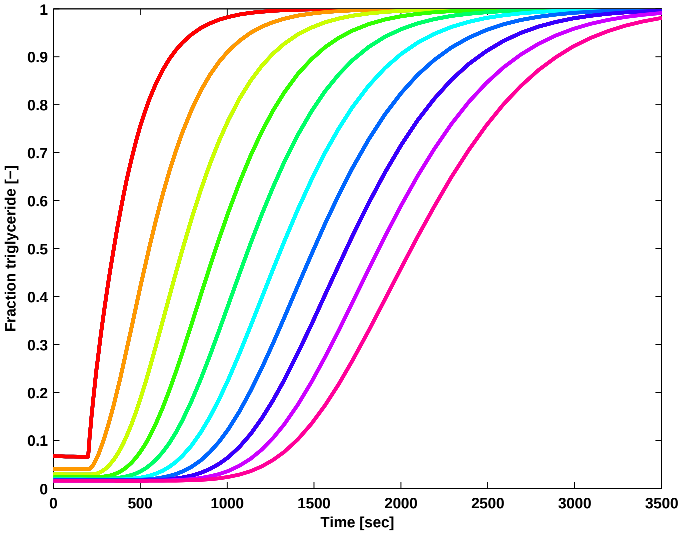

Figure 6.13: Case 4, No methanol in the inlet flow. The figure shows the changes for the first to the last reactor. The first reactor is to the left while the last reactor is to the right.

Case 5: Less methanol into the reactor than required by stoichiometry. It can be seen that by removal of methanol the reactions will not take place in the desired extend and it will end up with mainly triglyceride flowing through the reactors. It can be seen that the amount of diglyceride increases as the intermediate are not reacted further. Methanol will now be the limiting reactant for the reactions. The amount of products will now be given by the amount of methanol in the feed, and it can be seen that no glyceride will be produced. From Figure 6.14 it looks like only the first reaction is taking place since the amount of methyl ester is approximately 1/3 of the original.

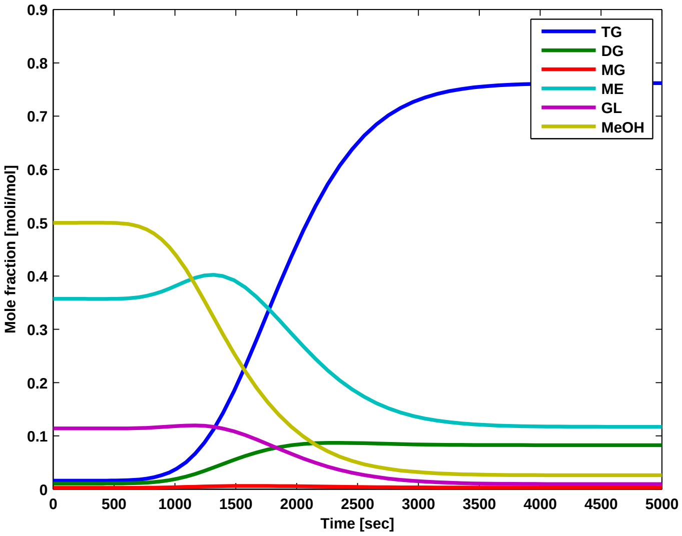

Figure 6.14: Case 5, Less methanol than required by stoichiometry in the reactor and the responding changes in the outlet flow composition.

Case 6: Some of the intermediate monoglyceride has been added to feed composition. From Figure 6.15 it can be observed that by adding MG the amount of methanol decreases while the flow of the products and intermediates increase. If DG was added instead of MG the amount of products increased more as expected by stoichiometry.

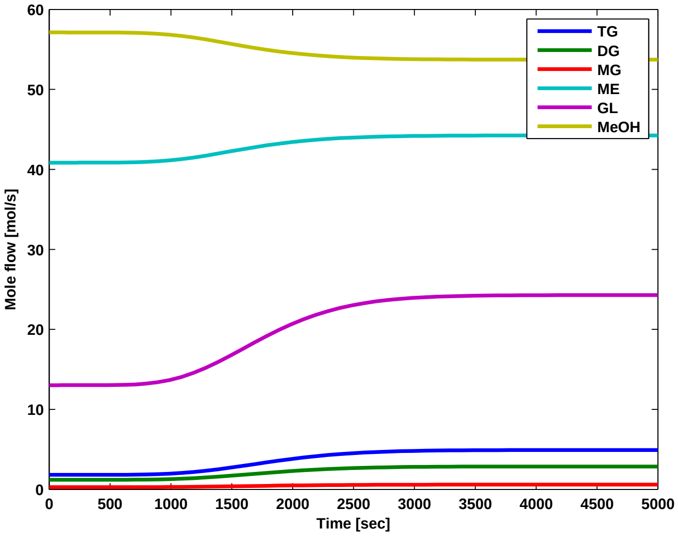

Figure 6.15: Case 6, Changes in outlet composition when some of the intermediate is added in the feed.

The cases given above indicate that the reactor response is as expected.

6.3 Settling tank

The case study for the settling tank was used to check that the flow was smoothed out and that the flows of the different phases were changing by disturbances in the inlet.

6.3.1 Result of case study of settling tank

From case 7 and 8 where a large τ_C has been introduced to make sure the controller is operating smoothly it looks like the settling tank is working with its purpose.

Case 7: Changing the inlet flow by + 10% to the settling tank without any other changes it can be seen in Figure 6.16 that the total outlet flow goes towards the new inlet flow, but over significantly larger time. This is the desired response to avoid disturbances in sensitive downstream equipment.

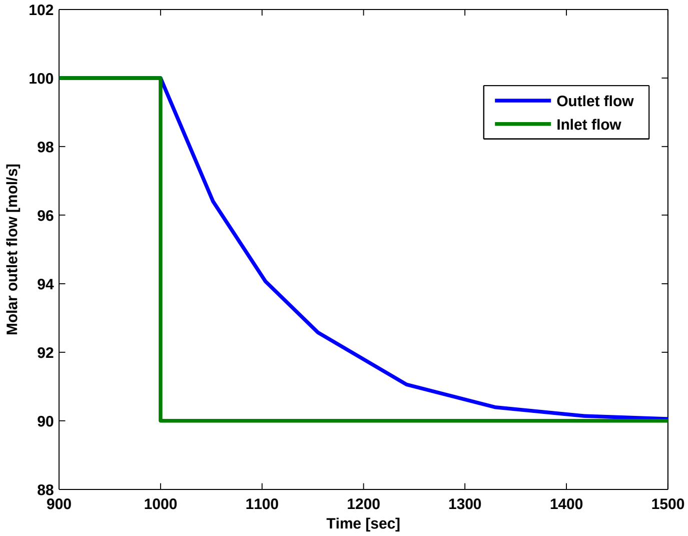

Figure 6.16: Case 7, Response in the total outlet flow from settling tank when a disturbance in the inlet flow was introduced.

From Figure 6.17 it can be seen that the flow of both phases changes with the same percentage as the disturbance in the inlet flow. This is expected as the composition is the same as before and only the amount changes.

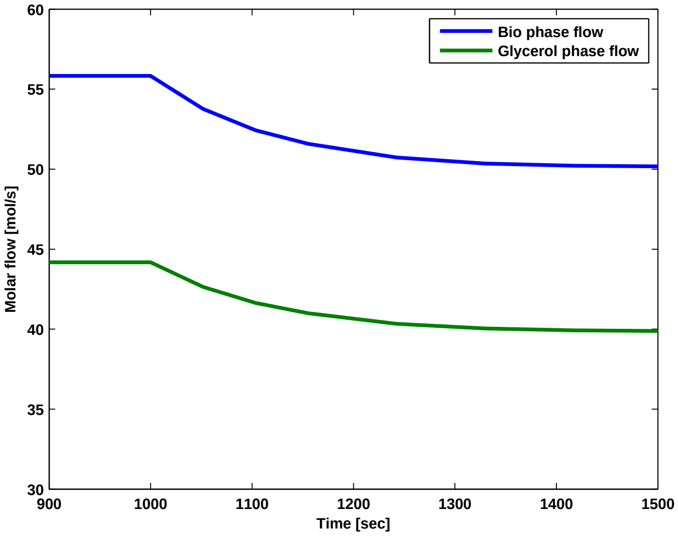

Figure 6.17: Case 7, Response in the flow of the different phases from settling tank when a disturbance in inlet flow occurred.

Case 8: The fraction of glycerol was reduced and the fraction of methyl linoleate was increased in the inlet flow. It can be seen from Figure 6.18 that the biodiesel phase increases while the glycerol phase decreases. It can also be observed that the changes happens very smoothly so that disturbances downstream will be small. The response is as predicted since the disturbance will be ”diluted” in the settling tank.

From Figure 6.19 it can be seen that the total outlet composition before splitting into phases changes slowly as the volume of the tank is significantly larger than the inlet flow. This shows how the composition in the tank changes with disturbances in the inlet composition. This is what could be expected when the tank is perfect mixing.

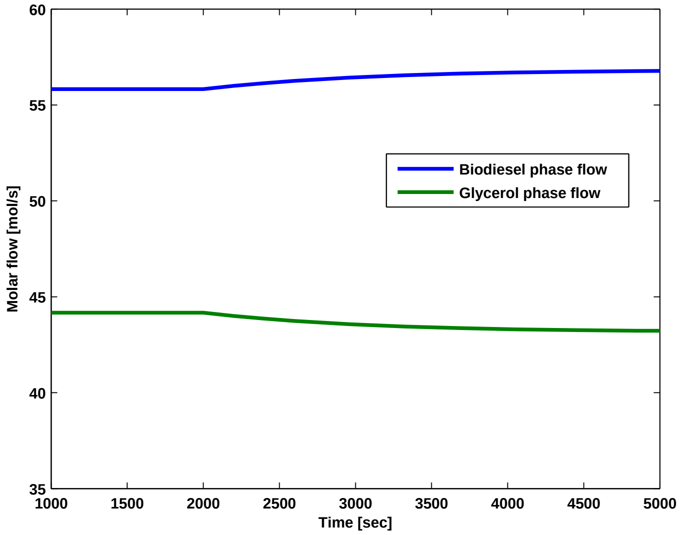

Figure 6.18: Case 8, The changes in flow of the different phases with a change in inlet composition.

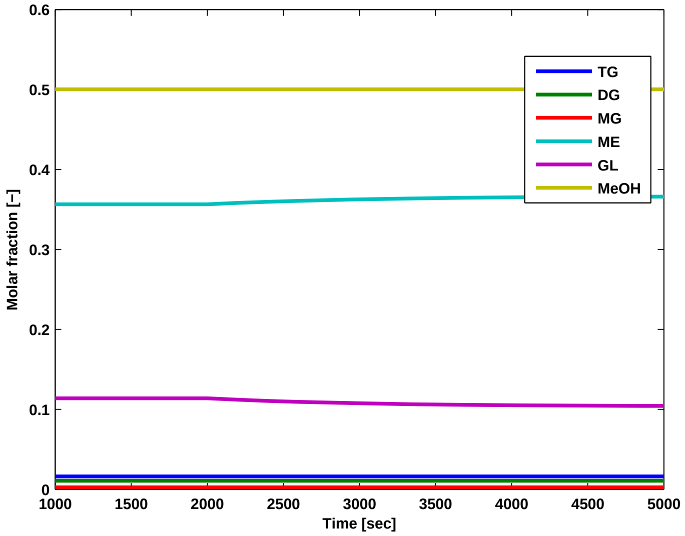

Figure 6.19: Case 8, The variation in outlet tank composition with a change in inlet composition.

6.4 Distillation

The distillation column is for purification of biodiesel phase.

6.4.1 Result of case study of distillation column

Case 9: Step change in the feed composition into the distillation column for purification of biodiesel, by increased amount of methanol.

When the fraction of methanol into the column increases and the bottom composition is tightly controlled to its setpoint the fraction of methanol in the vapour phase increases. From Figure 6.20 it can be seen that the controller for the bottom composition leads the composition back to the given setpoint. It could also be said that if the purity of biodiesel never should get below 99.6 % a backoff should be included and the setpoint in the model should be reduced by the shift rule. Biodiesel will not be sold directly as it is produced, but probably stored in tanks before shipped. Since disturbances in flow composition can fluctuate in both directions the setpoint probably do not need to be set as low as 0.002 from the peak in Figure 6.20 as the disturbances will cancel each other out when biodiesel is stored.

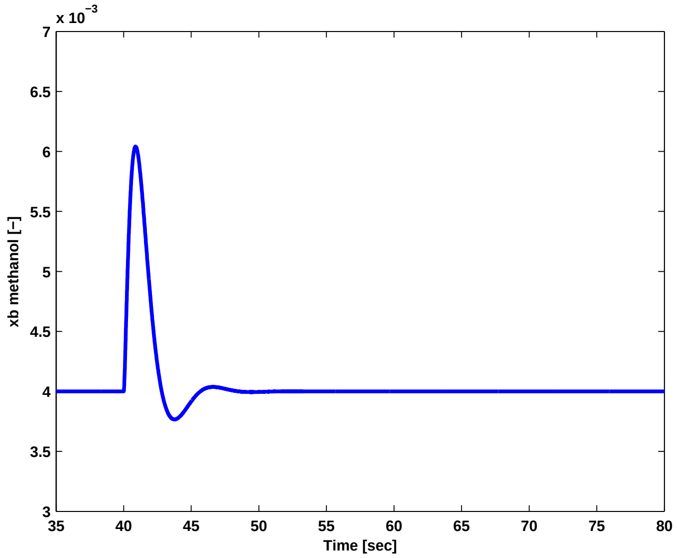

Figure 6.20: Case 9, Response in bottom composition when a step change was applied in the feed composition.

When the fraction of methanol in the inlet flow increases it can be expected that the vapour flow increases while the liquid decreases when the relative volatility is constant (Figure 6.21).

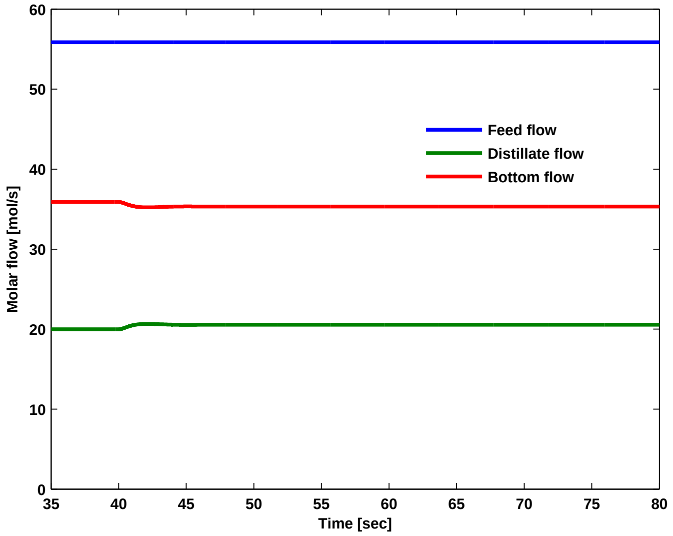

Figure 6.21: Case 9, Response in flows for distillation column when a step change was applied in the feed composition.

Case 10: Step change in the feed flow rate by +10%.

The response in distillate and bottom flow (Figure 6.22) shows that the total balance is fulfilled after the disturbance.

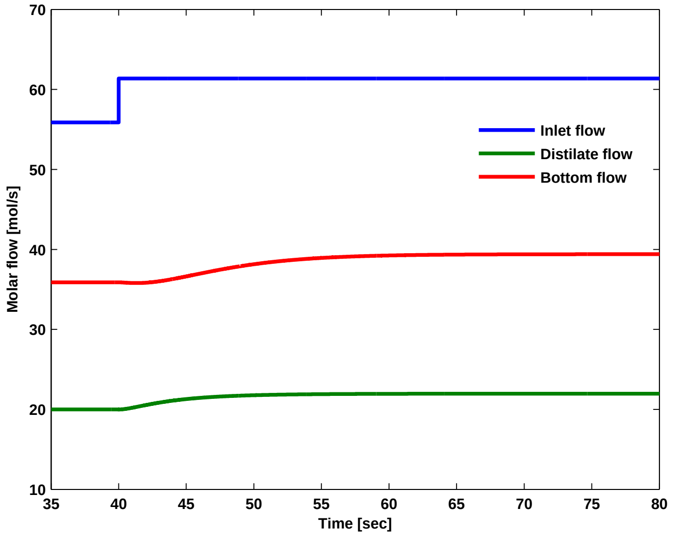

Figure 6.22: Case 10, Response in distillate and bottom flow in distillation column with a step in inlet flow.

When the flow in the column increases the required energy to get the required purity will increase as more methanol should be distillate off (Figure 6.23). The reflux will also increase to ensure the column performance.

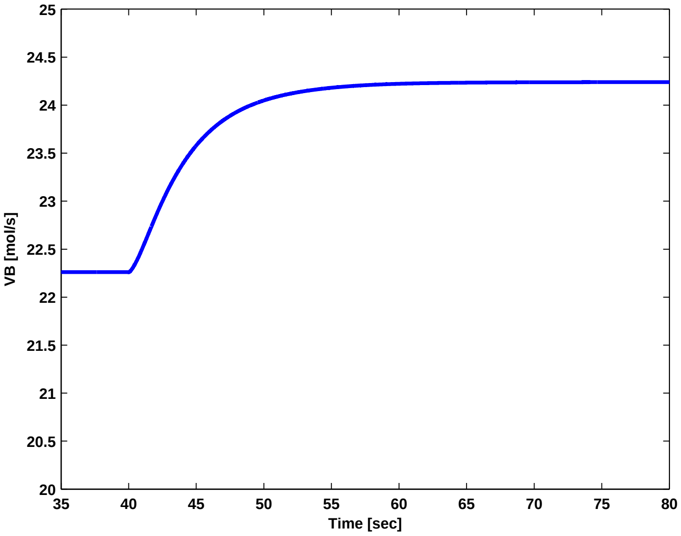

Figure 6.23: Case 10, Increased demand of boilup(VB), with increased inlet flow.

It is desired that the tight controller for the bottom composition always controls the expensive product at is specifications. The controller for the bottom composition leads the fraction in the bottom back to the set point after disturbance in the feed, see Figure 6.24. This is consistent with the desired response since biodiesel is the expensive product.

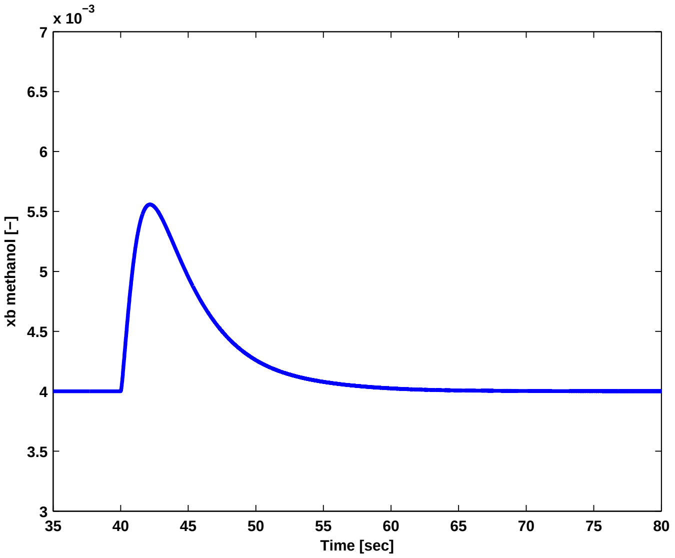

Figure 6.24: Case 10, Response in bottom composition when an increased inlet flow step was applied to the distillation column.

6.5 Flash tank

The flash tank is for purification of glycerol by removal of methanol.

6.5.1 Result of case study of flash tank

Case 11: Changing the inlet flow without changing the composition it could be expected that both flow will increase by the same percentage. The peaks in Figure 6.25 could be related to pressure build up before it get corrected for by the controllers. The opposite response was observed with reduced inlet flow since the pressure is reduced before the control units reduces the outlet stream so the inventory builds up again.

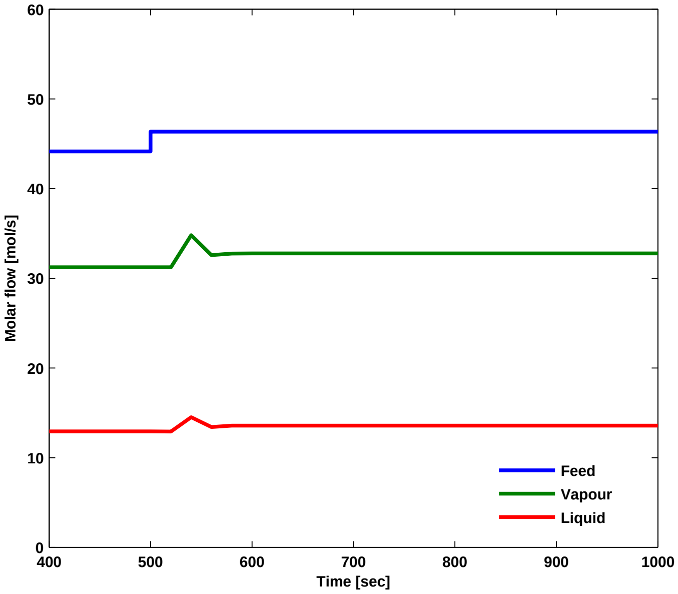

Figure 6.25: Case 11, The flow response in the flash tank due to increased inlet flow.

Case 12: Increasing the fraction of methanol in the inlet, it will be expected that the vapour flow increases while the bottom flow decreases (Figure 6.26). Due to the high relative volatility between the two components the vapour flow will mainly be the methanol entering the tank, and an increase in methanol fraction in will result in increased vapour flow. If the fraction of glycerol to the flash increases the opposite response was observed with an increased liquid flow and decreased vapour flow.

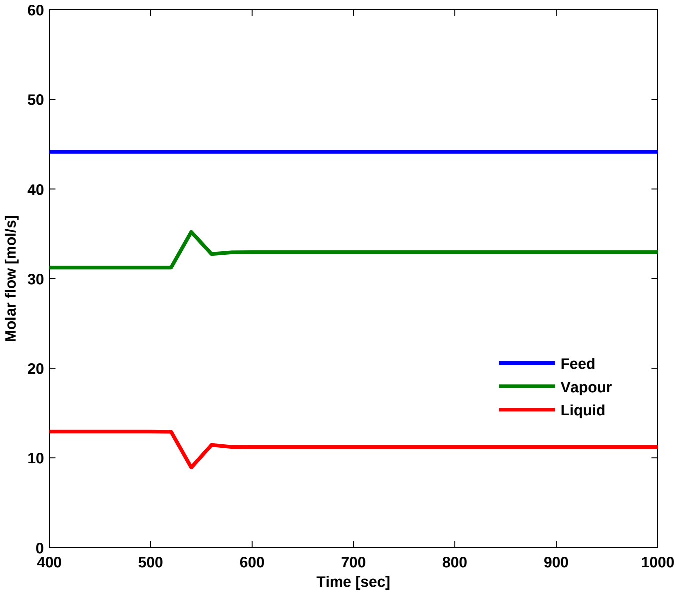

Figure 6.26: Case 12, Response in vapour and liquid flow due to increased fraction of methanol in inlet flow to flash tank.

Case 13: Mole fraction of methanol in the different phases at nominal operation. It can be seen in Figure 6.27 that the top product mainly contains methanol, while the bottom product contains glycerol in a purity above the required 92 % [1]. This high purification in the flash is due to the high relative volatility between the components and explains the behaviour observed in the two previous cases.

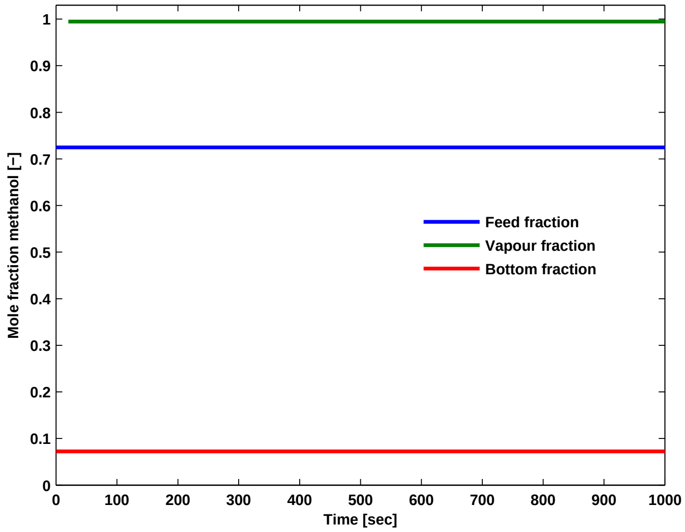

Figure 6.27: Case 13, Nominal fraction of methanol in flash tank streams.

6.6 System response to increased feed flow

By applying a step change to the inlet flow the responses out from the plant was as expected with an even percentage increase in all flows (Figure 6.28). The settling tank smooth out the disturbances downstream, but the total balance of the system is satisfied. It was also observed that the composition in the different flows was constant indicating correct performance of the model.

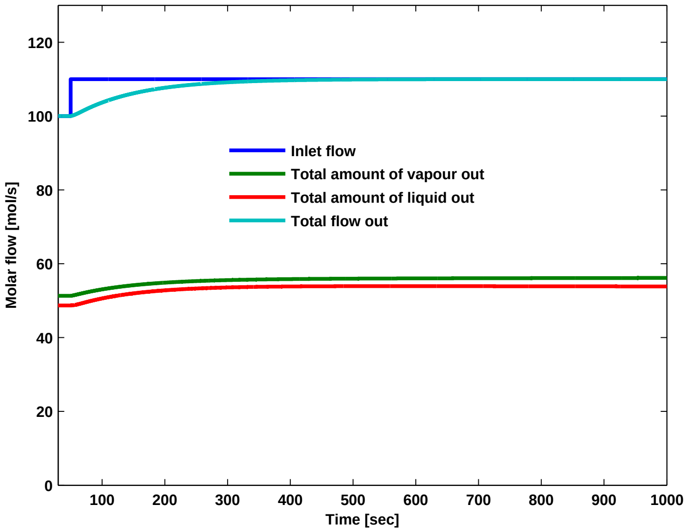

Figure 6.28: Overview response in the system with a step in the feed flow.

When the reaction conditions is nominal with an excess of methanol of 100 % the composition from the reactor is $\sim$50 % methanol and the rest is triglyceride, diglyceride, monoglyceride, methyl ester and glycerol. The given composition contains approximately $\sim$50 % light component and $\sim$50 % heavy component and as observed it is expected that the total vapour and liquid flows are approximately the same.

It was only performed a disturbance case for the amount of feed flow and none for composition disturbance due to slow model.

7 Discussion

From the case studies in front the model seems to operate as expected, but there is still room for improvements in tuning, better parameter fit, and more variable dependence like temperature, catalyst quality etc. The case studies are done for fictive disturbances and a better validation would be to know the range of an industry plant operating condition, tune and then perform disturbances expected in industry. If the model then respond as observed in the field, it can be used to predict the response of new disturbances. If the cases are unrealistic the reliability of the model can be less than first predicted. The model is very simplified and will therefore never represent a plant in detail, but it can reflect the main transfer of disturbance through the units. If disturbances to sensitive equipment are significantly larger or quicker than applied in model validation, the conditions might fall outside the operation range of the model.

Some of the values are taken from different articles or calculated from articles, and ideally all data should have been taken from one consistent source in industry to have the desired reliability. If all data are from the same source eventually impurities will be the same in all measurements and predicted values. The literature values given in different articles are over a wider range than desired and all data should be evaluated more extensively before the model is applied in industry.

The weakest units at the moment are the purification units. The flash tank and the distillation column should operate at nominal values and new steady states should be implemented before they are investigated more extensively to get desired model reliability. The control on the flash unit has not been tuned and checked in the desired extend for application on industrial cases. By including industrial nominal flash and resizing, the model could have practical use for checking responses.

The pairing for the control of the distillation column is taken as the most common configuration with LV. In reality another configuration might be the best suited and all the possible configurations should be checked. A better configuration might be to use a constant ratio between the boilup and feed flow for bottom composition control. A useful result of the model could then be to test new control structures, before applied on site.

Methanol from the two purification units will be a recycle stream and the model could be completed by including recycling. By including the recycle loop, the danger for snowballing can also be simulated.

At the moment the model script for all units together is slow and an improvement in solution time will be necessary to get the desired practical application. The long solution time is the reason for only one case study on feed flow for the system as one unit. With a quicker model more complex disturbances can be applied and the responses checked. In industry a disturbance seldom occur alone so the model should be able to handle complex disturbances with reasonable solving time.

8 Conclusion

The model including continuous-stirred reactor tanks in series, settling tank with phase separation, and purification of products by methanol removal has been created. A model for each units have been created separately for quick disturbance response check. The system model is slow and difficulties with case studies here are related to long computational time. The model is a very simplified version of a real plant and will only cover main aspects of disturbance response.

When disturbances are applied to the system, the model with its simplifications seems to react as expected (Figure 6.28). The very simplified model can be used for rough observation of system response to disturbances. The simplified model will further be used in connection with industry for plant response and control purposes. For connection to industry the model must be sized for the given flow, with the given equipment volumes.

Further work should focus on reducing model solution time and introduce more system affecting variables like temperature, catalyst, without making the model too complex. All units should in addition be made sure they are at steady state from the beginning by finding the optimal flow values for reflux, boilup, and outlet flows for setpoints. Literature values used in industry should be found and introduced for better validation and increased practical use of the model.

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A CD with Simulink model