

PAPER NAME

Sahra.Darabi.Thesis (Final Edited).docx

AUTHOR

Meshkat Dolat

WORD COUNT

15326 Words

CHARACTER COUNT

86600 Characters

PAGE COUNT

72 Pages

FILE SIZE

15.1MB

SUBMISSION DATE

Aug 27, 2023 11:30 PM GMT+1

REPORT DATE

Aug 27, 2023 11:31 PM GMT+1

● 48% Overall Similarity

The combined total of all matches, including overlapping sources, for each database.

- 30% Internet database
- 41% Publications database
- Crossref database
- Crossref Posted Content database
- 22% Submitted Works database

● Excluded from Similarity Report

- Bibliographic material
- Quoted material



Chemical Engineering Department-BIHE

Dissertation for Bachelor's Degree

Study on Production of Biofuel (Biogas, Biodiesel) and Process Simulation

Author: Sahra Darabi

Supervisor: Dr. Kamran Keynejad

Spring 2023

Acknowledgments

Studying at BIHE university was a great opportunity for me to meet very good professors who persuaded me to learn for my own growth. I would like to extend my deepest gratitude to Dr. Kamran Keynejad, who guided and supported me in the completion of my dissertation. I am also grateful to Chemical Engineering Department and Mr. Meshkat Dolat and appreciate efforts. In the end, I also wish to thank my family and friends for providing me unconditional supports during this era.

Abstract

In this research, the production methods of biodiesel and biogas, which are one of the types of renewable fuels, have been examined. In this report, fossil and renewable fuels are first introduced, and then more information is provided about biofuels. In chapter 2, recent researches related to biodiesel production methods and process simulation of these fuels have been examined and summarized. In chapter 3, one of these processes has been re-simulated by ASPEN HYSYS software, and a series of process factors such as temperature, pressure and current intensity have been investigated and presented as case studies. The result of this case study shows:

- 1-If the reactor temperature changes from 75°C to 30°C, the mole fraction changes from 0.2263 to 0.2275, which is equivalent to 0.57%.
- 2-If the mass flow of glycerin changes from 20 kg/h to 200 kg/h, the mole fraction changes from 0.2625 to 0.2650, which is equivalent to 0.95%.
- 3-If the flow temperature changes from 5°C to 100°C, the mole fraction changes from 0.2585 to 0.2700, which is equivalent to 4.44%.
- 4-If the inlet stream temperature changes from 20°C to 150°C, the mole fraction changes from 0.9994 to 0.9997, which is equivalent to 0.03%.

Chapter 1: Introduction	1
1.1 Fossil Fuels	2
1.1.1 Petroleum	2
1.1.2 Gasoline	2
1.1.3 Liquefied Petroleum Gas	2
1.1.4 Fuel Oil	3
1.1.5 Natural Gas	3
1.1.6 LNG Industry	3
1.1.7 Coal	3
22 1.2 Renewable Energy	4
1.2.1 Solar Energy	4
1.2.2 Wind Energy	4
1.2.3 Geothermal	5
1.2.4 Hydropower Energy	5
1.2.5 Ocean Energy	6
1.3 Biomass	6
1.3.1 Biomass Converting to Energy	7
1.4 Biofuel	8
1.4.1 Types of Biofuels	8
1.5 Biogas	9
Chapter 2: A Review of Articles	10
2.1 Simulation of Biofuel Production via Fast Pyrolysis	11
52 2.2 Biodiesel Production by Supercritical Methanol Transesterification	17
1 2.3 Thermochemical Waste Heat Recuperation by Steam Reforming of Liquid Biofuels	23
2.4 Biofuel Transportation Applications	27
2.5 Biodiesel Plant Assessment	38
2.6 Biodiesel Production from Waste Vegetable Oils	45
Chapter 3: Examining the Change of Some Parameters on the Conducted Studies	55
3.1 Biodiesel Plant Configurations	56
3.2 Equipment Information	57
3.3 Process Description	58
3.4 Case Study	58

21	3.4.1 Case Study 1	58
51	3.4.2 Case Study 2	59
	3.4.3 Case Study 3	60
	3.4.4 Case Study 4	61
	Chapter 4: Conclusion	63
	References	65

²⁶Chapter 1

Introduction

1.1 Fossil Fuels

Fossil fuels found in Earth's crust. They have hydrogen and carbon, so they can be burned to produce energy. Natural gas, coal and oil are fossil fuel examples. The energy for heat and electricity to homes and businesses, running cars and factories is supplied from coal, oil and natural gas. Fossil fuels take millions of years to form. They are unrenrenewable resources. Almost three-fourth of emissions from human activities are because of fossil fuels in the last twenty years. The effort is to reduce dependence on fossil fuels and try to burn these fuels cleaner for environment. Scientists are trying to solve fossil fuel challenges to have enough fuel and decrease environmental damages for healthier human life. The United States Department of Energy is trying to burn coal cleaner. Using more natural gas helps to emit 50% less carbon dioxide into the atmosphere than coal [1].

1.1.1 Petroleum: Petroleum has an important role in different organizations and cultures. Gasoline, liquid petroleum gas (LPG), mazut, paraffin waxes, naphtha and lubricants are some examples of petroleum products [2]. Oil and petroleum effect on life quality and government's economy. Contact lenses, medicines and bandages are provided by petroleum [3]. 1.65 trillion barrels of oil is proved in the world until 2016, which is shown in Figure 1. This amount is equal with 46.6 times using per year, which means 47 years of oil is left [4].

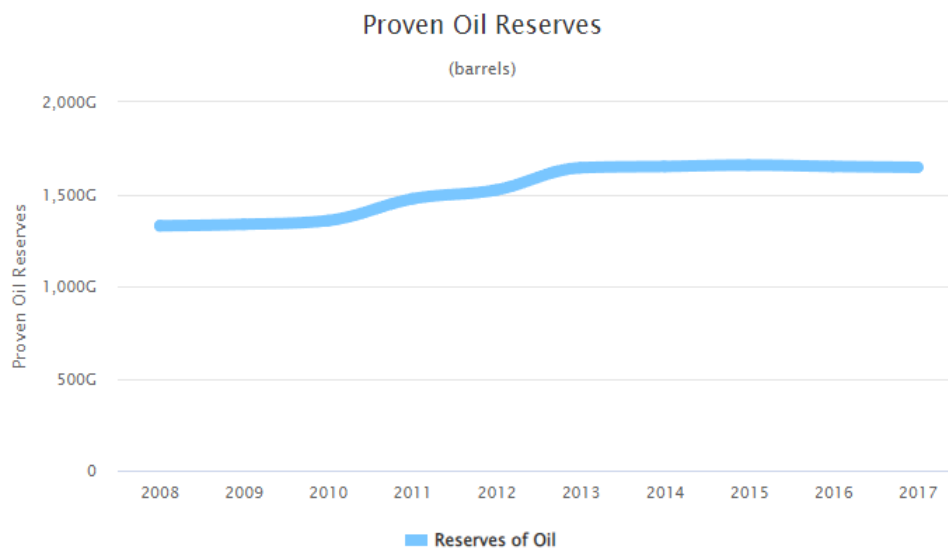


Figure 1-History of world's proven oil reserves.

1.1.2 Gasoline: Gasoline is a flammable liquid which is made of hydrocarbons and petroleum. Distillation produces gasoline. Polymerization, alkylation and isomerization are some methods which make better gasoline's quality [5].

1.1.3 Liquefied Petroleum Gas (LPG): LPG is used for cooking, heating and fuel for cars. It is a flammable fuel and also is mutagen and carcinogen. It is not corrosive, but it can dissolve some types of plastics, synthetic rubbers and lubricants. LPG can burn the skin and may be asphyxiate at high concentration [6].

1.1.4 Fuel Oil: Fuel oil (mazut) is a heavy, low quality fuel oil. Mazut can be used for house heating in Far East countries which do not have proper equipment to breakdown or blend mazut to form petrochemicals. Mazut is rated by its sulfur content, which means the feedstock effects on its sulfur content. The lowest amount of sulfur in mazut is 0.5% and the highest amount is 2-3.5% [7].

1.1.5 Natural Gas: Natural gas is an easy to burn gas which has no color and odor. Unprocessed natural gas is contained from methane, ethane, propane butane and pentane. In Alberta, a Canadian province, 25% of natural gas consumption is reported for commercial and residential. Petroleum refining, metal, plastic, glass industries and food processing use 75% of natural gas [8]. United states, Russia, China and Iran are the 4 top countries which use the most amount of natural gas [9].

1.1.6 LNG Industry: Liquefied natural gas (LNG) is formed by cooling down a natural gas about -162°C . LNG has a volume 600 times smaller than gaseous phase. LNG's volume reduction helps to store easier in tanks, Figure 2, for better shipping and transportation [10] [11]. LNG was used in different ranges such as residential, industrial settings for cooking, heating and electricity generation. LNG provided up to 75% of the commercial and residential's energy demand, 18% of electricity and 3% for vehicles in United States in 2009. LNG is safe to consume and transport and it is 90% less pollutant than diesel. It is also non-toxic, colorless, odorless and non-corrosive, so LNG is the cleanest fossil fuel. Global requirement for LNG is increasing due its low carbon production, easy to use for most of the applications and cost-efficient [12].



Figure 2-Huge tanks for LNG in the Rotterdam harbor.

1.1.7 Coal: Coal is formed from plants decomposition, which has rock form. Coal is cheaper than other fossil fuels and easy to store. Coal is used for heating, electricity generation and fuel. Anthracite Figure 3, bituminous, sub-bituminous and lignite are main types of coal [13] [14].



Figure 3-Anthracite, highest grade of carbon weight.

1.2 Renewable Energy

Renewable energy is energy that is produced from natural sources. They replenish at a higher rate than they consumed. The sun, Earth and wind have energy, so we can use this energy in different ways. Renewable energy produces lower amount of emissions than burning fossil fuels. Renewable energies are cheaper in the most countries, and also they present three times more jobs than fossil fuels. Renewable energy sources include: solar energy, wind energy, geothermal energy, hydropower, ocean energy and bioenergy (biomass) [15].

1.2.1 Solar Energy: solar power is a kind of energy that converts to electrical or thermal energy. Solar energy is the cleanest and the most abundant renewable energy source that is available. Photovoltaics or solar panels is shown in Figure 4, concentrating solar power and solar heating and cooling are kinds of solar technologies. Photovoltaics produce electricity from sunlight. It provides energy for calculators, commercial businesses and road signs. Concentrating solar power use the heat that generated of sun for large power stations like running traditional electricity-generating turbines in power plants. Solar heating and cooling uses for heating water [16] [17].



Figure 4-Solar panels.

1.2.2 Wind Energy: Wind energy uses wind to generate electricity or mechanical power. In this process, kinetic energy of the wind converts to mechanical energy or electricity. The power for

pumping water and grinding grain is supplied by mechanical power. In wind turbines aerodynamic force from rotor blades generates electricity, that work like an airplane wing. There is an air pressure difference across the two sides of the blades. The air pressure difference makes lift and drag forces. Lift force is stronger than drag, it causes rotor spinning. The rotor is connected to a generator which increase the speed of the rotation. The transformation of aerodynamic force to rotation of a generator generates electricity. There are two types of turbines: Horizontal-Axis Turbines and Vertical-Axis Turbines [18]. Here is a wind farm in Figure 5.



Figure 5-Wind power in Washington.

1.2.3 Geothermal: Geothermal energy, Figure 6, is a kind of energy which its heat produced inside the earth. The word geothermal is Greek, that means geo (earth) and therme (heat). Geothermal is used for generating electricity, heat buildings and bathing. Geothermal is renewable, baseload, domestic, small footprint and clean [19] [20].



Figure 6-Geothermal power plant (flash steam, combined cycle) in Iceland.

1.2.4 Hydropower: Hydropower, also called hydroelectricity or hydroelectric energy, is a kind of energy that uses the power of moving water to produce electricity. All types of hydropower facilities, use kinetic energy of water in motion. Hydropower plants are usually located near or on water sources, such as Cambodia's Hydropower plant in Figure 7. The producing electricity relies on the volume of

the flowing water and head. The more flow and higher head, the more electricity can be produced [21] [22].



Figure 7-Cambodia's hydropower project.

1.2.5 Ocean Energy: Each kind of renewable energy which its source is from sea. There are three main types of ocean technology: wave, tidal and ocean thermal. By converting the energy in the ocean waves to electricity, wave energy can be generated. There are multiple types of wave energy technologies for converting wave energy into electricity. Tidal energy has two forms, both of them generate electricity:

1-Tidal range technologies use potential energy which was created by height difference between low and high tides.

2-Tidal stream technologies catch the kinetic energy of currents flowing in and out of tidal areas, like beaches. Tidal stream devices work in an ordered series, like wind turbines.

Ocean thermal energy is produced by converting the temperature difference between ocean's surface water and deep water into energy. Ocean thermal plants can be floating or grazing [23].

1.3 Biomass

Biomass is renewable fuel that is based on plants and animals. Corn and soy are the most common biomass materials. Biomass can be burned directly for heat or be converted into electricity [24]. Biomass sources which are shown in Figure 8 include:

1-Waste from wood products factories, such as carpentry workshops, MDF factories, etc.

2-Agricultural waste bagasse from sugar cane factories

3- Production of biogas (renewable natural gas) from human sewage and animal manure

4- Molasses, factories for the production of sugar, production of ethanol- fuels resulting from biological reactions

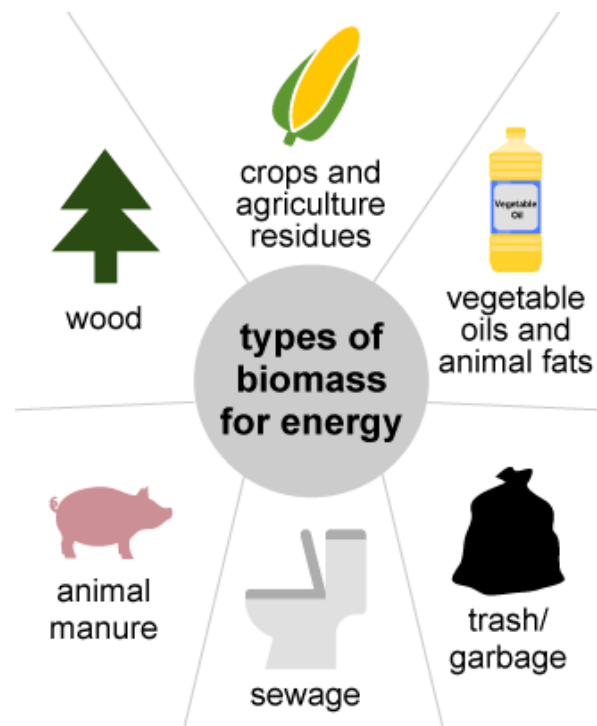


Figure 8-Biomass sources.

1.3.1 Biomass converting to energy

1-Direct combustion (burning) to produce heat: It is the most common way to convert biomass into necessary energy. Biomass sources can be burned directly for industrial process heat, heating water and buildings and for generating electricity in steam turbines.

2-Thermochemical conversion to produce solid, gaseous, and liquid fuels: Thermochemical conversion of biomass contains gasification and pyrolysis. These are both thermal decomposition processes. In these processes biomass feedstock materials are heated in closed, high pressure vessels. The difference in these two processes are amount of oxygen and process temperature.

Pyrolysis requires heating organic materials to 400-500 °C in the complete absence of free oxygen. Fuels like bio-oil, charcoal, methane, hydrogen and renewable diesel are produced from biomass pyrolysis. Bio-oil is produced by fast pyrolysis. Hydro treating is for processing bio-oil with hydrogen in high temperature and pressure with a catalyst. In hydro treating renewable gasoline, renewable diesel and renewable jet fuel are produced. Gasification process needs heating organic materials to 800-900°C. The steam injects to the vessel to produce syngas. Syngas can be used for heating, generating electricity in gas turbines and for diesel engines fuel. The processed syngas can be used in the Fischer-Tropsch process as a liquid fuel.

3-Chemical conversion to produce liquid fuels: Chemical conversion process or transesterification produces fats to produce biodiesel, such as animal fats, vegetable oils and greases into fatty acid methyl esters (FAME).

4-Biological conversion to produce liquid and gaseous fuels: Biological conversion includes fermentation and anaerobic digestion. Fermentation is a process to convert biomass into an alcohol like ethanol. Ethanol can be used as fuel in vehicles. Anaerobic digestion is a process to produce renewable natural gas at sewage treatment plants and at dairy and livestock operations. Renewable natural gas can be formed from solid waste landfills. Renewable natural gas which is refined well, has the same uses as fossil fuel natural gas such as water heating, transportation, cooking and electricity [25].

These are some of the advantages of biomass:

- 1-Biomass is carbon neutral.
- 2- It is always available as a renewable source of energy.
- 3-It is cheaper than fossil fuels.
- 4-it produces less garbage on landfills.

It should be noted that biomass has some challenges:

- 1-biomass plants need a lot of space.
- 2-it is not as efficient as fossil fuels.
- 3- that is not entirely a clean fuel [26].

1.4 Biofuel

The fuels that are driven from biomass, that is based on plants and animal wastes.

1.4.1 Types of Biofuels

Biomass sources can be burned to produce heat, like wood, grass and other kinds of biomass. The heat can be used for running generators to produce electricity in power plants. Liquid biofuels have been considered for many uses, especially for transportation. The most production of liquid biofuel is ethanol. It is produced by fermenting sugar or starch. The two important producers of ethanol are Brazil and the United states. Gasohol is produced in the United States. Gasohol is a kind of ethanol biofuel which is produced primarily from corn grain, and it is blended with gasoline. It consists of 10% ethanol.

As it is shown in Figure 9, “second generation” or cellulosic ethanol is derived from wood chips, municipal waste and crop residues. Cellulosic ethanol is usually made of waste products from sugar processing than can be get on low quality lands. The conversion ratio is lower than first generation.

Biodiesel is the second most common liquid biofuel. It is made primarily from oily plants like oil palm or soybean. Biodiesel is used in diesel engines. It is blended with petroleum diesel fuel in different percentages. Algae and cyanobacteria can be used a source of “third generation” of producing biodiesel, but it is a little bit challenging in economical way. Some kinds of algae include 40 weight percent lipids. It can be converted into synthetic petroleum or biodiesel. There are some evaluations mention that algae and cyanobacteria can produced 10-100 times more fuel than second generation biofuels per unit area. Biofuels which contain biogas and methane, methanol, butanol and dimethyl ether are in development [27].

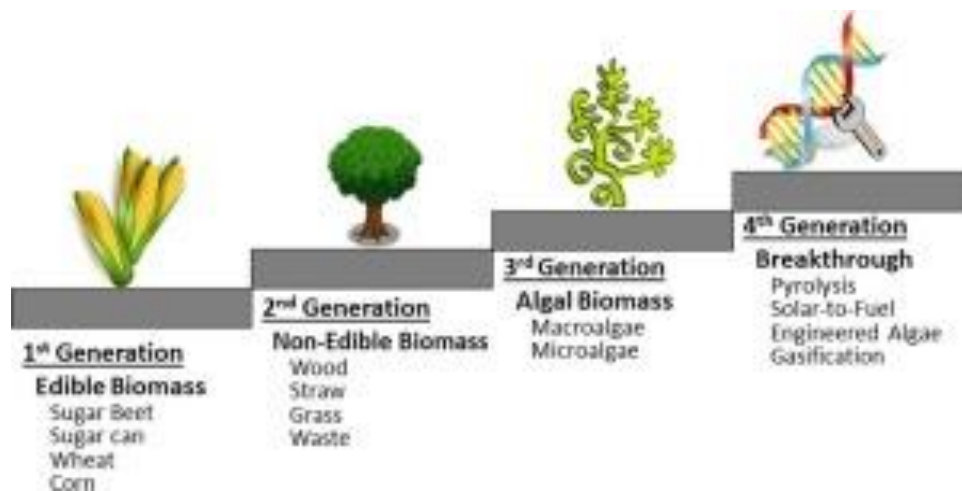


Figure 9-Biofuel generations.

1.5 Biogas

Biogas is a renewable fuel which is produced by the breakdown of biomass. It is a renewable energy source and environmentally friend. It is produced when biomass, such as animal waste or food are broken down in the absence of oxygen. Biogas can occur naturally or as a part of industrial processes to be created as a fuel. Compressed biogas can be used as vehicle fuel. Biogas can be used instead of natural gas if it refined properly. It is known as bio methane and can be used like methane such as, heating, cooking and industrial transportations [28].

Biogas is produced from a natural process in a closed area, so methane-carbon dioxide ratio can be variable. 60% methane-40% carbon dioxide is the most common ratio. It is expectable that biogas include 45 to 75% methane- 55 to 25% carbon dioxide. Here are some of the advantages of using biogas:

1. It is renewable and clean source of energy which is depended on carbon neutral process. It does not release new amounts of carbon into atmosphere.
2. It reduces water and soil pollution because of human feces and animal manure. It helps to have a clean, healthy and safe environment entire the world.
3. It reduced the amount of methane released into the atmosphere. It counters climate change which has important effect on living animals and human.

Here are some of the disadvantages of biogas:

1. Biogas is produced from a natural process, so it is challenging to control its compounds of constituent ratios.
2. Biogas works better in warm climates. It means that it is not available entire world identically [29].

Chapter 2

A Review of Articles

In this chapter, we will have an overview of 6 articles that we studied in the field of biodiesel production process and simulation, and briefly stated here to identify the factors.

2.1 Simulation of Biofuel Production via Fast Pyrolysis

Jens F. Peters and et al. published an article entitled “Simulation and life cycle assessment of biofuel production via fast pyrolysis and hydro upgrading” in 2014.

The process is done by Aspen Plus. The simulation includes the pyrolysis plant and bio-refinery. The bio-refinery includes hydro-treating, hydrocracking, distillation and steam reforming sections. The obtained synthetic biofuels are compared with their fossil fuel equivalents in order to quantify their potential environmental benefits. Biofuels are considered as a solution for greenhouse gas (GHG) reduction. Bio-oil is produced from fast pyrolysis. Bio-oil is high density and has moderate heating value. It can be upgraded to gasoline and diesel in a bio-refinery. Biofuel can lead to save 60-88% GHG vs fossil fuels. LCA applies to bioethanol and biodiesel processes. The production is assumed in central Spain. The functional unit (FU) used in this work is 1 MJ of energy content of the obtained synthetic biofuel mix (gasoline and diesel). Biofuels are produced by fast pyrolysis in this system. The entire system includes these subsystems which is shown in Figure 10: agriculture and cropping, biomass transport, pyrolysis plant, bio-oil transport and bio-refinery plant.

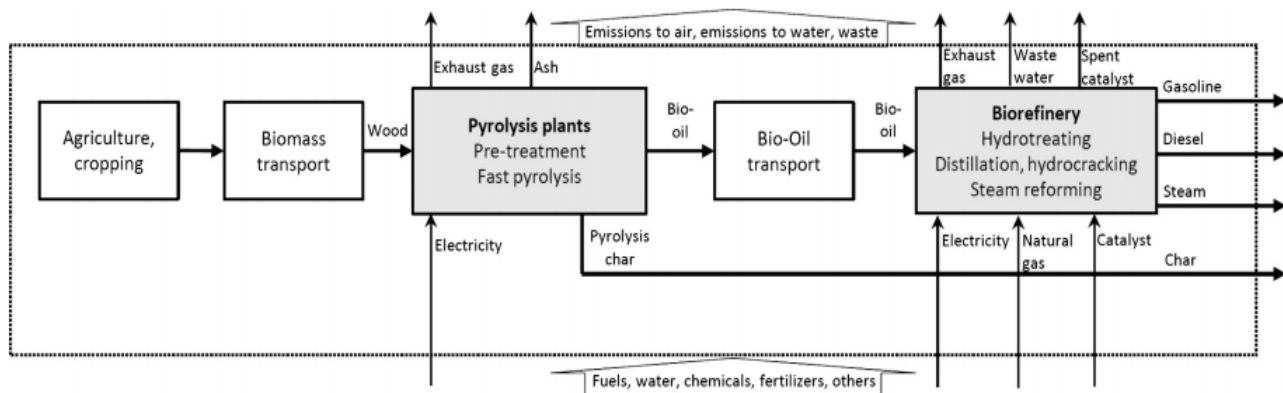


Figure 10-Block diagram of the biofuel system.

Process simulation

Pyrolysis plant: Raw biomass converts into bio-oil and char (by product) in this plant.

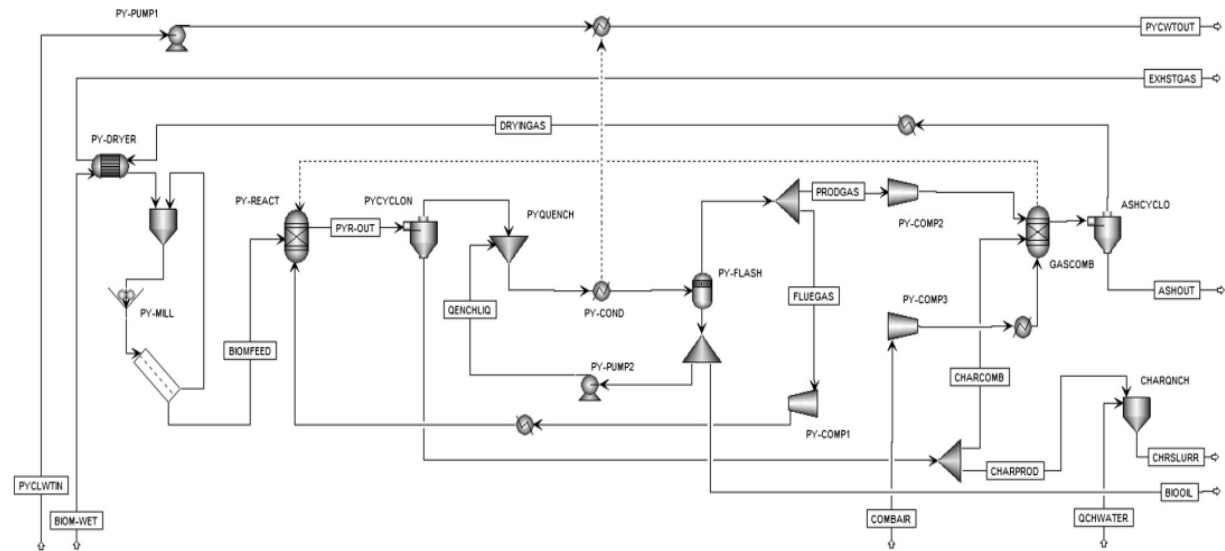


Figure 11 Aspen Plus flowsheet of the pyrolysis plant.

Pretreatment

Hot exhaust gases from chamber and coal dry wet biomass to reach biomass moisture to 7%.

Pyrolysis Reactor

Dry biomass decomposes into bio-oil or biogas in the pyrolysis reactor. Here are common conditions in a circulating fluidized bed reactor: 520°C, vapor residence time of 0.5 s, bed residence time of 2 s and gas to feed ratio of 1.0 by weight. The products are modeled in details. Bio-oil includes of more than 31 model compounds. coal is an unconventional component with H, N, S, O and Cl content.

Product Recovery

The pyrolyzed products should pass certain number of cyclones for residual vapors and coal separating. The products are quenched with cold bio-oil. It prevents secondary decomposition reactions. A water cooler is needed for temperature reduction to reach the liquid recovery to maximum point. 50% of alkali metals, except Cd, shifted into oil at pyrolysis temperature which is 500°C. Some parts of recycle liquid does not return to the quench coolers. They leave pyrolysis plant as an oil by-product.

Gas and Char Combustor

One of the gas fraction parts returns to the pyrolysis reactor, and the other part is burned in combustion chamber. Some pyrolysis coal fraction is needed to burn to provide enough heat for pyrolysis reactor. The coal separated in the cyclone into product fraction and fuel fraction. Combustion exhaust gases are needed to dry the biomass. The biomass dryer defines the exhaust gas flow and air flow to the combustion chamber.

Bio Refinery

Hydro treatment

A two stage catalyst hydro-treatment transforms the bio-oil into an oxygen-free hydrocarbon product which has C4-C18 chain length. The product includes alkanes, naphthenes, mono- and poly-aromatics, phenols, alcohols and furans. The catalyst is commercial Co-Mo catalyst. The bio-oil and hydrogen are fed to the first reactor at the pressure of 170 bar and temperature of 270°C. The bio-oil is stabilized for its more processing in the reactor. The stabilized oil is deoxygenized to <2% of oxygen content at the temperature of 350°C and the pressure of 150 bar in the second hydrotreating reactor. After cooling the product, the aqueous part of the product is separated in a high-pressure flash unit. The aqueous fraction includes 1% organics, mainly about alcohol and phenols. A cooling water circuit is needed to cool the products of the hydrotreater. Aspen Plus cannot simulate catalyst consumption in the hydrotreaters.

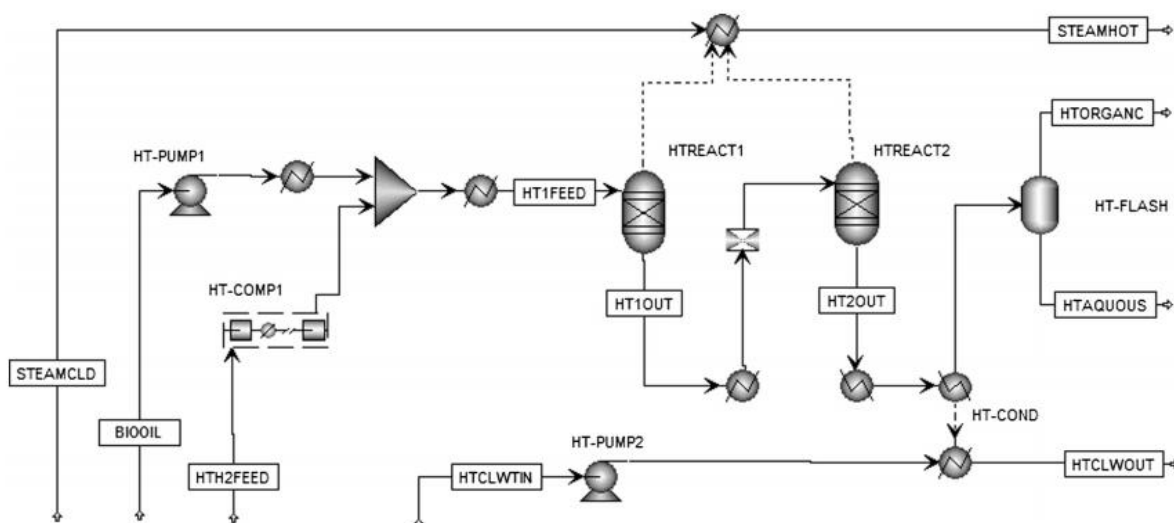


Figure 12 Aspen Plus flowsheet of the hydrotreating section.

Distillation

The organic fraction from hydrotreatment is dewatered and separated into fuel fractions by distillation. By hydrocracking, the heavy bottom transforms into lighter compounds. The organic fraction includes unreacted hydrogen from hydrotreating part. A pre-flash unit cracks the feed stream into a gas fraction and a liquid fraction to separate hydrogen from organic fraction. Then the separated fractions go to the distillation process. First distillation column has 8 stages and operates under atmospheric pressure. Gasoline fraction is the lighter product of the heavier fraction. There is also a gas fraction as a product that cannot be condensed in cryogenic condition. The bottom stream goes to the second column. The operation is done in 9 stages and separates diesel fraction under vacuum.

Hydrocracking

The heavy fraction is mixed with hydrogen and pressurized. It is fed to the hydrocracker to crack the heavy hydrocarbons into lighter molecules in a temperature of 670°C, the pressure of 90 bar and a Ni catalyst. There is a pressure drop for product stream. It is cooled and recirculated for mixing with the organic fraction from hydrotreating. The condensers of distillation columns need a cooling water circuit. The steam product from the hydrotreating section and combustor in steam reforming section provides heat for reboiler.

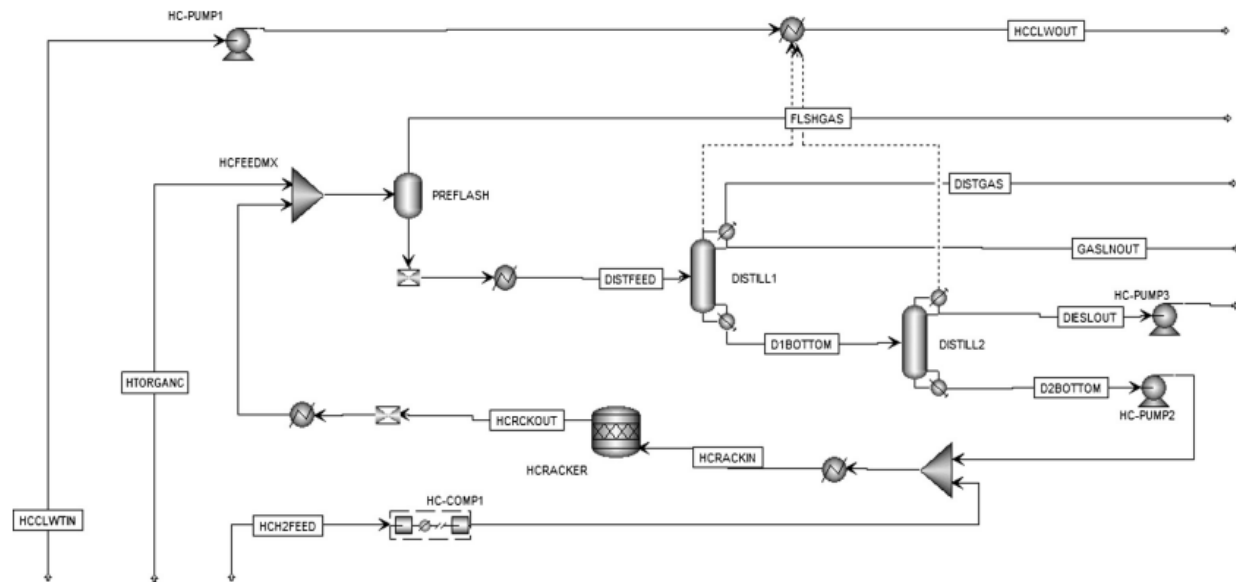


Figure 13 Aspen Plus flowsheet of the distillation and hydrocracking section.

4 Steam Reforming

The gases from pre-flash unit in distillation section are divided into a fraction for reforming and a fraction for direct combustion. Gas fraction for reforming is mixed with water. It is heated and fed into the steam reforming reactor with demanded amount of natural gas. The temperature of 950°C shows best results for gas feed composition which includes high amount of non-methane gases.

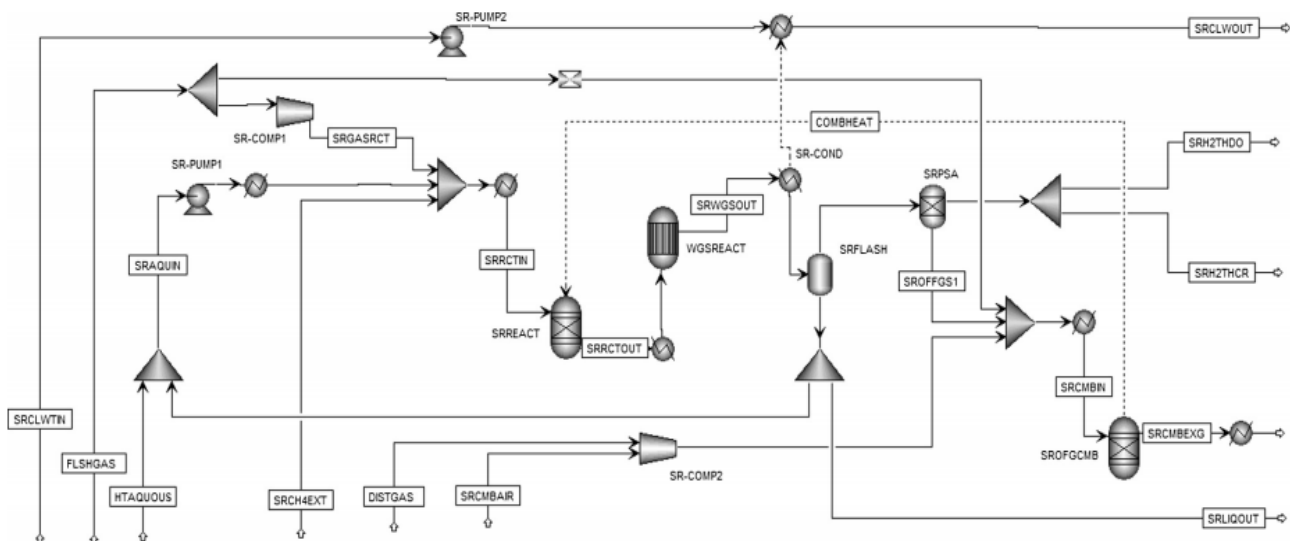


Figure 14 Aspen Plus flowsheet of the steam reforming section.

4 Water gas shift

The reactor product stream goes to the water gas shift reactor after cooling down. The water gas shift reactor calculates the products by Gibbs free energy. The operation condition is under 350°C, the conversion of CO and H₂O to CO₂ and H₂ the amount of hydrogen is increased. The water fraction

is separated from gases after product stream cooling down. There is also a PSA unit which separates 90% of the hydrogen from gases, then they will be sent to the hydrocracker and hydrotreater sections.

Combustor

The stream is gas-free, which includes CO_2 and unreacted hydrocarbons. It is mixed with gas stream from distillation column, combustion air and separated fraction from flash gas stream to combust directly. The demanded heat for steam reforming reactor is provided in the combustor. A part of condensed water is separated in SRFLASH. It is recirculated and enters to the steam reforming process. The excess water exists the plant as wastewater. A cooling water circuit condenses the aqueous fraction.

Pyrolysis plant

The information about the reactor efficiency and product compositions is obtained from the simulation. The yields are 68.8% bio-oil, 14.3% gas and 16.9% char.

These yields are reported for a hybrid poplar feedstock by Jones et al. 75% bio-oil, 12% gas and 13% char. Ringer et al. 73% bio-oil, 12% gas and 15% char. Oasmaa et al. report yields of 25% water, 30% sugar-derived, 25% aldehydes and ketones, 17% degraded lignins and 3% others for eucalyptus wood under similar reactor conditions. The values are close to simulation results. In addition, Dong et al. mentioned 12% anhydrosugars and furans, 15% aldehydes, 6% ketones, 18% acids and 25% phenols and degraded lignin for poplar wood pyrolysis in a condition with 500°C and a residence time of 5. Organic acid has higher content than degraded sugar in simulation. It may be cause of longer residence time, which leads to sugar derived fraction, levoglucosan and xylose, decomposition.

Bio-refinery

In bio-refinery, 0.96 MJ of bio-oil is demanded to produce 1 MJ of bio-synfuels, 0.27 MJ of natural gas and 0.04 MJ of electricity. Final product compositions for two-stage hydro-treating is shown in Table 1.

Table 14 Final product composition for the two-stage hydrotreating process according to simulation results.

Product	Compound group	Yield (%)
Gasoline C ₅ -C ₁₂	C ₅ -C ₁₀ paraffins	15.70
	C ₅ -C ₁₀ naphthenes	31.08
	Polynaphthenes	0.00
	Benzenes, phenols	4.75
	(Total Gasoline)	51.53
Diesel C ₈ -C ₁₈	Propylbenzene, propylphenol	2.38
	Naphthalene	1.06
	C ₁₁ -C ₁₈ (Poly-)naphthenes and paraffins	25.58
	(Total Diesel)	29.02
Heavies	Chrysene	14.28
	(Total Heavies)	14.28
Others	Furans	3.29
	Alcohols	1.88
	(Total others)	5.17

Electricity consumption: Electricity is the main external source of energy in this process: The pyrolysis plant provides 70% required electricity, and the main consumer is combustion air compressor. The high electricity demand causes high air flow that enters to the dryer with high pressure. In bio refinery plant, hydrogen compressor of hydro treating part needs the most electricity.

Comparison with fossil fuels: Figure 15 shows the comparison of the potential environmental impacts of synthetic biofuels. The impact of the pyrolysis fuels is lower than fossil fuels for ADP and CEDnr. It is higher for AP and EP. They showed a higher impact for EP in agricultural phase. Synthetic fuels have similar properties to fossil fuels, so they show similar emission profiles. We can use similar GHG emissions factors.

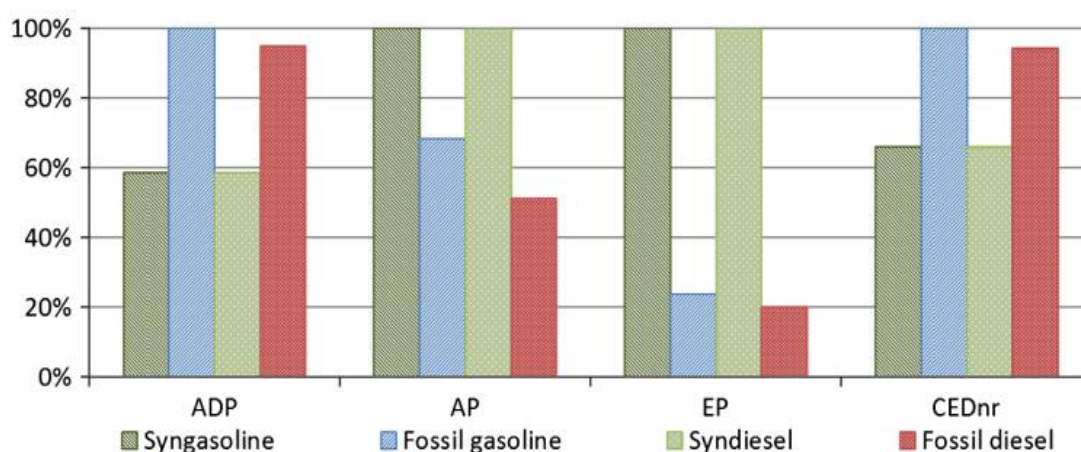


Figure 15-Comparison of the potential environmental impacts of the synthetic biofuels with fossil gasoline and diesel.

EMEP/EEA: GHG emission potential = 39.41 CO_2 eq/MJ, 39.13g CO_2 eq/MJ are for synthetic gasoline and synthetic diesel. In comparison with conventional gasoline and diesel causes GHG emission savings of 55.9% gasoline and 53.0% diesel, based on RED method. Fuel production mix (0.51 MJ gasoline, 0.49 MJ diesel) the equivalent saving is about 54.5% which is close to the target 60%. For hybrid poplar as feedstock and natural gas which used as hydrogen source in hydro-treating the GHG saving is 53%, which is a value that was similar to what was calculated in this project.

The simulation of the biofuel process chain based on fast pyrolysis of poplar biomass showed good results. It is possible to investigate the effects of emission of elements such as chlorine and sulfur on nature from modeling. GHG savings of 54.5% for produced fuel mix is visible. Non-renewable energy demand and abiotic depletion potential are lower than gasoline and fossil diesel. Although, acidification and eutrophication are typical patterns for biofuels. There is a method which is good for improving the performance of the plant. It is using of wood with lower amount of moisture or installing a passive pre-drying during biomass tank. The drying stage is really important because the biomass dryer demands the thermal energy which is generated by the combustor. Significant progress was seen in the agricultural stage. Irrigation water demand is reduced. It reduced environmental impacts on this stage. All together, the system showed high GHG savings. It can be considered a choice to produce fuels from lignocellulose biomass [30].

2.2 Biodiesel Production by Supercritical Methanol Transesterification

Víctor Fernando Marulanda published an article entitled “Biodiesel production by supercritical methanol transesterification: process simulation and potential environmental impact assessment” in 2012.

Process simulation

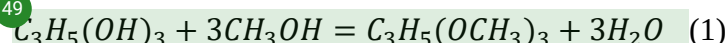
It is important to specify the experimentally determined reaction conditions, model component for the triglycerides mixture, suggested chemical reactions, plant capacity and thermodynamic models to set up the supercritical transesterification process.

Experimental studies supporting the model

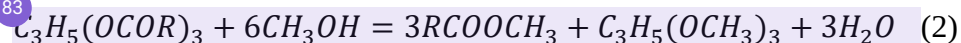
Marulanda et al. studied the continuous supercritical transesterification of chicken fat at these conditions: temperatures (350, 375 and 400°C), pressures (100, 200 and 300 bar) and molar ratios (3:1-12:1). Good quality biodiesel was produced at 400°C, with pressure of 200 bar and a molar ratio of 9:1. The residence time was between 6 and 10 minutes. Some of biodiesel components such as those derived from unsaturated fatty acids, were decomposed to linear alkanes, alkanes and small chain methyl esters because of high temperature condition. Some of them are fuels which are known, but glycerol produced glycerol ethers, alcohols and diglycerol compounds under various reactions. Sawangkeaw et al reported similar results when checked the batch supercritical transesterification of refined palm oil with methanol at 400°C, pressure of 15 MPa and a molar ratio of 12:1.

Chemical reactions

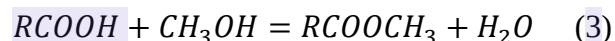
Marulanda et al. (2010) offered a model reaction. The whole etherification reaction between methanol and glycerol to produce glycerol trimethyl ether is shown here:



This reaction can be connected with overall transesterification reaction to delete glycerol:



It shows the stoichiometric ratio at least higher than 3:1 due methanol using for glycerol ethers production. If the FFA contained is high, the esterification reaction can be considered here:



Experimental results showed that the stoichiometry of side reactions of isomerization, thermal cracking and decarboxylation are unknown and they are not considered at this stage. This assumption is also credible for triglyceride sources like palm oil and waste vegetable oils that are decomposed at higher than 300°C temperatures.

Simulation results

Figure 16 shows the supercritical process flowsheet and a summary of stream simulation results in Aspen Plus 2006. Inlet feed streams, triolein and methanol are pressurized to 200 bar separately (pumps B2, B3) to flow in heat exchangers (B13, B21). Feed streams are mixed at reactor inlet (heater B4) to heat to the reaction temperature. This recovers the reaction product and also it prevents preheating the triolein at temperature higher than 350°C, that could lead pyrolytic decomposition reactions.

There is a reactor model (B6) and its reaction stoichiometry is shown in reaction (2). A 99.5% triolein conversion in continuous lab scale unit. The inlet streams pass the heat exchanger and the reactor outlet stream is depressurized. It is sent to a flash unit (B9) at 95°C and 1 bar. The vapor phase contains mostly water and methanol is sent to a distillation column (B12, 6 stages and reflux ratio 2). Methanol is recovered in distillation column and recycled back to the inlet stream. It is mixed with make-up methanol in inlet stream. The liquid phase which contains biodiesel product, unreacted triolein, by-product glycerin trimethyl ether and a small amount of methanol and water, is sent to the distillation column (B19, 5 stages and reflux ratio 1.5). biodiesel is purified in distillation column.

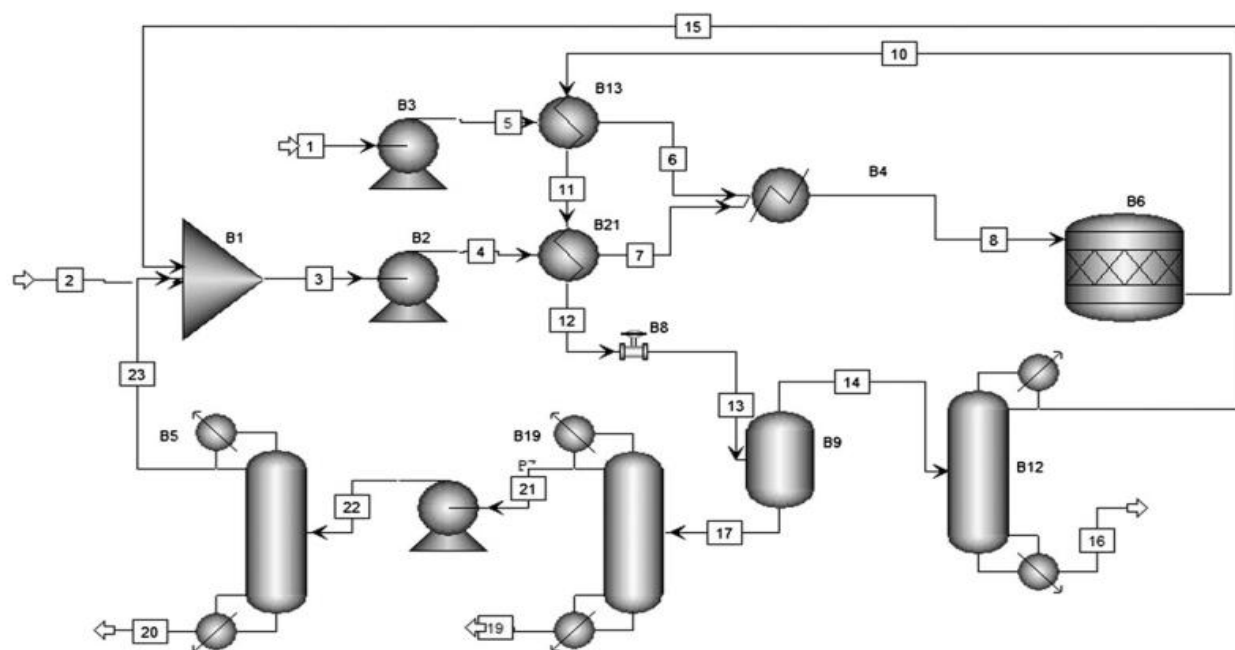


Figure 16-Proposed supercritical process flowsheet.

As it is noted in Table 2, the flash separation of the reactor outlet stream forms a vapor phase which is a methanol rich stream. It is mostly recovered in distillation column (B12). It is recycled with a specific amount of water to the methanol inlet stream. Glycerol trimethyl ether and FAMEs are got from bottom stream of the distillation column (B19). The top stream contains composed of methanol, a small amount of glycerol and water, is sent to a distillation column (B5) to recover methanol. Additional yield attributed to glycerol decomposition reactions is reported based on experimental results. Sawangkeaw et al reported an additional 5% of fuel in supercritical methanol of palm oil with 12:1 molar ratio at 400°C. The formation of gaseous products that are the result of glycerol by-products decomposition in batch reaction time, is reported by the authors. So, the additional fuel yield can be higher than 5%.

Table 2-Streams summary.

Stream name	2	4	5	8	10	12	14	15	17	16	19	20	23
Temperature, K	298.1	333.6	332.7	673.1	673.1	585.5	363.1	302.4	363.1	386.6	417.1	387.2	302.6
Pressure, bar	1	200	200	200	200	200	1	0.2	1	1.8	0.8	1.8	0.2
Mass fraction													
Methanol	1	0.991	0	0.252	0.091	0.091	0.55	0.975	0.015	0.041	Traces	0.031	0.966
Triolein	0	0	1	0.742	0.004	0.004	Traces	0	0.005	0	0.005	0	0
Methyl Oleate	0	Traces	0	Traces	0.742	0.742	Traces	Traces	0.865	Traces	0.889	0	Traces
Triglycerol	0	Traces	0	Traces	0.112	0.112	0.162	Traces	0.103	0.357	0.104	0.168	Traces
Water	0	0.009	0	0.006	0.051	0.051	0.287	0.025	0.012	0.602	0.002	0.802	0.034
Total flow (kg/h)	288.4	444.6	1282	1726.6	1726.6	1726.6	245.682	134	1480.9	111.7	1440.6	18	22.3

Simulation results for required energy consumption of process units are shown in Table 3. The total energy consumption was 573 kW for this flowsheet. This figure is different with previous one which

had 2407 kW for a supercritical and 2400 kW for the conventional base catalyzed processes energy consumption. This difference is because of excess methanol which is in supercritical process (42:1), that defines into high energy consumption in methanol heating up and recycling, methyl esters recovery from unconverted triolein in conventional base catalyzed process with a 97% triglyceride conversion. Low energy consumption is due to energy using of the reactor outlet stream for flash separation performing, instead of reaction cool down to separate the immiscible glycerol and biodiesel phases, which are carried out in conventional processes. In this work, this method lets separating most of the low boiling components, water and methanol without any more energy.

Table 3-Process equipment energy consumption.

Process equipment	Energy consumption (kW)	Energy carrier
Triolein pump (B3)	20.8	Electricity
Methanol pump (B2)	3.1	Electricity
Heater (B4)	84	High pressure steam
Reactor (B6)	229	High pressure steam
Methanol column (B12)	131	Medium pressure steam
Biofuel column (B19)	88	Medium pressure steam
Methanol column 2 (B5)	17	Medium pressure steam
Total energy	573 kW	

A supercritical process with a 42:1 molar ratio showed a higher triolein conversion, but there is only some decreasing energy consumption to eliminate triolein FAME methanol distillation step. Glisic and Skala simulated the supercritical process on ASPEN PLUS with a 42:1 molar ratio and 99.5% conversion. They found a decreasing of 300 kW while the previous results showed 640 kW with a 97% conversion in FAME purification distillation. There are similar results for the same distillation steps in the conversion process. Methanol recovery in the supercritical process (1560 kW) and salt removing in the conventional process (1039 kW) are the most energy intensive operations that do not belong to specific conversion.

Environmental impact assessment analysis

The war algorithm (Waste Reduction) is a methodology which is developed by the Risk Management Research Division of the Environmental Protection Agency (EPA). The EPA is based on a potential environmental impact (PEI) balance for a chemical process. The PEI is a measurement of the potential for a chemical to check the effect on environmental and human health. This scheme includes these categories: global warming potential (GWP), ozone depletion potential (ODP), acidification or acid rain potential (AP), photochemical oxidation (PCOP), human toxicity by ingestion (HTPI), human toxicity by inhalation or dermal exposure (HTPE), aquatic toxicity potential (ATP) and terrestrial toxicity potential (TTP). The categories are based on experimental measures for chemical materials like the threshold limit value (TLV) and lethal dose (LD50). The eight categories where mentioned above, do not show the fate and transport of materials when they are emitted to a special media. EPA's TRACI, IMPACT 2002, USETOX and CALTOX are Life Cycle Impact Assessment (LCIA) methods which report for three different factors such as the fate, exposure and the toxicity factors. They can define more realistic methods for environmental indicators.

The software come close to a pollution index based on these information: participating chemical components, inlet, outlet, product and waste stream, total energy consumption, the software and a PEI balance. The index is used as a comparison with some kinds of process alternatives to choose the best environmental friendly alternative. The suggested supercritical process, which is analyzed as supercritical 9, was compared to the previous supercritical process with a 42:1 molar ratio at 300°C, which is analyzed as supercritical 42 in this work. Glisic and Skala reported some results from ASPEN PLUS. The experiments showed that not all of the produced glycerol was completely etherified. Glycerol, methyl glycerol and dimethyl glycerol were also present.

Both supercritical processes have lower output PEI per mass of product than conventional process which is shown in figure 17. Supercritical 9 has the lowest PEI. Previous LCA assessments stated that super critical processes have higher environmental impact than conventional processes or a little lower impact after decreasing the molar ratio to 24:1 by using a co-solvent. There is a negative PEI for all process options. It shows that the products which are formed from transesterification and decomposition reactions are more harmless than reactants which they are formed from so PEI is used in the process.

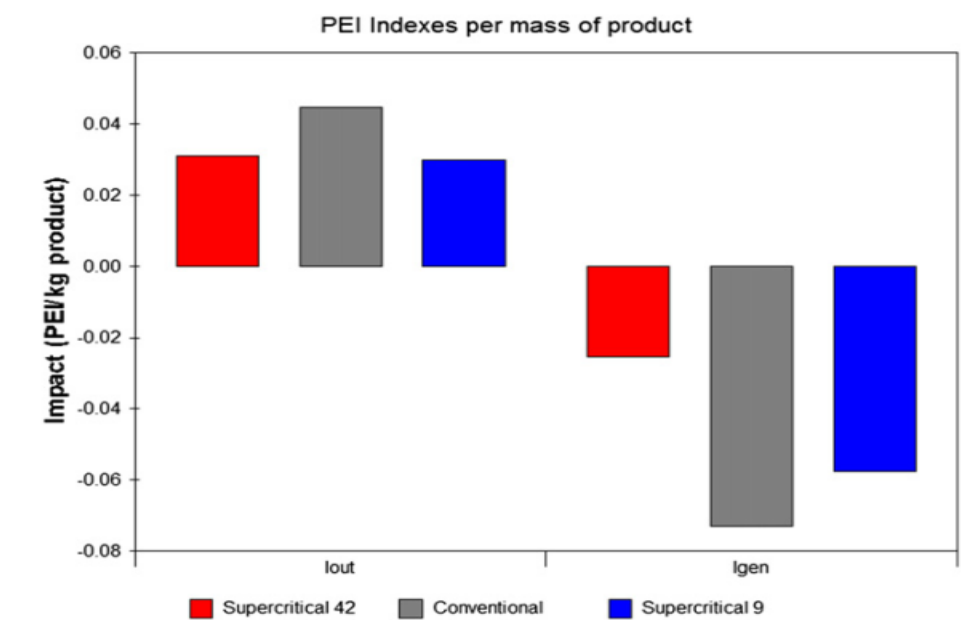


Figure 17 Total output and generated PEI for biodiesel production processes.

Figure 18 presents that the supercritical 42 uses the most of the PEI because of high energy consumption of the process, while the supercritical 9 uses PEI because of waste streams that contain unrecovered glycerol trimethyl ether and methanol.

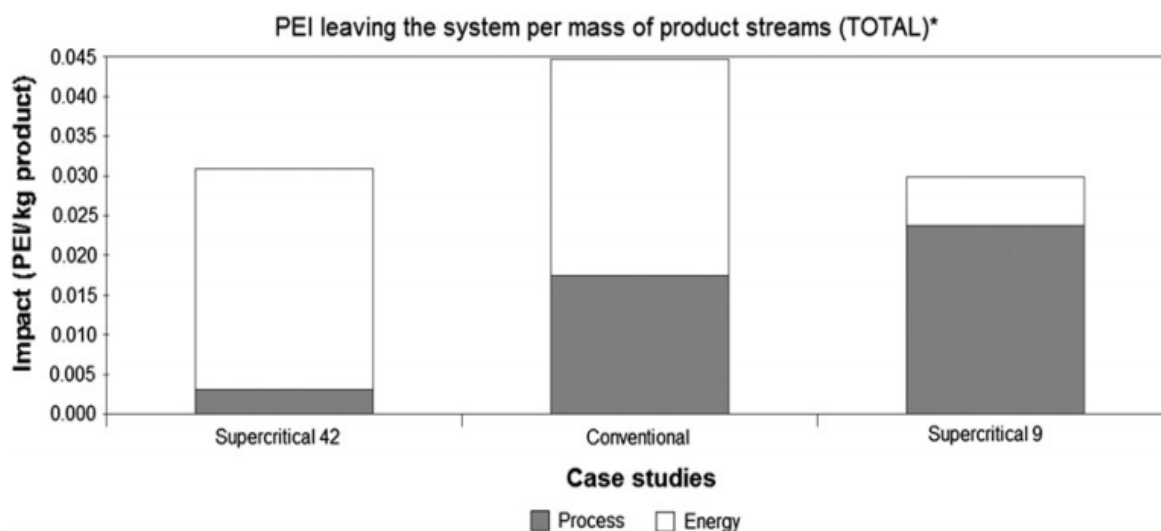


Figure 18 Total output PEI due to process and energy consumption.

The indexes of photochemical oxidation (PCOP) and acidification potential (AP) are the sources of total PEI/kg which are shown in Figure 19. The AP index is lower for supercritical 9, but the PCOP is higher because of the unrecovered glycerol trimethyl ether. However, a part of the glycerol trimethyl ether can be used as a part of the fuel. Glycerol decomposition produces water, which makes glycerol recovery difficult for conventional distillation, whereas almost the whole by-product glycerol is recovered with high purity in supercritical 42 and conventional processes because of easy separation of glycerol from methanol and FAMEs.

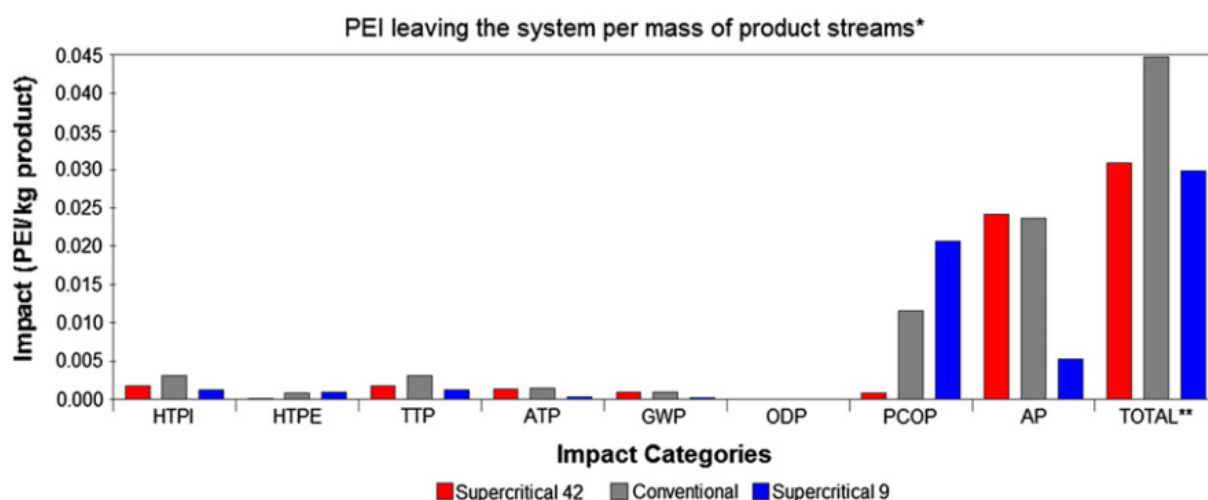


Figure 19 Contribution to total PEI/kg product of each impact category.

In Figure 20, the total output PEI of supercritical 9 is about 3 times lower than the PEI for supercritical 42 and conventional base catalyzed processes. FAME stream (19) includes glycerol trimethyl ether as a product, which leads to the lower pollution index of supercritical 9, whereas supercritical 42 and conventional base catalyzed processes consider glycerol as a waste. Supercritical 9 has a negative PEI amount because of glycerol decomposition, whereas glycerol is considered as a waste.

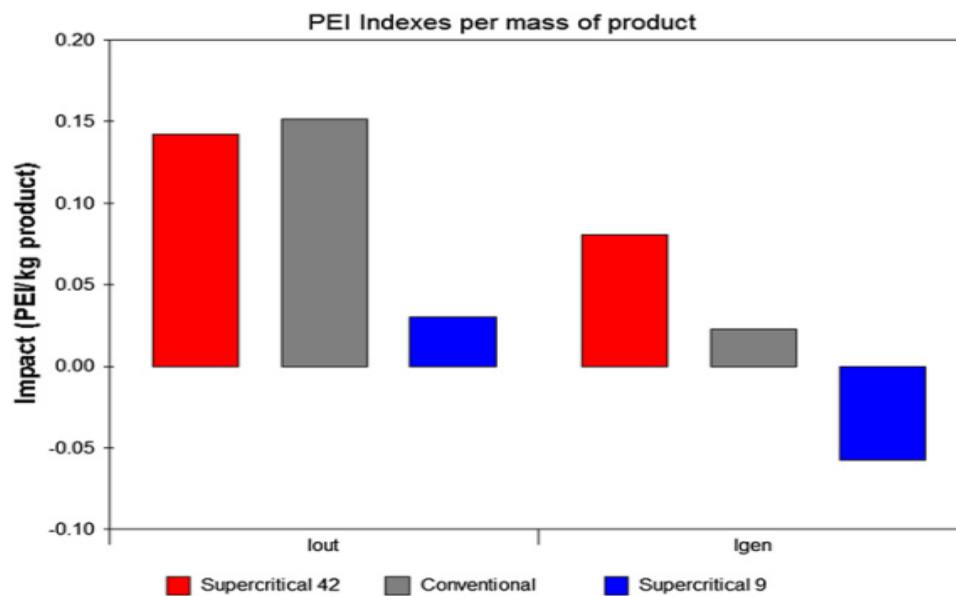


Figure 20 Total PEI per mass of product without glycerol.

A supercritical transesterification process for biodiesel production, based on available experimental information, reaction conditions, biofuel yield and products and by-products was investigated and simulated in Aspen Plus 2006. Simulation results presented that the supercritical process with a 9:1 molar ratio at 400°C has lower energy consumption than supercritical with a 42:1 molar ratio and conventional process at 300°C.

Simulation results were used to check environmental impact via developed tool which is EPA. The environmental impact assessment presented that supercritical process with a 42:1 molar ratio, has a lower environmental potential impact than the supercritical process with a 9:1 molar ratio and conventional process. The supercritical process with 9:1 molar ratio has the lowest output environmental potential impact because of low energy consumption. Moreover, the profit increase due to lower energy consumption and increased yield got from glycerol decomposition at suggested conditions is reported for the supercritical process with 9:1 molar ratio [31].

2.3 Thermochemical Waste Heat Recuperation by Steam Reforming of Liquid Biofuels

Dmitry Pashchenko and et al. published a paper entitled “Comparison study of thermochemical waste-heat recuperation by steam reforming of liquid biofuels” in 2019.

On this article Thermochemical exhaust heat recuperation is considered. Thermochemical recuperation is a kind of hydrogen production technology. The thermodynamic analysis is done by Gibbs free energy minimization. The simulation is done by ASPEN and HYSYS. Here is thermochemical analysis: T: 400-900K, for steam to fuel of 1 bar, maximum fuel conversion: Methanol: -600K, Ethanol: -730K, n-butanol: -860K, Glycerol: -890K. maximum heat transformation coefficient :1.187.

Biofuels are used in transport, chemical industries, energy and other industries widely. Simplest biofuels are ethanol and methanol, which they are obtained from alcohol. Thermochemical

recuperation of the exhaust heat is a way that we can use bio-fuels in transport and energy. This article suggests an overview of research on fuel reforming in the internal combustion engines (ICE). The authors tested different reforming processes for ethanol, methanol, gasoline and other fuels of ICE application. Thermochemical waste-heat recuperation is used in industrial plants. It has been used in high temperature plants, especially in glass melting furnaces. Rue and co-authors tested a glass melting furnace with TCR in a pilot scale process unit. The authors presented that waste heat in furnace with TCR, is used for natural gas reforming. Simulation and experimental investigation showed higher energy recovery in TCR system than heat exchangers or thermal regenerators.

Thermochemical recuperation concept

Thermochemical heat recuperation is using exhaust gas heat for an endothermic change of primary fuel. New synthetic fuel is the product of this change. The product has higher LHV than initial fuel. A schematic diagram is shown in Figure 17, which includes: 1-thermochemical recuperation system (fuel reformer, steam generator (boiler), mixer (steam ejector)). 2-the fuel consuming system (fuel consuming equipment itself, burner assembly).

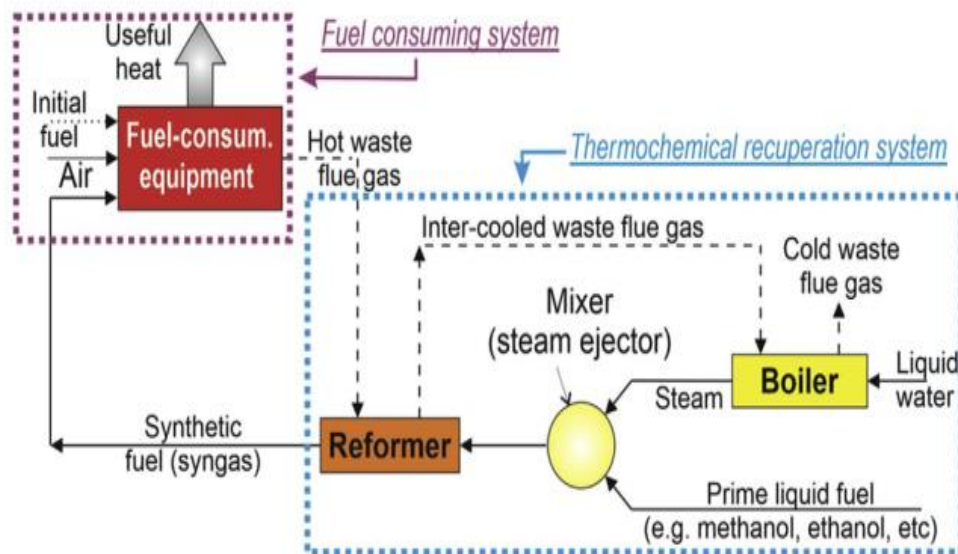
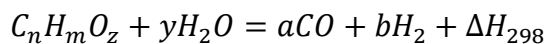


Figure 21-Schematic view of the fuel-consuming equipment with thermochemical recuperation by steam reforming of liquid fuel.

The exhaust gas after fuel consuming equipment is sequentially passing through the fuel reformer and the boiler (steam generator). The fuel reformer performs as a catalytic heat exchanger. The reaction mixtures before the reformer contain steam and fuel vapor. Inside the reaction space of the reformer, fuel and steam are reacted and to the mixture than dominantly consist of hydrogen is produced. The overall chemical endothermic reaction of the fuel reforming process can be written as follows:



after the thermochemical reformer syngases leads to the combustion chamber of the fuel-consuming equipment. In the combustion chamber the combustion process of combustion components of syngases occurs.

Liquid fuel reforming process reactions include the water gas shift reaction, fuel reforming and other reactions. The mechanism of these reactions is dependent on parameters like temperature, steam to fuel ratio, catalyst composition and pressure. Fuel reforming process produces synthetic fuel. synthetic fuel is fed to a burner after reformer. It is done for heat production in the fuel consuming material. Thermodynamic analysis determined equilibrium gas composition, enthalpy of fuel reforming reaction and fuel reforming. The author introduced the algorithm of the thermodynamic analysis by the Gibbs free energy minimization (GFEM). GFEM method is used to find equilibrium compositions of product gas. The system is ideal at low pressure before 5-10 bar and high pressure. Four liquid biofuels such as methanol, ethanol, n-butanol and glycerol were compared on this study. The enthalpy of the reforming reaction, which is determined by initial fuel conversion, reveals the effectiveness of the thermochemical recuperation system. The thermochemical heat recuperation is absent when the initial fuel is zero.

Fuel conversion: Equilibrium fuel conversion: $X_{fuel} = \frac{Fuel_{in} - Fuel_{out}}{Fuel_{in}}$, fuel is the number of moles of fuel.

If the initial fuel does not join to the reaction, the fuel conversion will be 0. If the total fuel reacts with steam, the fuel conversion will be 1. Fuel conversion is dependent on process temperature. The reason is reforming reactions are reversible. The equilibrium of reactions at low temperature, leads consuming reforming products.

Figure 22 checked the relation between temperature and fuel conversion. Reforming reactions are endothermic. Therefore, when the temperature increases, the fuel conversion also increases. In the interval of 500-700K: glycerol at 600K is 0.31 of conversion, but at same temperature methanol is close to unity. All fuels in temperature above 900K have a conversion close to unity.

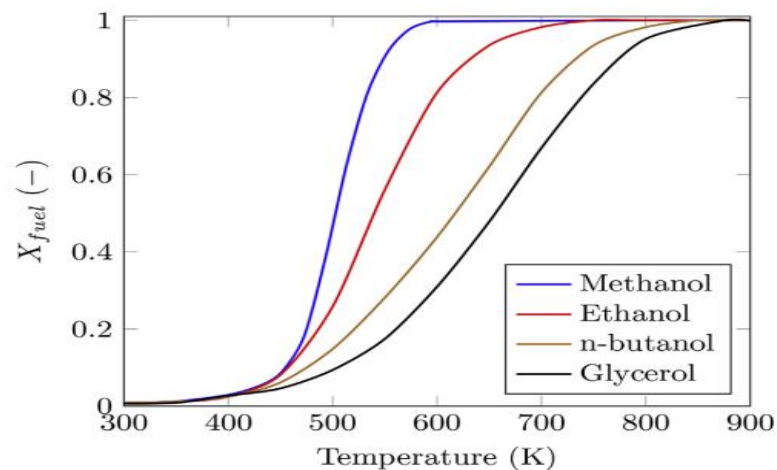


Figure 22. The fuel conversion as a function of temperature at $p=1\text{bar}$ and fuel-to-steam ratio of 1.

Reaction enthalpy for a steam reforming process is presented in Figure 23. Enthalpy changes during the reaction which changes with temperature, at a pressure of 1 bar, steam fuel ratio=1. In temperature range above 600K, n-butanol has the maximum reaction enthalpy. Methanol has the least reaction enthalpy. Reaction enthalpy shows exhaust heat transformation into new synthetic fuel. In conclusion, 1 mole of n-butanol helps to transform the maximum amount of exhaust heat into the new synthetic fuel. The considerable difference in enthalpy of reaction is because different compositions of fuels.

Initial fuels have different LHV. In conclusion, to check the fuel efficiency in thermochemical recuperation system, it should be noted that finding how many times the LHV of new synthetic fuel is bigger than the LHV of initial fuel has importance.

Heat transfer coefficient: $n_q = LHV_{synfuel}/LHV_{initial\ fuel}$

In endothermic reforming reactions, the heat transform coefficient is bigger than unity.

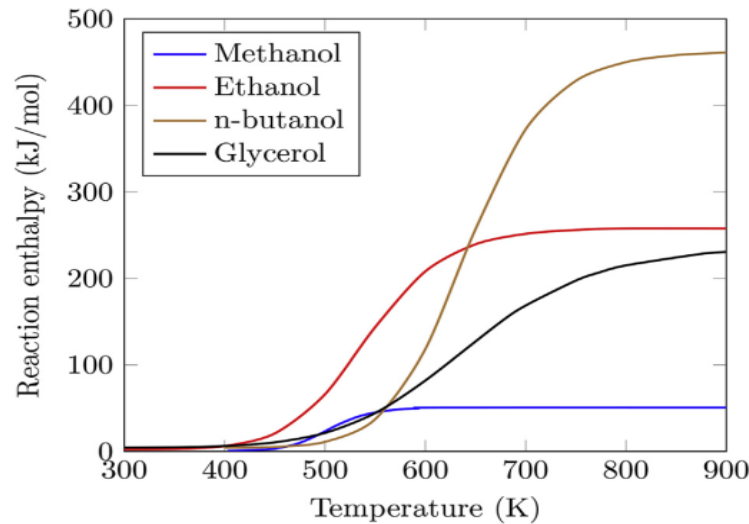


Figure 23 Reaction enthalpy for a steam reforming process as a function of temperature.

The reaction enthalpy increases with increasing the temperature of the reaction, which is shown in Figure 24. Ethanol has the maximum heat transfer coefficient at 500-900K of temperature range, which is 1.187. Ethanol and methanol have a close value at 500K, and ethanol and n-butanol have close value of heat transfer coefficient above 900K. Heat transferred in the reformer for fuel reforming reactions and syngas defines the efficiency of the TCR systems. The efficiency will be zero, if steam fuel reformer does not occur in reformer. When exhaust heat is used for the generation of system, it has negative effect.

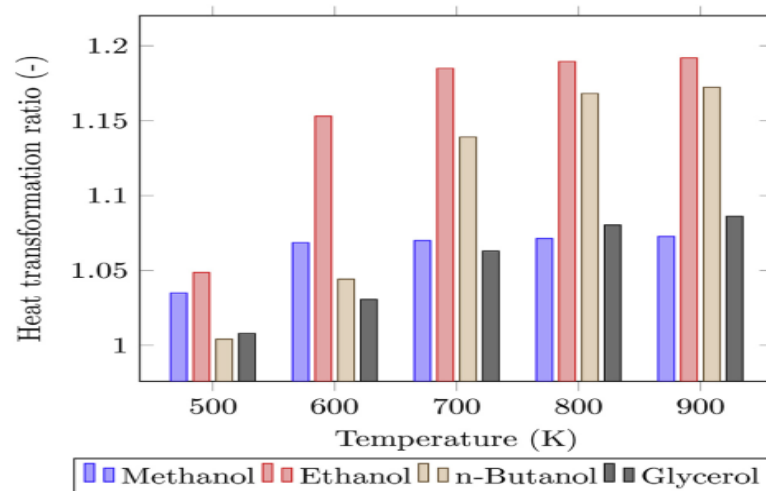


Figure 24 The transformation coefficients for various fuels vs. temperature.

Conclusion

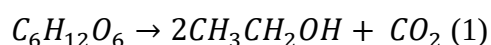
Four types of biofuels are checked like ethanol, methanol, glycerol and n-butanol. The thermodynamic analysis is done based on Gibbs free energy minimization method and the simulation is done by Aspen HYSYS software.

The increasing of fuel conversion is because of temperature increase in process. There are temperatures which fuel conversion reaches its maximum amount: methanol- 600K, ethanol- 730K, n-butanol- 860K, glycerol- 890K. The enthalpy of the reforming process defines the effectiveness of the thermochemical recuperation system. The reforming enthalpy is depended on the process temperature. In addition, maximum enthalpy of the process for reforming methanol is 5 times less than for reforming n-butanol. Enthalpy of the reaction finds the heat transfer coefficient, that shows the ratio of the low heat value of synthetic fuel and low heat value of the initial fuel. The maximum value of transformation coefficient is found for steam reforming of ethanol which is 1.187. The obtained results help to select proper type of fuel for thermochemical recuperation due to steam reforming. The results on this article can be used for first law energy analysis of the thermochemical waste-heat recuperation system by steam reforming of liquid biofuels [32].

2.4 Biofuel Transportation Applications

Wei-Ru Chang, Jenn-Jiang Hwang, Wei Wu published an article entitled “Environmental impact and sustainability study on biofuels for transportation applications” in 2015:

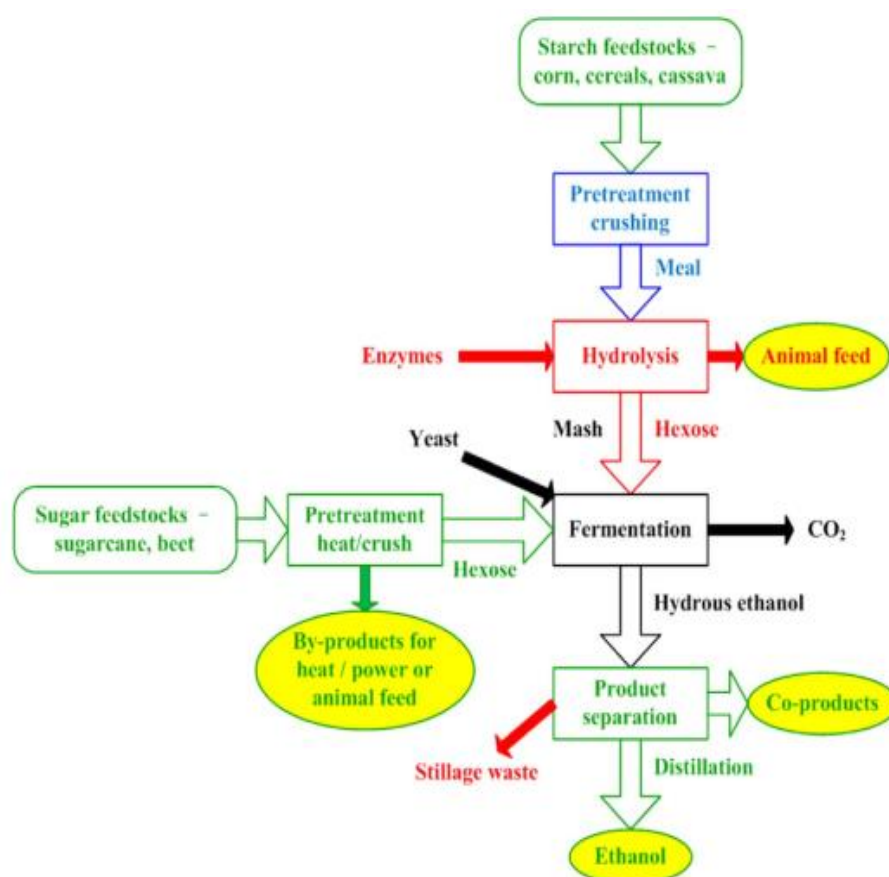
Bioethanol is a kind of alcohol which is generally produced from biomass. Glucose fermenting with insufficient amount of oxygen, when anaerobic respiration occurs in yeast, so glucose is converted into ethanol and carbon dioxide. Here is bioethanol production reaction:



Lately, cellulosic biomass, which is derived from nonfood sources like woody biomass, herbaceous and waste residues, is using as feedstock to produce ethanol. Bioethanol which is based on starch biomass or sucrose is called first generation bioethanol, while the bioethanol that is based on

lignocellulosic biomass is known as second generation bioethanol. They are defined in following sections:

10 First generation bioethanol: Figure 25 shows production of first generation bioethanol. Two kinds of feedstocks are used in this reaction which are starch based biomass and sucrose based biomass. The juice of sucrose based biomass like beet or sugarcane are pressed from cooked biomass mechanically. Then they'll be fractionated. Yeasts metabolize sucrose for ethanol fermentation to the hexoses. Finally, the separated ethanol will be recovered by distillation. Starch based biomass such as corn, cereal, wheat and barley are pretreated by crushing and milling. The starch crops meal is hydrolyzed by enzymes into the hexose. Mash hexose is converted into ethanol biochemically by yeasts. Distillation will purify the hydrous ethanol. As a point, it should be noted that the starch based route uses more energy than the sucrose based route because of an additional step for converting of starch into the glucose.



9 Figure 25 Conversion routes for sugar and starch feedstocks.

9 Second generation bioethanol: Second generation bioethanol is produced from lignocellulose which is made of cellulose, hemicellulose and lignin. It forms almost 50% of biomass whole the world. Figure 26 presents the process diagram of lignocellulose to ethanol by biochemical process. 1 Agricultural and forest residues such as switchgrass, corn stover, wood chips and miscanthus grass species are lignocellulosic materials to produce ethanol. In addition, 9 urban municipal solid waste

biomass streams are useable. It is visible in figure 2, the conversion of lignocellulose to ethanol process include three main steps: pretreatment of feedstocks, enzymatic hydrolysis and fermentation.

Pretreatment of feedstocks: Feedstocks pretreatment consists of these steps: feedstock harvesting, handling, recovery and transport, size reduction, polymer fractionation, solid lignin separation and end product recovery.

Enzymatic hydrolysis: Biochemical conversion step uses enzymes to destroy lignocellulose into its basic polymers. It breaks down cellulose and hemicellulose into glucose and xylose. It should be noted that, in addition to enzymatic hydrolysis, acid agents are used in hydrolysis steps. Acid hydrolysis causes equipment corrosion and low glucose yield. Little is known about this technology.

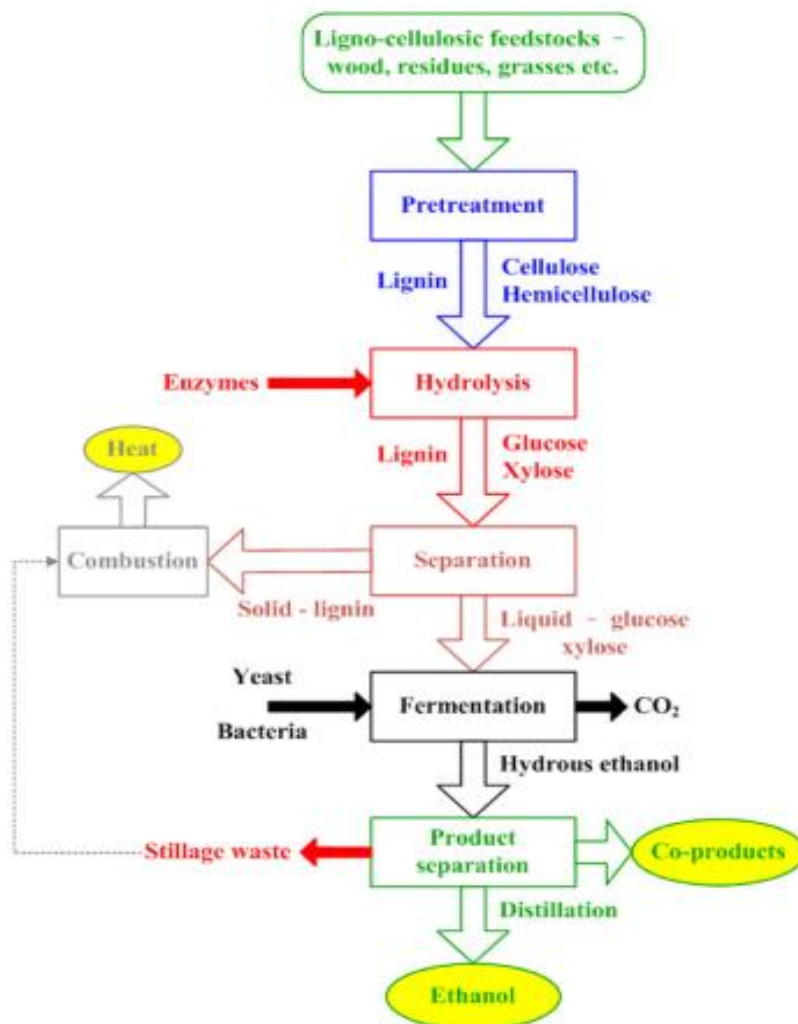
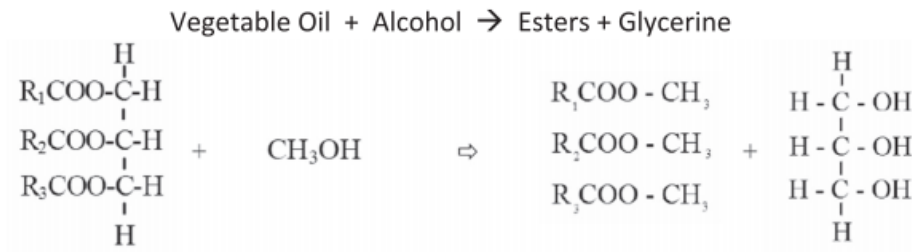


Figure 26 Bioethanol productions from lignocellulose via the biochemical route.

Fermentation: Monomeric sugars will be fermented into ethanol.

Biodiesel is a renewable fuel that is produced from animal fats or vegetable oils for using in diesel engine vehicles. It is made of a mix of mono-alkyl esters of long chain fatty acids chemically. Standard diesel engines use biodiesel, and fuel converted diesel engines use vegetable oils. Figure 27 is biodiesel production process diagram. The main step in biodiesel production is transesterification reaction. It is the reaction of methanol with triglycerides to produce fatty acid methyl ester (FAME) and glycerin which is shown below:



(2)

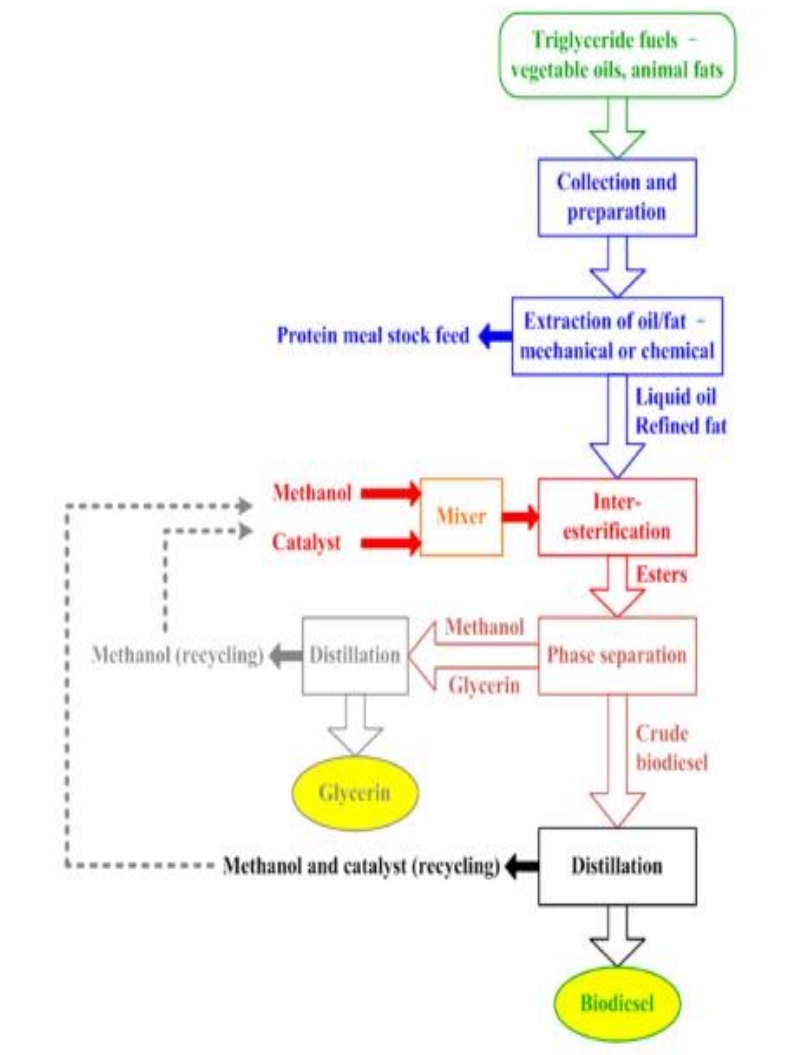


Figure 27-Production pathway of biodiesel.

Ethanol can be used for fatty acid ethyl ester (FAEE) biodiesel production, too. Higher alcohols such as butanol and isopropanol are also used. Using higher molecular weight alcohols in this reaction, improves the cold flow properties of produced ester with a less efficient transesterification reaction. It should be noted that, raw or refined plant oil or recycled greases which are not processed into biodiesel, are not biodiesel and should not be used. Triglycerides such as oils and fats are more viscous than biodiesel. Low level vegetable oil blends lead to long term engine deposits, lube oil gelling, ring sticking and other problems which decrease life of the engine.

Methodology

The GREET code (Greenhouse gases, Regulated Emissions and Energy use in Transportation) is explained in this article. Here is a scope of a well-to-wheels analysis for biofuel vehicle systems which is shown in Figure 28. The boundary of this fuel-cycle model is divided into two stages which are the tank-to-wheel stage (TTW) and the biomass-to-tank stage (BTT). The BTT stage begins with feedstock production (farming, harvesting and transportation), it ends with available biofuels in the vehicles tank fuel.

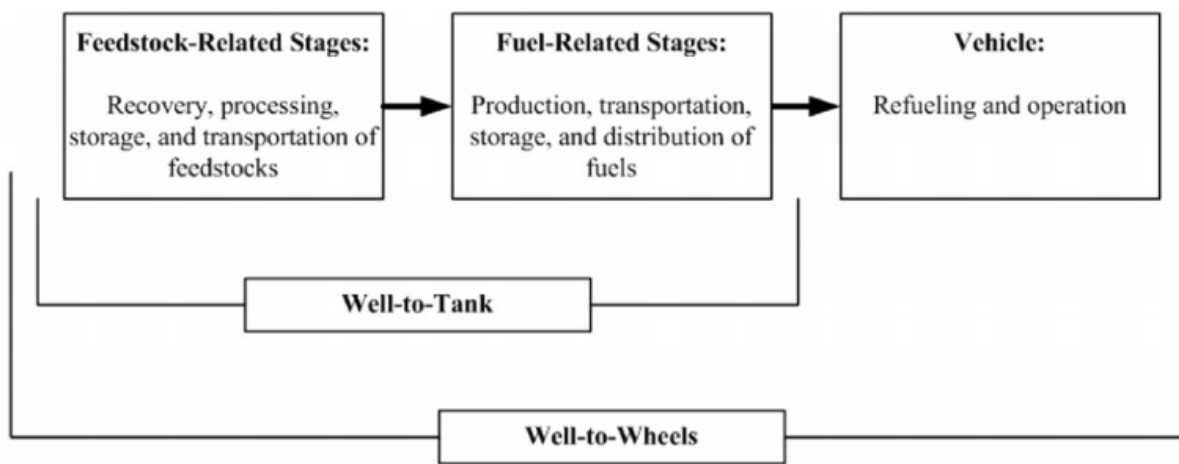


Figure 28 Scope of a biomass-to-wheels analysis for biofuel/vehicle systems.

Here are two kinds of land-use change: 1-Direct, which is growing biofuel feedstocks on land that was forest before;

2-Indirect, is the displacement of biofuel production of other commodities, which are produced on converted lands elsewhere (foreign or domestic land).

Results and discussion

Fuel economy

City mode, a highway mode and a combined mode are fuel economy types of a vehicle. When a vehicle starts in the morning after being parked all night, and then is driven in traffic in urban area is on city mode. Highway mode represents a longer trip with free-flowing traffic with a mixture of rural and highway driving. A combination of both city mode and highway mode is the combined-mode fuel economy.

Biomass-to-tank efficiency

Energy intensity and carbon intensity are shown in Figure 29 and Figure 30. It is visible that higher energy intensities are belong to biofuels. However, conventional gasoline has less energy intensity. The energy intensity of E10 is less than E85 with switchgrass ethanol or corn ethanol. Moreover, blended corn ethanol with E85 uses more energy than blended switchgrass ethanol with E85. It is because of consuming more energy in corn-to-ethanol process than switchgrass-to-ethanol process in feedstock and fuel processes. Negative value for E85 blended with switchgrass ethanol in carbon intensity means that the feedstock process of switchgrass can attract carbon. The highest carbon intensity belongs to bio-hydrogen from corn ethanol reforming, because of its highest energy intensity.

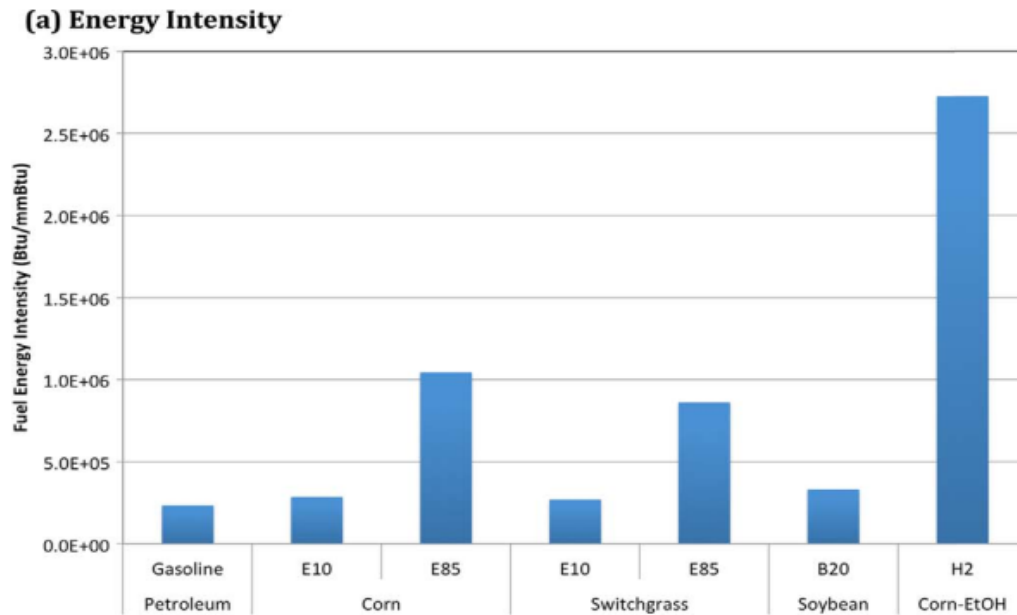


Figure 29: Energy intensity of various biofuel pathways.

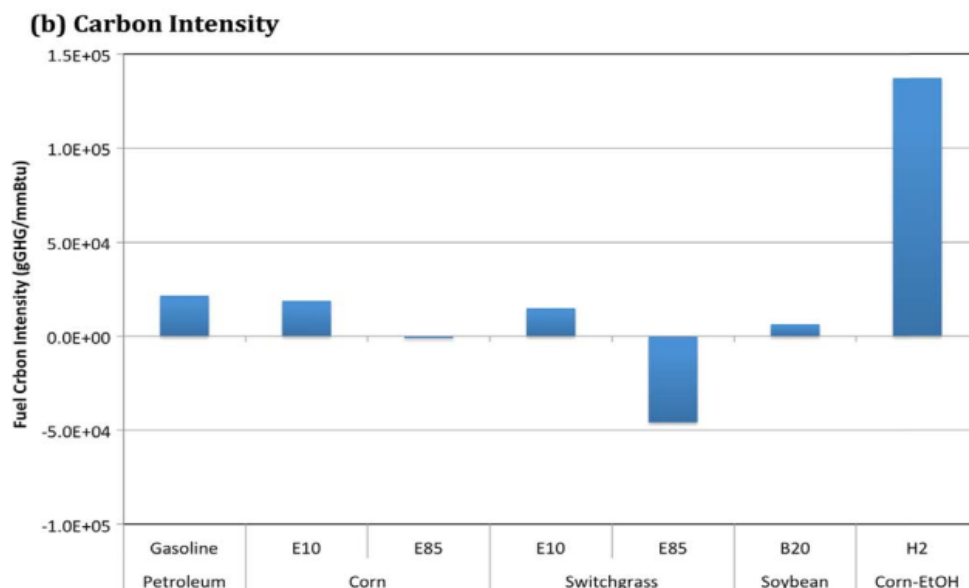


Figure 30: Carbon intensity of various biofuel pathways.

The biomass-to-tank efficiency of six different biofuel pathways is shown in figure 31. It is shown here; the biomass-to-tank efficiencies are lower than the well-to-tank of gasoline from a petroleum refinery for all biofuel pathways. Switchgrass ethanol for E10 has the highest biomass-to-tank efficiency (78.7%), as the bio-hydrogen from corn ethanol has the lowest biomass-to-tank efficiency (26.8%). Hydrogen production from corn-ethanol reforming and corn-to-ethanol fermentation have the lowest biomass-to-tank efficiency, which are inefficient processes.

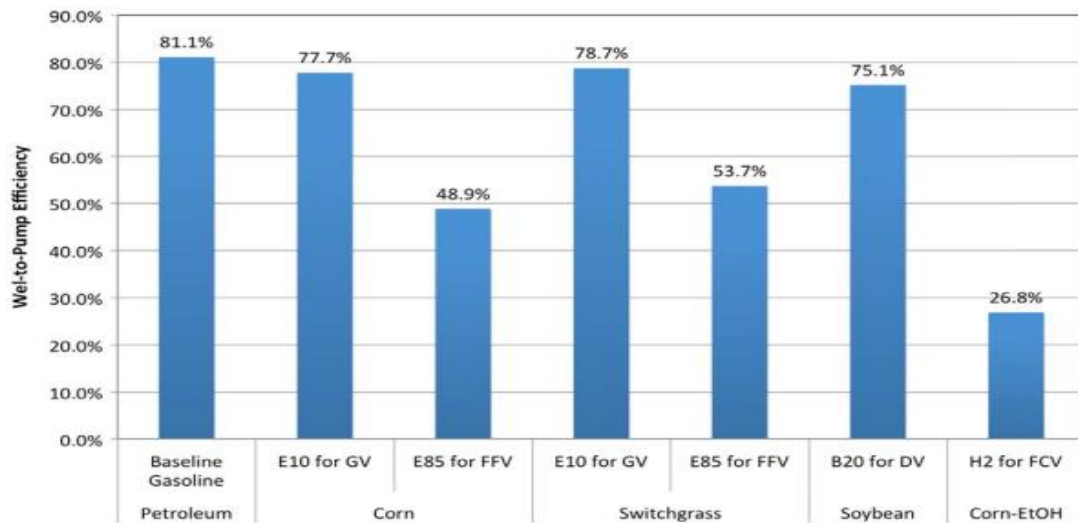


Figure 31 Biomass-to-tank efficiency for various fuel pathways.

Figure 32 shows that, the flexible fuel vehicles fueled by E85 blended with corn ethanol consume the most energy in fuel stage and vehicle operation stage. It has the largest total energy consumption up to 11,126 Btu/mile. The diesel vehicle/B20 which is derived from soybean biomass has a little higher energy consumption than gasoline vehicle/gasoline. The higher fuel economy for diesel vehicle/B20 decreased its total energy consumption. Fuel cell vehicle/H2 has an excellent fuel economy (tank-to-well efficiency) which can make up the energy consumed in the fermentation and reforming fuel processes. Total energy consumption of fuel cell vehicle/H2 is higher than gasoline vehicle/gasoline.

(a) Stage energy consumption

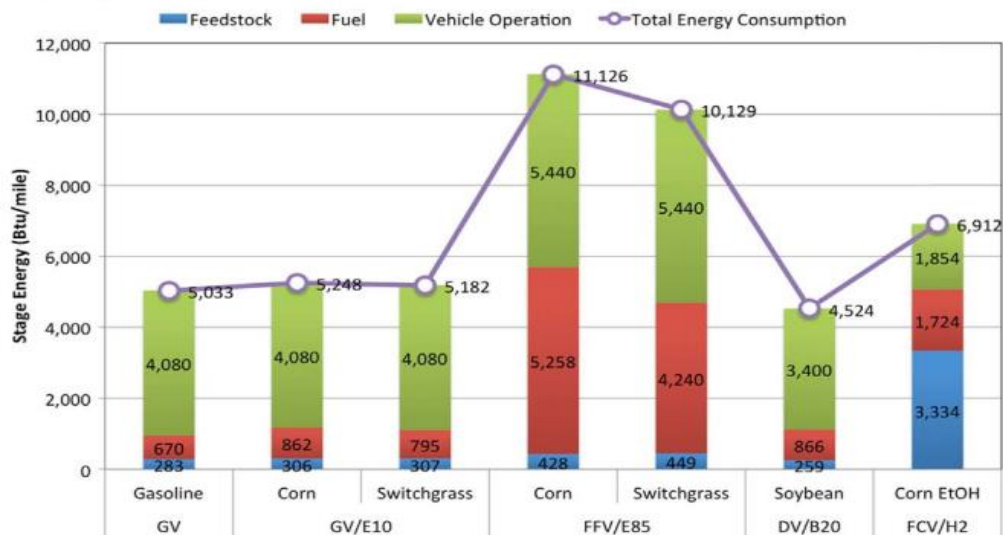


Figure 32-Stage energy consumption for various biofuel/vehicle systems.

Figure 233 presents the results of stage GHG emissions for various biofuel/vehicle systems. The flexible fuel vehicles fueled by E85 which is blended with corn ethanol has considerable GHG

emission in vehicle operation stage. Carbon can be captured during feedstock stage, that can make up the GHG emissions during the vehicle operation stage. In conclusion, the flexible fuel vehicle fueled by E85 blended with corn ethanol has the lowest GHG emissions between the other biofuel/vehicle systems. The fuel cell vehicle/H₂ does not send out GHGs when vehicle operation stage is running so the fuel stage covers all GHG emissions. The fuel process for corn ethanol uses fossil fuel which effects on GHG emissions. It is concluded that the fuel cell vehicles which use bio-hydrogen derived from ethanol are second best in GHG emission reduction among the other biofuel vehicle systems.

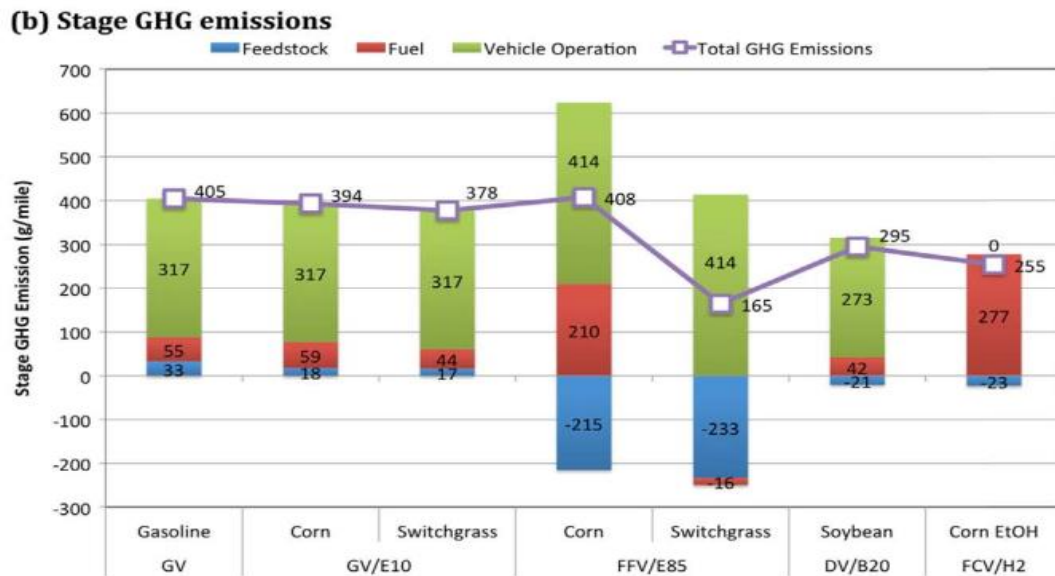


Figure 33 Stage GHG emissions for various biofuel/vehicle systems.

Figure 34 shows that all biomass derived fuels suggest a specified reduction in fossil energy assumption (5.0-68.5%). It is due to the renewable non-fossil feedstock used. The Flexible fuel vehicle (FFV) that is fueled with E85 blended with switchgrass ethanol offers the largest fossil fuel consumption decrease which is about 68.5%.

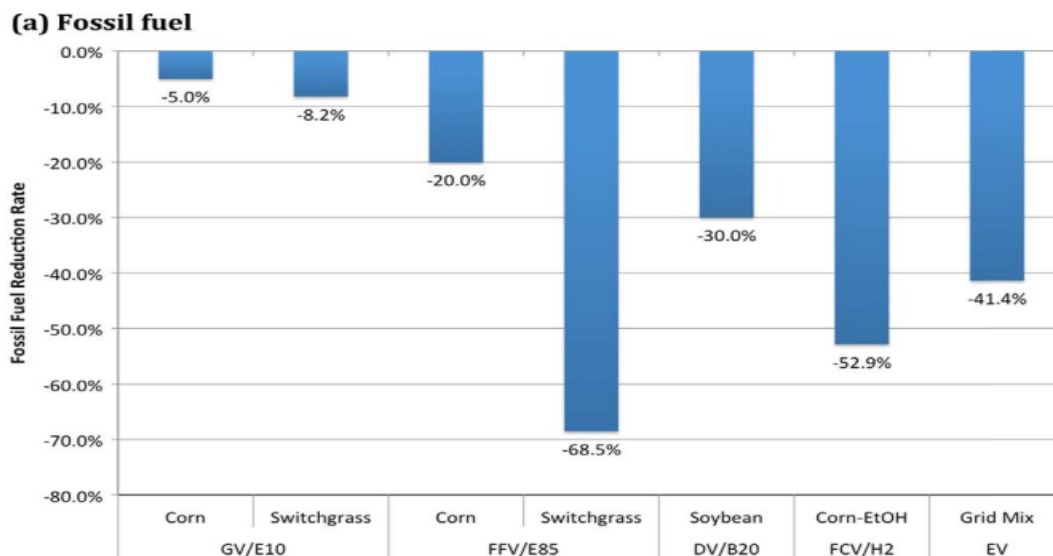


Figure 34-Fossil fuel rate for various biofuel/vehicle systems.

All other biofuel vehicle systems save petroleum significantly except GV/E10, which is shown in Figure 35. FFV/E85, DV/B20 and FCV/H2 use lower petroleum than GV/CG. The soybean diesel produces various amount of co-products which can be replaced with petroleum fuels. The DV/B20 saves less petroleum than FFV/E85. The FFV/E85 can reduce petroleum consumption about 50% and more. For the FCV/H2 from corn ethanol, the petroleum reduced about 94.7% due to petroleum absence in TTW stage.

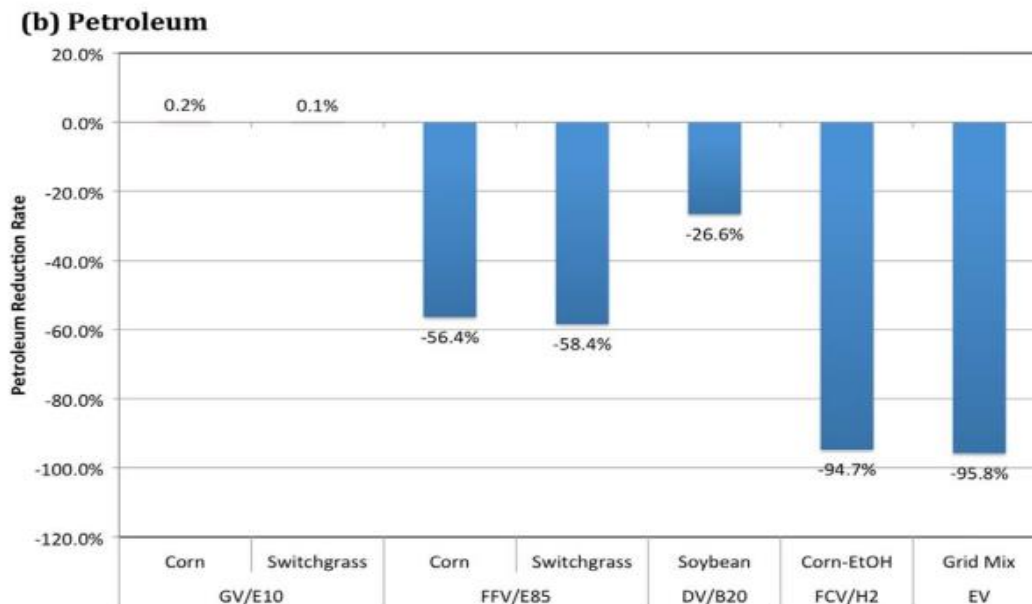


Figure 35-Petroleum reduction rate for various biofuel/vehicle systems.

Relative changes in GHG emissions for different biofuel/vehicle systems is shown in figure 36. All biofuel/vehicle use more energy than GVs, except for DV/B20. The DV/B20 reduced total energy consumption by 10.1% in comparison with conventional GV/gasoline. The FFVs fueled with switchgrass blended with E85 reduce GHG emissions more than 59%. It is due to using co-products for heat and power production and are replaced with fossil fuels. It should be noted that the FCVs fueled with bio-hydrogen from corn ethanol reduces the GHG emissions about 31.1%, but it increases the total energy about 37.4% in comparison with GVs.

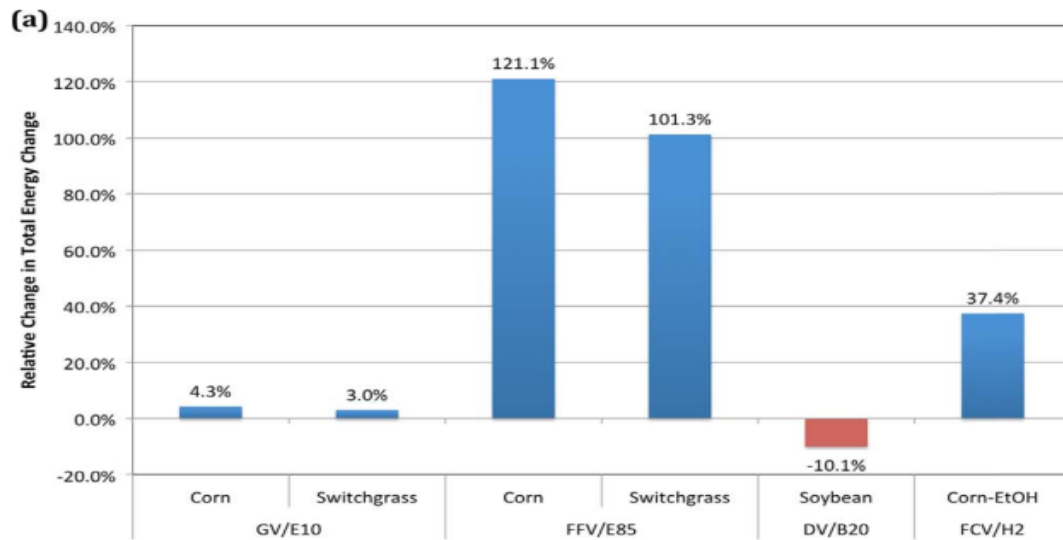


Figure 36 Relative change in total energy for various biofuel/vehicle systems.

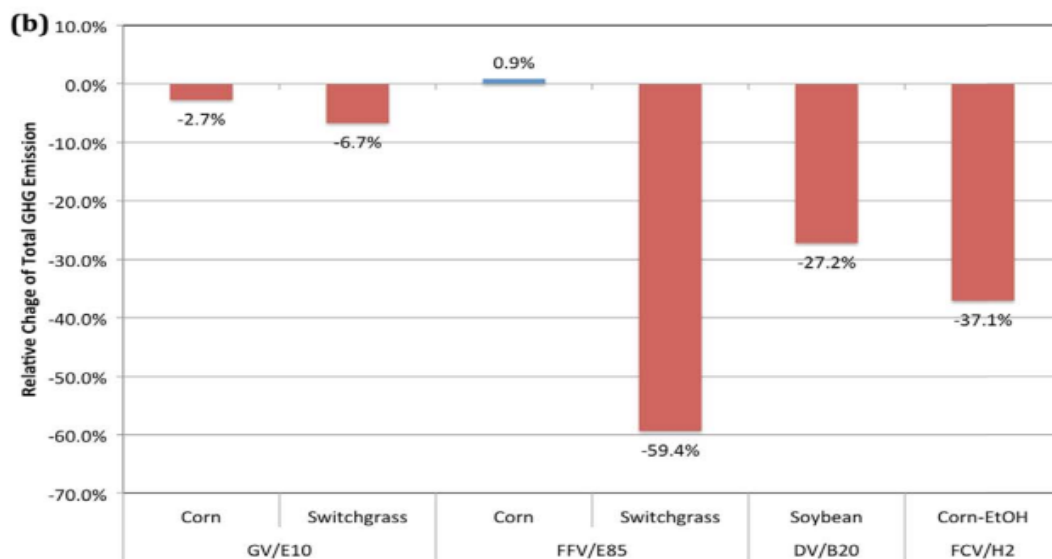


Figure 37 Relative change in GHG emissions for various biofuel/vehicle systems.

Conclusion

There has been an investigation on assessment of lifecycle energy consumption and GHG emission of different biofuel vehicles. Biodiesel from soybeans, bio-hydrogen from corn ethanol, and bioethanol from corn and switchgrass were options for transportation. There are comparisons of biofuel-to-wheel (BTW) efficiencies with conventional GVs. Conclusions are mentioned below.

1. FFVs/E85 blended with switchgrass ethanol had the best potential in GHG emissions minimizing.
2. It is not suggested to use FFVs/E85 blended with corn ethanol because it has higher energy consumption and GHG emission in feedstock step than the GVs.
3. FCVs which are fueled with bio-hydrogen from corn-ethanol have low GHG emission but they are high in energy consumption.

4. Even with using alternative fuel and biomass, the renewable fuel/vehicle choices can still get to a special amount of fossil energy reduction and petroleum consumption [33].

2.5 Biodiesel Plant Assessment

Thibério P.C. Souza, Luiz Stragevitch, Augusto Knoechelmann, Jose G.A. Pacheco, Jose M.F. Silva published an article entitled “Simulation and preliminary economic assessment of a biodiesel plant and comparison with reactive distillation” in 2014. Glycerin is a valuable by-product, which could add an appreciable credit to reduce the total manufacturing cost by approximately 10%.

Batch process simulation

The industrial batch plant of simulation was in Caetes, Brazil. The capacity of the plant was 270 kg/h or 562 ton/year of vegetable oil. The pilot plant operates 40 hours/week. The plant works with vegetable oils as raw material. The process is showed in Figure 38, it includes reaction step, biodiesel purification and alcohol recovery. The process was simulated in steady state mode in ASPEN/HYSYS. Mass and energy balance were considered. In this work, the pressure drops from pipe-lines were considered but the simulation did not consider pressure drops from heat exchangers. The cottonseed oil and methanol with alkaline catalyst were pumped into a batch reactor. The product mixture was sent to a decanter to separate glycerol from biodiesel after 60 minutes (reaction time). The biodiesel is in the light phase. It will be purified by washing process and alcohol. The alcohol is in the heavy phase which is mixed with glycerol. The alcohol is recovered by distillation column.

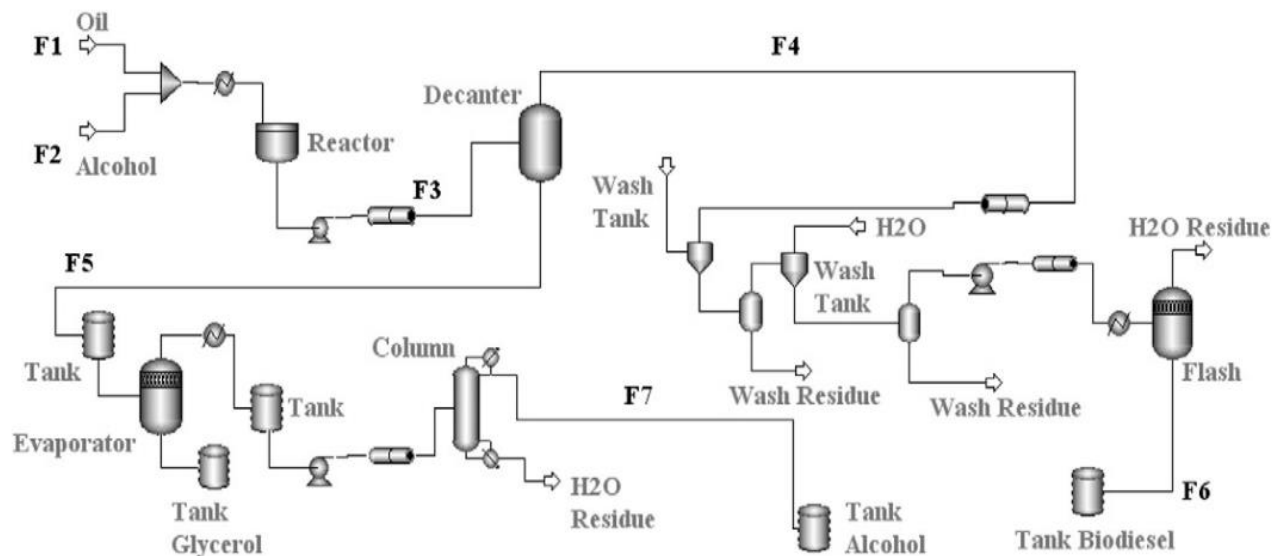


Figure 38. Process flow diagram for the biodiesel batch plant at Caetes/Brazil.

Table 4 Operational data from the plant Caetes/Brazil for biodiesel production from cottonseed oil.

Variable	Value
Oil feed flow rate	270 kg h ⁻¹
Oil temperature	25 °C
Oil pressure	1 atm
Mass fraction of oleic triglyceride	0.2412
Mass fraction of palmitic triglyceride	0.1375
Mass fraction of linoleic triglyceride	0.5755
Mass fraction of stearic triglyceride	0.0458
Alcohol feed flow rate (methanol)	60 kg h ⁻¹
Temperature of alcohol	25 °C
Alcohol pressure	1 atm
Time batch reactor	60 min
Reaction temperature range	40 °C to 60 °C
Reactor pressure	1 atm
Reaction phase	Liquid
Flash temperature (biodiesel drying)	100 °C
Flash pressure (biodiesel drying)	660 mm Hg
Wash water flowrate	70 kg h ⁻¹

Kinetic Model

A pseudo-homogeneous kinetic model is considered for transesterification of cottonseed oil with methanol in batch reactor. The process occurs in a 1 L stirred batch reactor, at the temperatures of 40, 50 and 60°C, with a 6/1 molar ratio of methanol/cottonseed oil and a 1 wt.% concentration of NaOH catalyst of vegetable oil mass. Here are the kinetic model equations:

$$\frac{dC_{TG}}{dt} = -k * C_{TG} * C_A \quad (1)$$

$$C_A = C_{A0} - 3 * (C_{TG0} - C_{TG}) \quad (2)$$

$$k = k_0 * \exp\left(-\frac{E_A}{R*T}\right) \quad (3)$$

C_{TG} is triacylglycerols concentration, C_A is alcohol concentration, C_{TG0} and C_{A0} are initial feed concentrations, k is kinetic constant, k_0 is frequency factor of reaction rate, E_A is activation energy and T is temperature. The activation energy is 29.3 kJ/mole and k_0 is 3320 dm³/mole*min.

Operational conditions of the industrial plant

The flowrate of the biodiesel plant was 270kg/h of cottonseed oil and 60kg/h of methanol. The concentration of catalyst NaOH was considered 1wt.% of vegetable oil in simulation batch plant, that was similar to the industrial plant. NaOH catalyst was blended with alcohol then fed into the alcohol stream. Table 5 shows the properties and operational conditions of the main streams.

1 Table 5-1 Properties and operational conditions of the main streams of the batch industrial plant.

	F1	F2	F3	F4	F5	F6	F7
Temperature (°C)	25	25	50	25	25	110	41
Pressure (bar)	1.013	1.013	1.013	1.013	1.013	0.880	1.013
Mole Flow (kmol h ⁻¹)	0.310	1.860	3.214	2.411	0.803	2.493	0.200
Mass Flow (kg h ⁻¹)	274.48	59.60	788.70	714.74	73.96	716.19	6.41
Mass fraction							
Cotton oil	1.0000	0.0	0.0	0.0	0.0	0.0	0.0
Alcohol	0.0	0.9560	0.0	0.0	0.0	0.0	1.0000
Glycerol	0.0	0.0	0.0930	0.0001	1.0000	0.0	0.0
Biodiesel	0.0	0.0	0.9060	0.9999	0.0	0.9979	0.0
Water	0.0	0.0	0.0	0.0	0.0	0.0021	0.0
NaOH	0.0	0.0440	0.0	0.0	0.0	0.0	0.0

6 Continuous reactive distillation process simulation

There is a simulation of reactive distillation process. The capacity for processing cottonseed oil feedstock is 270kg/h. The process has ten stages. Oil feed is in stage 2 and alcohol feed is in stage 8. The columns should work with high liquid hold-up on trays. It helps facilitating mass transfer in high rates and kinetic of the chemical reactions. Here is Table 6, which includes operational data used in this simulation:

6 Table 6-Operational data of reactive distillation.

Variable	Value
Oil feed flow rate	270 kg h ⁻¹
Oil temperature	25 °C
Oil pressure	1 atm
Mass fraction of oleate	0.2412
Mass fraction of palmitate	0.1375
Mass fraction of linoleate	0.5755
Mass fraction of stearate	0.0458
Alcohol + NaOH feed flow rate	60 kg h ⁻¹
Temperature of alcohol	25 °C
Configuration column	Top down
Alcohol pressure	1 atm
Number of separation stages	10
Reflux ratio	4
Stage of oil feed	2
Stage of alcohol feed	8
Operating pressure	1 atm
Type of condenser	Total
Temperature on the top	65 °C
Temperature at the bottom	80 °C

In this process, the cottonseed oil enters into the column in stage 3. The alcohol enters into the column in stage 8. The product exits from the bottom of the column. it passes via a decanter where the biodiesel-rich stream is recovered from light phase. Washing process purifies the biodiesel. The glycerol rich stream was sent to the purification process. Alcohol recovery is done at the top of the column.

Results and discussion

The produced biodiesel based on vegetable oil used, cottonseed, is made of methyl stearate, methyl palmitate, methyl linoleate and methyl oleate. These makeups almost 89% of the mixture. The results of simulation of batch process are really close to the experimental results, which are shown in Table 7.

Table 7-Composition and flowrate of experimental and simulated biodiesel product.

Biodiesel flow	Experimental	Simulated	Residue ^a
Volume flow rate	270 kg h ⁻¹	271.8 kg h ⁻¹	1.8
Fraction of palmitic ester	0.1270	0.1016	0.0254
Fraction of stearate ester	0.0412	0.0539	0.0127
Fraction of oleic ester	0.2148	0.2018	0.013
Fraction of linoleic ester	0.5048	0.4673	0.0375
Methanol fraction	0.0004	0.0010	0.0006
Water content	<500 mg kg ⁻¹	400 mg kg ⁻¹	100 mg kg ⁻¹
HCl content	–	0.000007	–
NaOH content	–	0.000009	–
Glycerol content	0.0018	0.0016	0.0002

^a Residue is the difference between the simulated and the experimental value.

According to economic analysis of simulation, three parameters were focused on: the quality of the final product, the produced biodiesel flow rate and the fixed cost of the simulated process. Simulation process has close results to experimental data with few differences. Table 8 shows the evaluation for the quality of final biodiesel product.

Table 8-Biodiesel quality specification: experimental, simulated and standard.

Characteristics (unit)	Standard ^a	Experimental	Simulated	Residue
Water content, max (mg kg ⁻¹)	500	500	400	100
Total contamination, max	24	7	16	9
Ester content, min (% mass)	96.5	97.2	97.0	0.2
Total Glycerin (1% mass)	0.25	0.18	0.16	0.02
Methanol or ethanol, max (% mass)	0.20	0.038	0.11	0.072

^a ANP (Brazilian Petroleum Agency).

Simulation results based on Table 4 parameters, showed a biodiesel production with the rate of 270kg/h. This plant, is located in Caetes, invested USD\$344,262.00 for fixed capital expenses such

as equipment, buildings and automation and invested USD\$179,234.00 on outsourcing and personnel, which is showed in Table 9.

Table 9-Investment costs (USD\$) of the industrial batch plant Caetes/Brazil and reactive distillation process.

Expense	Industrial plant (Real data)	Reactive distillation (Estimated values)
Equipment	273,224.00	183,744.00
Building	16,393.00	16,393.00
Automation	54,645.00	36,748.00
Personnel	98,360.00	66,147.00
Outsourcing	80,874.00	54,388.00

The total cost of equipment is estimated USD\$273,224 which is showed in Table 9. The cost of equipment for simulation is calculated based on industrial plant which is represented about USD\$67,442 for pumps, distillation columns, flash drum, reactors, decanters, valves, filter press, fittings and pipes. The Lang factor was calculated about 3.90 based on data's in Table 6 and 7. It was multiplied by the cost of equipment for simulation about USD\$67,442. Final cost was calculated about USD\$263,026, which was 96% close to real investment in plant. The total annualized unit cost (TAUC) was calculated by simulation for Caetes, Brazil plant. This value for the TAUC gives a preliminary economic feasibility of 15%. An analysis was done on the cost of the operation. The cost of the raw feedstock (oil and alcohol), the yield of the product biodiesel and the cost of required energy in the process was calculated.

Figure 39(a) shows operating cost of the process. It is visible that the feedstock cost is 96% and the energy cost is 4%. Figure 39(b) shows required energy consumption by the reactor. It is about 58% of total energy used in the whole process.

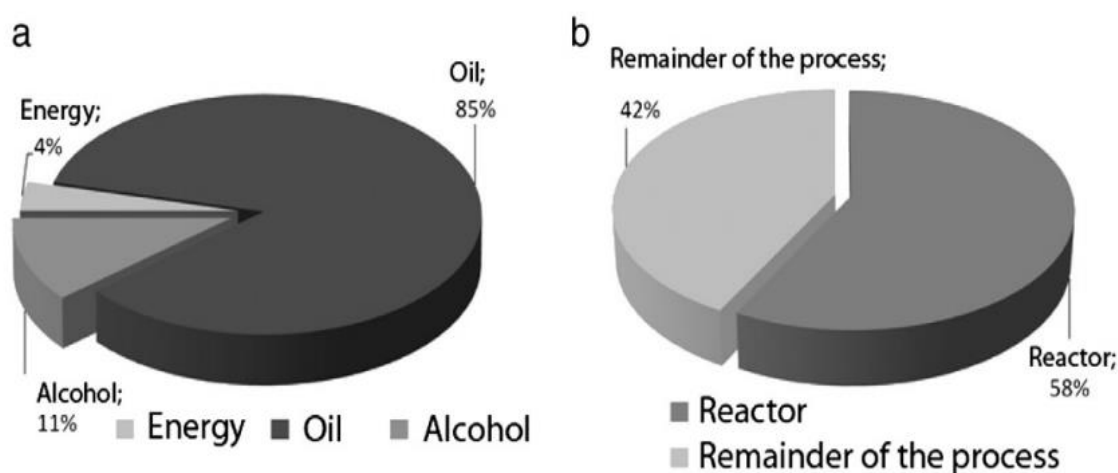


Figure 39-(a) Relative operating cost of the batch process. (b) Relative energy consumption.

Figure 40 shows the variation of the annualized unit cost which is a function of reactor temperature. When the temperature of the operation was between 48 °C and 60 °C, total annualized unit cost had its minimum value. The amount of produced esters is not enough to compensate the energy consumption at temperatures below 48 °C. At temperatures above 55 °C, the reaction occurs so fast because of this the increasing of energy is not necessary for obtaining products. In conclusion, the ideal reactor temperature is in the range between 48 °C to 60 °C. In these ranges the total annualized unit cost has minimum value.

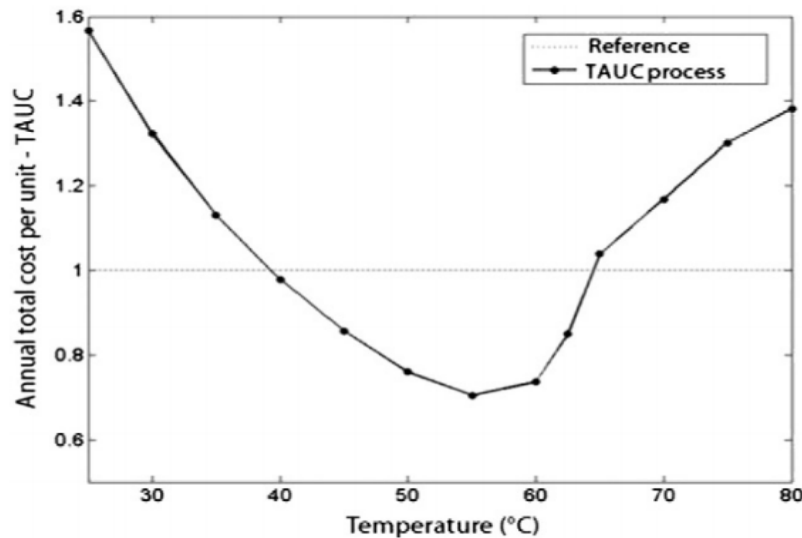


Figure 40. Total annualized unit cost (TAUC) vs. temperature.

A simulation of the reactive distillation process was done based on same calculation of 270kg/h of biodiesel production, which is visible in figure 41. The reaction and separation steps occur in same equipment. The flow of oil and alcohol and the reactive distillation column work as a counter flow. It effects on increasing the mass transfer efficiency during reaction.

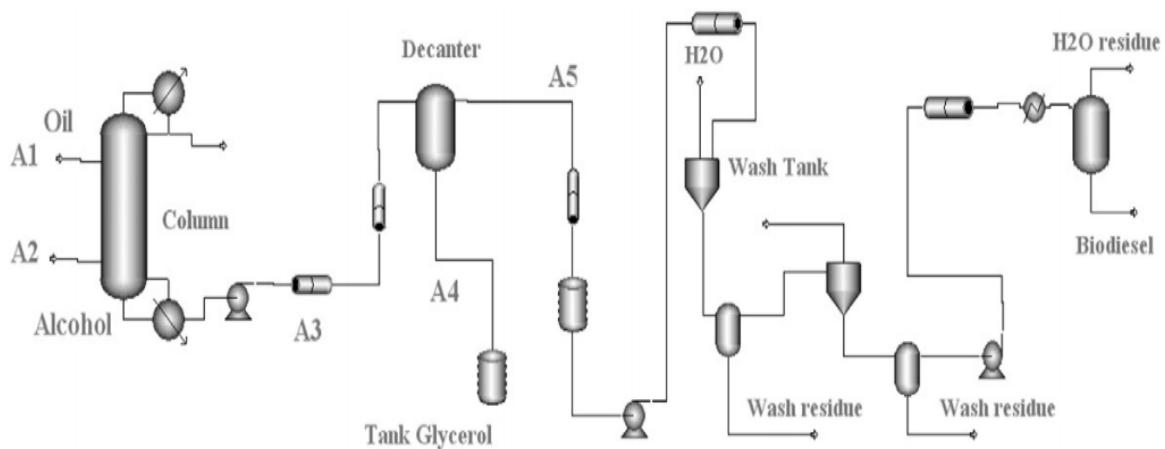


Figure 41. Process flow diagram of the continuous reactive distillation process.

The simulated concentration profile of oil, alcohol, glycerol and ester is shown in figure 42. There are 10 stages in the reactive column, where the first stage is located at the top of the column. The vegetable oil was fed into the column rectification zone in stage 2, while the alcohol was fed into the stripping zone in stage 8. It is concluded from figure 5 that a 10 stage column is enough for a 97% conversion of triacylglycerols (oil).

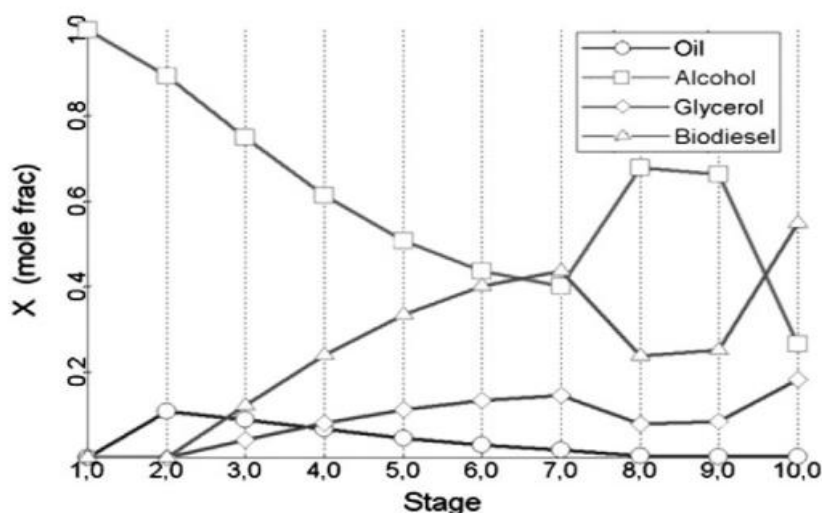


Figure 42. Profile of concentration along the column at a reflux ratio of 4:1.

Figure 43 presents that the triacylglycerols (oil) conversion increases with the increase of the oil to alcohol molar ratio. The results of the simulation showed that using same plant operating conditions of 270kg/h for a 97% conversion, a 0.74 total annualized unit cost (TAUC), the previous batch process had a 0.85 TAUC value. A 11% reduction in TAUC was visible that depends on increase in economic viability from 15% in batch process to 26% in reactive distillation process. In addition, the processing time in reactive distillation process is about 10-15 times faster than reaction time in batch process, which increases the viability of the process in large scale biodiesel production.

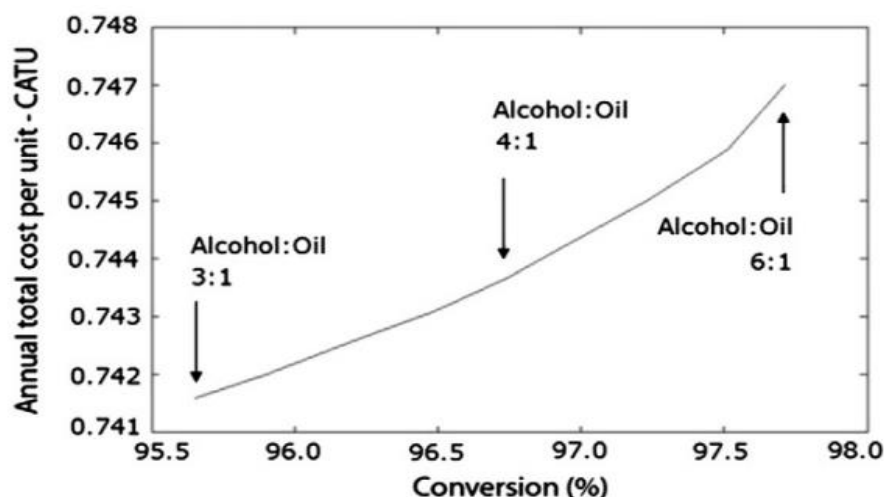


Figure 43. Total annualized unit cost of the reactive distillation process vs. conversion (Number of Stages is 10 and reflux ratio is 4).

The relative operating cost of the continuous reactive distillation process is shown in figure 44. Figure 44(a) presents the energy cost and feedstock cost which are 3% and 97%. These amounts are similar to the batch process results. Figure 44(b) presents the relative energy consumption which is needed by reactive distillation column, is about 39% and lower than operating cost of batch reactor which is 58%. In this process, oil cost is higher than the other costs.

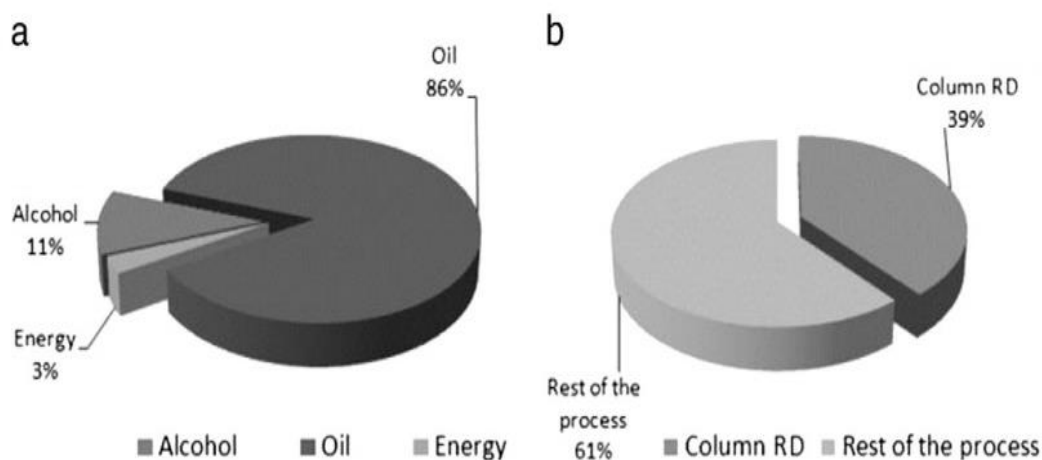


Figure 44 (a) Relative operating cost of the continuous reactive distillation process. (b) Relative energy consumption.

Conclusion

The price of feedstock effects on the cost of biodiesel production. Raw cottonseed vegetable oil has better price than soybean oil, which is used widely for biodiesel production. An industrial batch plant for producing biodiesel with rate of 270kg/h (561.6 tons/year), from transesterification of cottonseed oil, was simulated by ASPEN/HYSYS. The simulation results were matched to the experimental industrial plant. In addition, there is a study of the economic viability of batch process which is based on estimation of total annualized unit cost of the process. The relative energy consumption which is needed by the reactor is 58% of the whole energy used in the process. Temperature ranges between 48 °C to 60 °C is the ideal range, which the total annualized unit cost has its minimum value. A simulation of a continuous process operating with reactive distillation is done based on the same biodiesel production of 270kg/h. A reflux ratio of 4:1 and 10 stages for process is enough for oil producing with 97% conversion. So, increasing in alcohol/oil ratio from 3:1 to 6:1 increases the conversion from 95.6% to 97.6%. The simulation of the reactive distillation process showed economic viability of 26%, that is 11% higher than in the batch process in that the viability was about 15% [34].

2.6 Biodiesel Production from Waste Vegetable Oils

Sérgio Morais, Teresa M. Mata, António A. Martins, Gilberto A. Pinto, Carlos A.V. Costa published an article entitled "Simulation and life cycle assessment of process design alternatives for biodiesel production from waste vegetable oils" in 2010.

Transesterification is the most usual method to produce biodiesel, which uses a catalyzed chemical reaction includes a vegetable oil or fat and an alcohol, produces biodiesel and glycerol. Alcohols such

as methanol, ethanol and butanol can be used and the produced esters are called methyl, ethyl and butyl esters.

Alkali-catalyzed process

There are different methods for biodiesel production from lipidic feedstocks. Transesterification of triglycerides with low molecular weight alcohols is the most widely used way. It occurs in the presence of a homogenous alkali-catalyst and in a batch mode. It is suggested to use an excess methanol in the presence of the alkali-catalyst to change the reaction to a maximum production of biodiesel. Freedman et al. (1984) suggested a 6:1 molar ratio (methanol to oil), at a temperature of 333.25 K which is close to the methanol boiling point. The alkali-catalyzed transesterification reaction is very sensitive to the presence of free fatty acids and water in the lipidic feedstocks. Adding an alkali catalyst to the feedstocks, leads free fatty acids react with the catalyst and produces soap and water. The soap formation consumes catalyst and also leads to form emulsions, it makes biodiesel recovering and purifying difficult. Freedman et al. (1984) suggested to use refined vegetable oils with an FFA content lower than 0.5% (w/w) to enlarge methyl esters formation. In addition, water presence causes ester saponification under alkaline conditions.

Acid-catalyzed process

Pre-treatment operation can be avoided by an acid catalyst such as sulfuric acid. Pre-treatment operation is less sensitive than alkali-catalyzed transesterification to the presence of free fatty acids and gives high conversion rates. It needs longer times and higher temperature reaction. In addition, higher methanol to oil molar ratio helps to promote triglycerides to esters high equilibrium conversions. Canacki and Van Gerpen informed a 98.7% conversion in 48 hours at a 30:1 molar ratio of methanol to oil, at a temperature of 333.15 K. Zhang et al. and Zheng et al found a 97% conversion for a 4-hour reaction with a 50:1 methanol to oil molar ratio in 353.15 K.

Supercritical methanol process

Triglyceride transesterification with supercritical methanol is taken into consideration for biodiesel production. It is a catalyst-free process and high reaction rate. This performs the reaction in a few minutes (about 4 minutes). The insensitivity of this process to the impurities in vegetable oil such as, free fatty acids and water, can esterify free fatty acids simultaneously with triglycerides transesterification. Kusdiana and Saka reported that this process needs a very high molar ratio of methanol to oil which is about 42:1 and a very high temperature and pressure which are 623.15 K and 43 MPa.

Study goal and scope definition

This study performs an environmental evaluation of three process design alternatives for biodiesel production from waste vegetable oils, using process simulation and life cycle assessment. Here are the process design alternatives in this study: the alkali-catalyzed process with a free fatty acid pre-treatment (AICP), the acid-catalyzed process (AcCP) and the supercritical methanol process using propane as co-solvent (ScMP). This unit produces 1000 kg of biodiesel based on a process with 3500 tons per year capacity.

Process design and simulation

5 Alkali-catalyzed process with FFA pre-treatment

The alkali-catalyzed process model, with free fatty acid pre-treatment is shown in Figure 45. Stream 104 which is a waste vegetable oil stream with 428.50 kg/h stream is pre-heated in a heat exchanger. Stream 106A is the esterification reactor product that is fed into the esterification reactor (R-100) where the free fatty acids are converted to methyl esters. The free fatty acid content is assumed about 6% (w/w) in the vegetable oil. A fresh methanol stream flowrate of 9.50 kg/h (101) is mixed with a recycled methanol stream (110) and the sulfuric acid catalyst (103) to perform esterification. The esterification reaction occurred at 343.15 K, 405.3 kPa, a 6:1 methanol to oil molar ratio with 5% (w/w) of sulfuric acid catalyst in methanol. The conversion of free fatty acids in methyl esters is considered 95%. Stream 106A as the esterification products are cooled to 333.15 K in a heat exchanger that used to preheat the oil feed simultaneously. The products are sent to a glycerol washing column (X-100) where fresh glycerol (stream 108) is sued to wash out sulfuric acid and water. The treated vegetable oil leaves the glycerol washing column (X-100) and then exits from top stream (107). It contains 0.30% content of non-reacted free fatty acid. Glycerol, water and acid catalyst are remaining components which leave the glycerol washing column (X-100) in the bottom stream (109). Remaining components enter into a distillation column (T-100) where most of the non-reacted methanol (stream 110) is recycled and recovered to fed into the esterification reactor (R-100) again. Glycerol and sulfuric acid leave the distillation column (T-100) in bottom stream (111), that is fed to a neutralization reactor (R-101). Sulfuric acid is removed from glycerol by calcium oxide (stream 112). Precipitated calcium sulfate is removed in a gravity separator (X-101) and then treated as a waste stream (114). Glycerol stream (115) leaves the gravity separator (X-101). The glycerol stream is purified in a flash evaporator (T-101). The remaining methanol and water are removed in the top stream (117) in the flash evaporator. The remaining methanol and water stream (117) are treated as a waste stream because of its small mass flowrate (0.97 kg/h). The flash bottom stream (118) is recycled back to the glycerol washing column (X-100). This stream (118) is mixed with a fresh glycerol stream (108). The pretreated oil stream (107) from esterification process is sent to the transesterification reactor (R-200) with a 6:1 molar ratio of methanol to oil, 1% (w/w) of sodium hydroxide to do the reaction. Transesterification reaction occurs at 333.15 K, 405.3 kPa with a 95% conversion of oil to fatty acid methyl ester (FAME) after 2 hours. A fresh methanol stream with a 42.98 kg/h flowrate is mixed with anhydrous sodium hydroxide before entering the transesterification reactor (R-200). The products (stream 205) of transesterification reactor are fed to a vacuum distillation column (T-300). 94% of methanol is recovered in the vacuum distillation column in 4 theoretical steps with 1.5 reflux ratio. The column top stream is recovered from methanol (301) is recycled back to the transesterification reactor and mixes with fresh methanol stream. The column bottom stream (302A) includes biodiesel and glycerol and it should wash a column (X-400). Water washes biodiesel, and separates methanol, soap, glycerol and catalyst from fatty acid methyl ester in the washing column. The top stream leaves the washing column (402A), and it contains methyl esters and unconverted oil. Top stream is fed to a vacuum distillation column (T-500) in six theoretical steps. It is operated at a 1.5 reflux rate to separate remaining water and methanol from non-reacted oil and fatty acid methyl ester. A partial condenser is placed in the distillation column (T-100) overhead. It is due to fatty acid methyl ester separation from methanol and water. Fatty acid methyl ester is produced from bottom stream (502A) with 411.13 kg/h mass flowrate and 99.10% purity of the column overhead condenser. Water and methanol is got from the same condenser top stream (501) and are treated as a waste stream. Unconverted oil is got from the column bottom stream (503). It can be considered for recycling conversion and it is not

salts are removed in gravity separator (X-200) and they are treated as waste. Biodiesel and glycerol purification units (T-400, T-500) and remaining water washing column (X-300) are similar to the alkali-catalyzed process in operating conditions and equipment sizing. FAME is taken from the bottom stream (402A) of the condenser, with a mass flowrate of 408.67% and 99.14% purity. The glycerol by-products are taken from bottom stream of the column (T-500) with 46.57 kg/h flow rate and 91% purity.

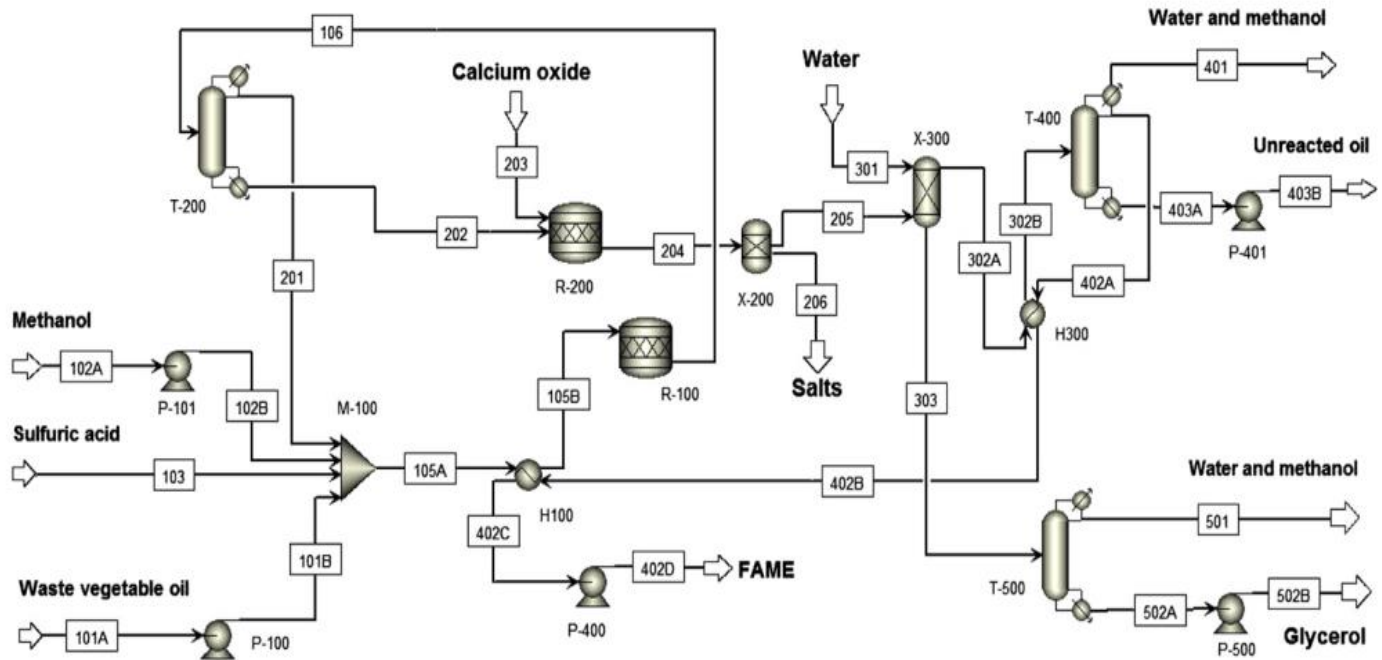


Figure 46 Acid-catalyzed process for biodiesel production from waste vegetable oils.

Supercritical methanol process using propane as co-solvent

Figure 47 shows the supercritical methanol process biodiesel production from waste vegetable oils. A stream of waste vegetable oil (stream 101A) with a flowrate of 410 kg/h is mixed with a fresh methanol stream (stream 102A) with a 45.33 kg/h, recycled methanol (stream 202B) and propane (stream 102) and entered to the transesterification reactor (R-100). The reaction occurs at 553.15 K, 12.7 MPa and a molar ratio of 1:24 for oil to methanol and 1:0.05 for methanol to propane. The reaction is done completely after 12.6 minutes of residence time in a 10 cm diameter and 7 m length plug flow reactor. The reaction products (stream 105) are sent to a flash evaporator (X-200) and the pressure reduced to 506.6 kPa. The pressure drop leads liquid methanol and propane transferring to gaseous form. The flash gas stream (201), which contains 92.2% methanol and 7.5% propane, is recycled back to the reactor with a 279.93 kg/h flowrate. The bottom flash stream (203A) is sent to settler unit (X-201). The FAME (stream 204A) from remaining methanol and glycerol (stream 205A) are separated there. A flash evaporator (X-300) is used to remove remaining methanol and propane in order to purify methyl esters (stream 204A). A FAME (stream 302B) is formed with a flowrate of 412.69 kg/h and 99.15% purity. A flash evaporator (X-400) purifies the glycerol by-product (stream 205A) which leads to form glycerol in flash bottom stream with a flowrate of 42.90 kg/h and 91% purity. Propane and methanol flash top stream (401) is recycled back to the transesterification reactor.

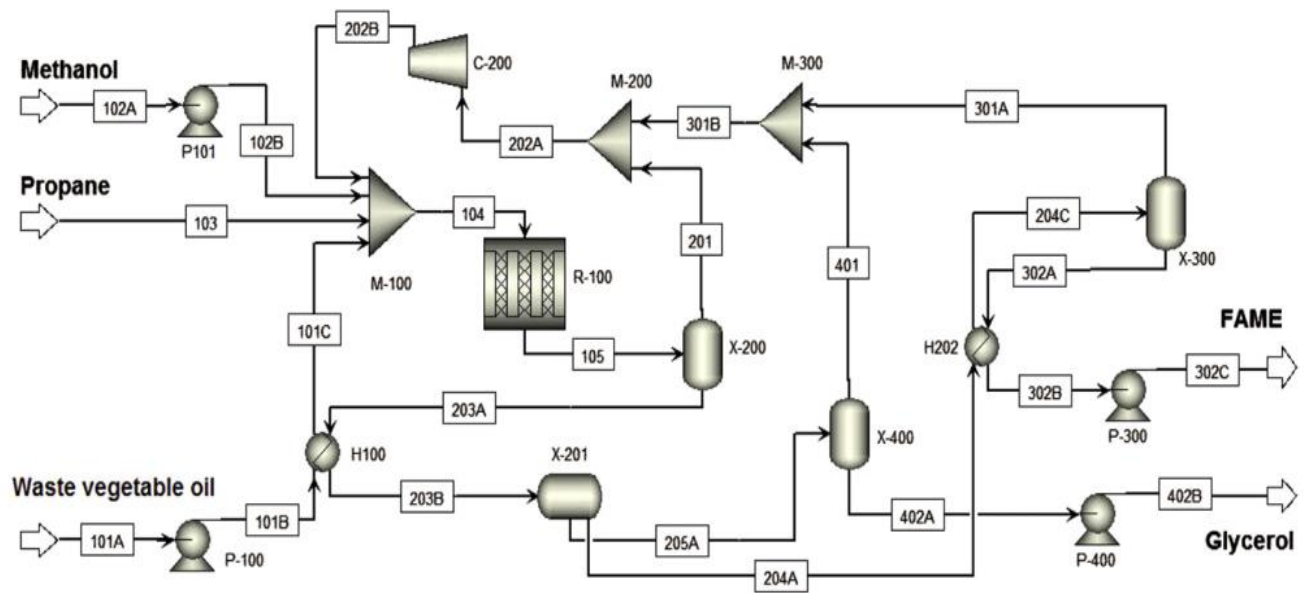


Figure 47. Supercritical methanol process with propane as co-solvent to produce biodiesel from waste vegetable oils.

Table 10 presents material and energy inventory data for each of the three process alternatives analyzed:

alkali-catalyzed process with FFA pre-treatment (AICP), acid-catalyzed process (AcCP) and supercritical methanol process using propane as co-solvent (ScMP). It is concluded from Table 10, the higher methanol to oil molar ratio for acid catalyzed transesterification reaction causes higher methanol flowrate (670 kg/h) in recycle step, which is 297.5 kg/h for ScMP and 23 kg/h for AICP.

Table 10. Material and energy inventory data for the three process alternatives.

Inventory	AICP	AcCP	ScMP
Products			
Biodiesel (kg)	1000.00	1000.00	1000.00
Glycerol (kg)	106.37	114.80	105.62
Feed			
Waste vegetable oil (kg)	1042.25	1035.32	995.51
Methanol (kg)	126.80	214.45	110.09
NaOH (kg)	9.80	—	—
H ₂ SO ₄ (kg)	0.15	149.09	—
H ₃ PO ₄ (kg)	7.95	—	—
CaO (kg)	0.10	85.24	—
Propane (kg)	—	—	0.02
Glycerol (kg)	0.05	—	—
High pressure steam (300 °C) (kg)	—	—	196.55
Medium pressure steam (250 °C) (kg)	935.30	933.24	239.53
Low pressure steam (100 °C) (kg)	1750.81	3366.96	—
Electricity (kWh)	1.01	0.95	4.01
Water (Process) (kg)	48.65	39.44	—
Water (Cooling) (kg)	3143	5031	510
Waste			
Salts (kg) (to landfill)	16.00	205.71	—
Hazardous liquid waste (kg) (to wastewater treatment)	37.92	172.21	—

Normalized potential environmental impacts of the conventional alkali-catalyzed process with FFA pre-treatment (AICP) is shown in Figure 48. The most considerable impact category is marine aquatic eco-toxicity. Steam use is the most important participant for all the PEI categories in the AICP process

alternatives. Methanol recovery and FAME purification in the multi-stage distillation unit demand the most energy.

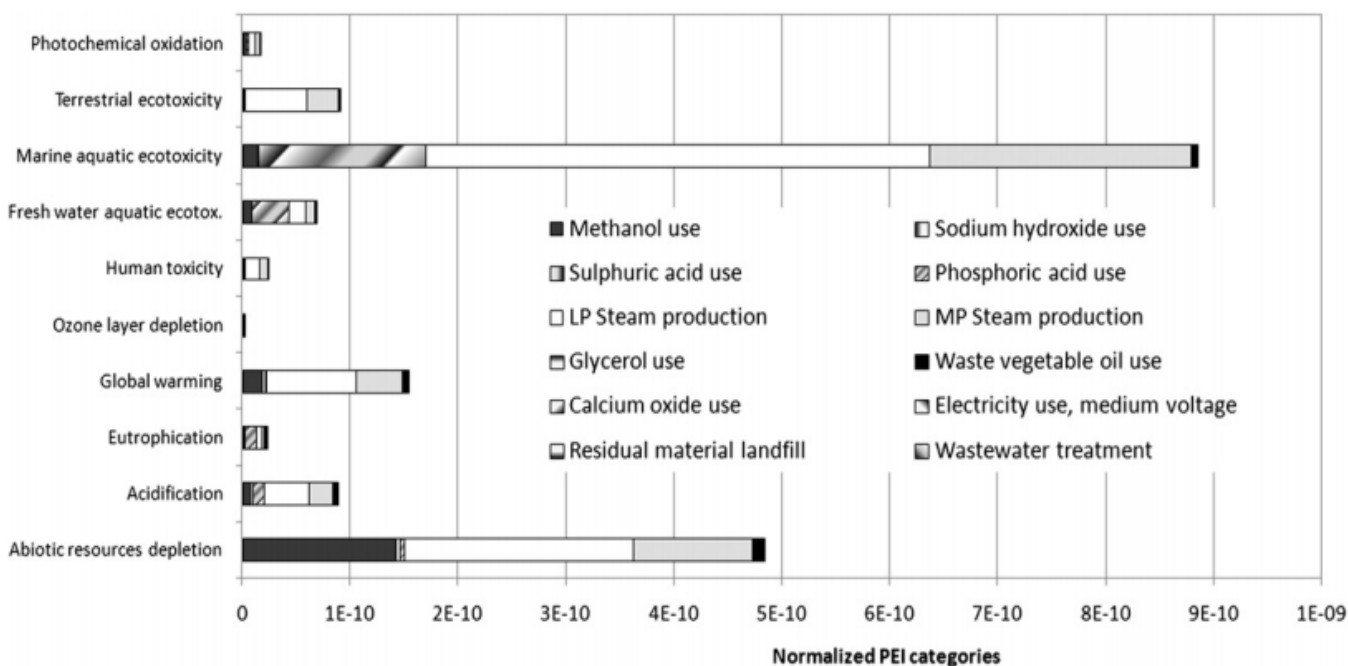


Figure 48 Contribution of resources use and waste treatment to the normalized PEI categories of the alkali-catalyzed process with FFA pre-treatment.

Normalized PEI categories for AcCP is presented in Figure 49. Using low pressure steam has an important role to all PEI categories in methanol recovery distillation column.

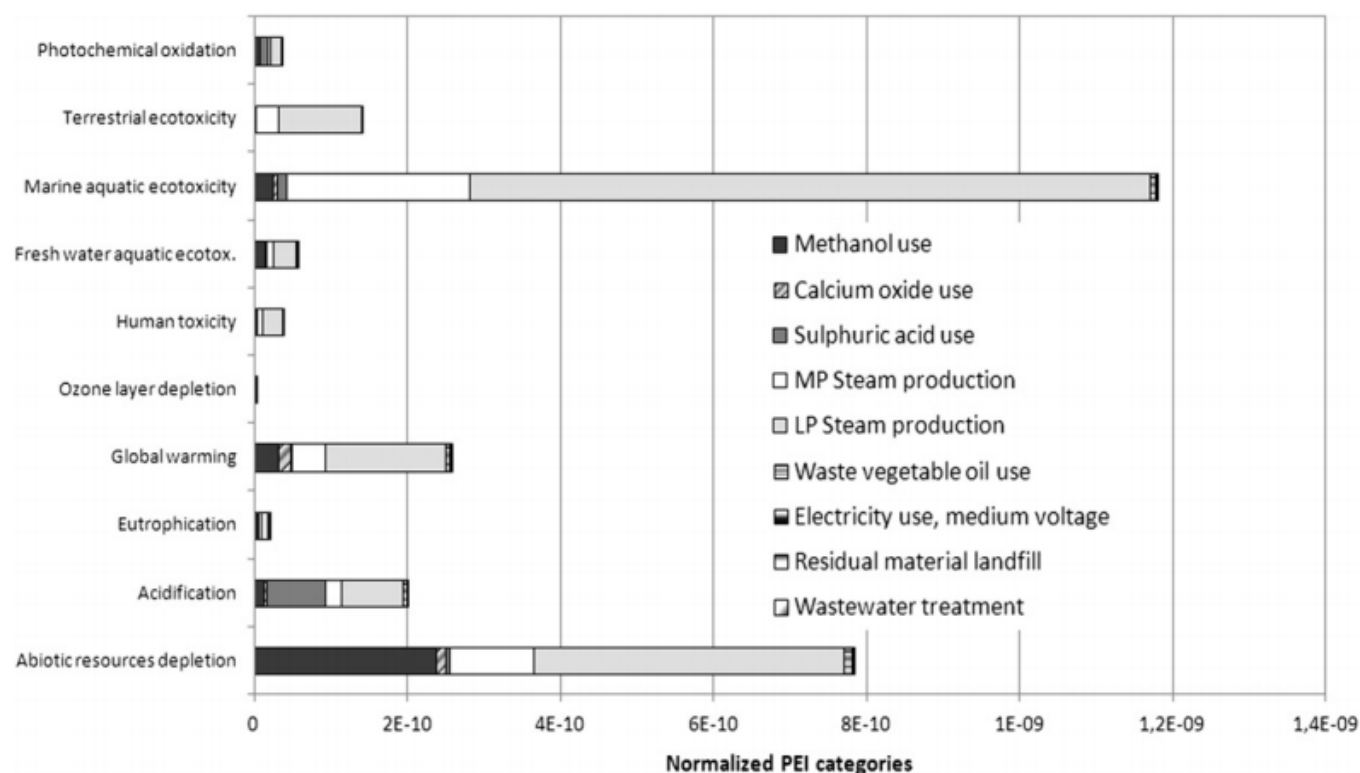


Figure 49 Contribution of resources use and waste treatment to the normalized PEI categories of the acid-catalyzed process.

Normalized PEI's associated with the ScMP is presented in Figure 50. The most important impact category is depletion of abiotic resources and marine aquatic eco-toxicity is the second important impact category, in this process. Methanol is formed in a fossil oil based refinery which leads to having an important participation with abiotic resources depletion.

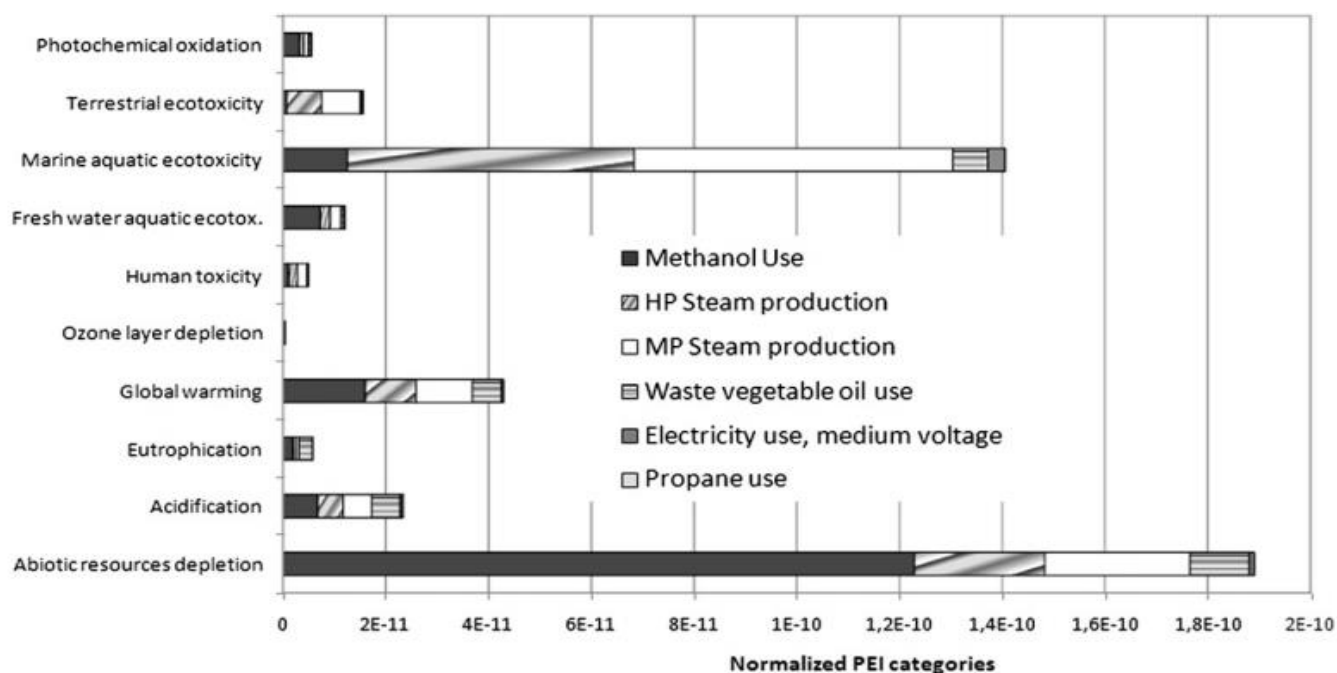


Figure 50 Contribution of resources use to the normalized PEI categories of the supercritical methanol process using propane as co-solvent.

Comparison of normalized PEI categories for the three process design alternatives is shown in Figure 51. The PEI includes these categories: eutrophication, ozone layer depletion, human toxicity, fresh water aquatic eco-toxicity and photochemical oxidation. The AcCP showed some results relatively to the AICP, an increase of 62% in abiotic resources depletion, 67% in global warming, 33% in marine aquatic eco-toxicity and 126% in acidification because of using large amount of sulfuric acid and low pressure steam. Acid-catalyzed transesterification reaction needs a higher molar ratio of 50:1 for methanol to oil to prepare higher energy for methanol recovery.

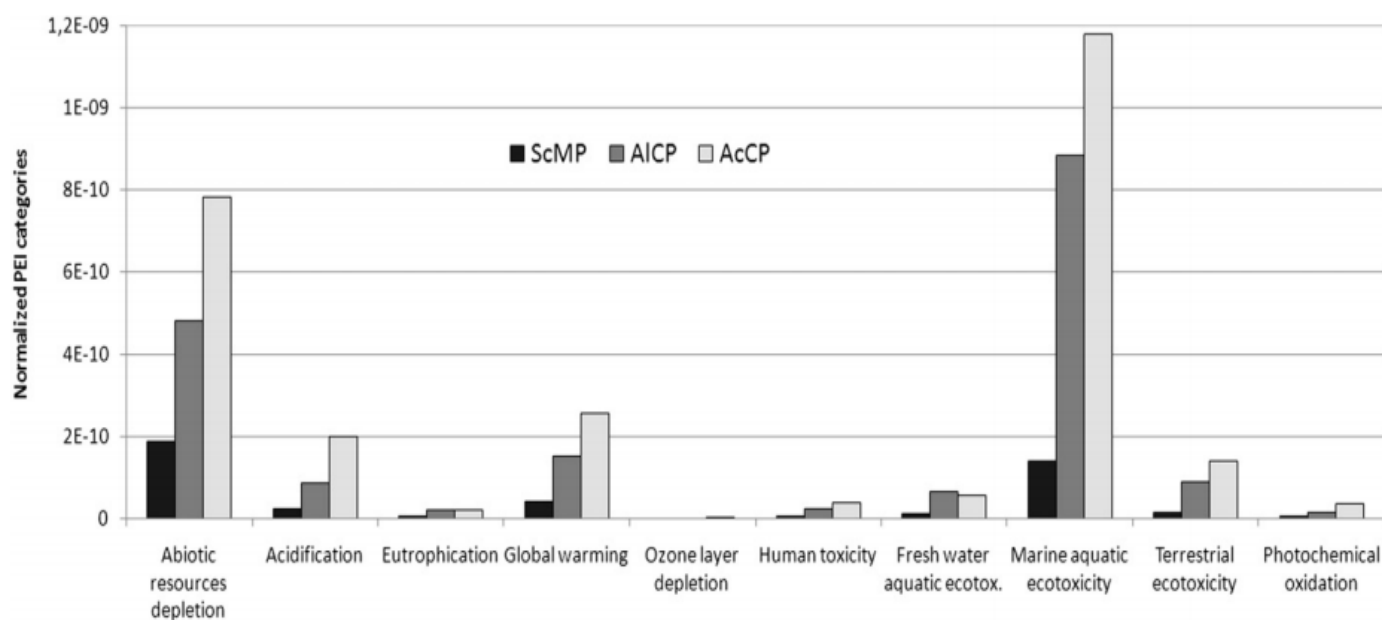


Figure 51 Comparison of normalized PEI categories for the three process design alternatives: supercritical methanol process using propane as co-Solvent (ScMP), alkali-catalyzed.

The ScMP has the least contribution with potential environmental impacts (PEI's), due to it the ScMP is the most environmental friendly for biodiesel production. In contrast with AICP, the ScMP decreases acidification by 754%, global warming by 496%, abiotic resources depletion by 313% and marine aquatic eco-toxicity by 793%. The downstream operations which are related to the supercritical methanol process are easier than other process alternatives. Methanol recovers by pressure depression in a flash evaporator. Glycerol separated from FAME in flash evaporators and no catalyst is consumed here. Kiwjaroun et al. (2009) concluded that the supercritical process has higher PEI than the conventional alkali-catalyzed process with FFA pre-treatment. It is because of higher amount of methanol demand for supercritical transesterification reaction. Avoiding waste production is visible by using a co-solvent in the ScMP at low temperature.

Applications such as hydrodynamic cavitation reactor in alkali-catalyzed process are attractive by economics and environmental. They minimize mass transfer resistance during transesterification reaction. Mancosky et al (2007) claimed that the mentioned alternative with a lower reaction time, allows using different of feedstocks various kinds of free fatty acid concentrations and avoiding FFA pretreatment due to less emulsification. Boocock et al (1998) also stated that, the co-solvent using in the alkali-catalyzed process decreases the mass transfer resistance of the reaction, which decreases the reaction time to 7 minutes and lead to FFA conversion to methyl esters.

Conclusion

Marine aquatic eco-toxicity and depletion of abiotic resources are related to the PEI categories for analyzed alternatives. Higher PEI for acid-catalyzed process is reported, that is pollutant because of high energy demands for methanol recovery unit. The supercritical methanol process with propane as a co-solvent is the most environmentally friendly between three process alternatives. Despite high energy intensive for supercritical methanol process, methanol recovery and purification products have simple structures. It decreases the overall energy consumption in contrast with other alternatives for process.

Steam production is one of the most important participant in PEI of acid and alkali-catalyzed processes. So, it is a good chance to decrease environmental concerns by reducing steam demand for three process alternatives [35].

Chapter 3

Examining the Change of Some Parameters on the Conducted Studies

3.1 Biodiesel Plant Configurations

Here are four biodiesel plant configurations which are investigated: 1- a homogeneous alkali-catalyzed pure vegetable oil process

2- a two-step process to treat waste vegetable oils

3- a single step homogeneous acid-catalyzed process to treat waste vegetable oil

4- a homogeneous acid-catalyzed process using hexane extraction to help purify the biodiesel

The suitable conditions for the homogeneous alkali-catalyzed process are at a pressure of 1 atmosphere, 60°C, a 6-1 alcohol to oil molar ratio and a catalyst weight percent of 1.

The acid-catalyzed process needs 48 hours at 60°C, at a molar ratio of 30:1 for alcohol-to-oil to have a 98% conversion. The reaction time of this process can be reduced to 8 hours in a temperature of 100°C and a pressure of 3.5 bar for a 99% conversion.

Supercritical transesterification processes achieve to high conversion at high temperatures, up to 350°C and a 42:1 molar ratio of alcohol-to-oil in just a quarter of time. Free fatty acids (FFA) and water can be tolerated up to 36 wt.% and 30 wt.% in feed stock. Unit operation conditions for each process is presented in Table 11.

Table 11- Unit operating condition for each process.

	Pre-treated alkali-catalyzed	Acid-catalyzed	Heterogeneous acid-catalyzed	Supercritical process
<i>Transesterification</i>				
Catalyst	H ₂ SO ₄ ^a /NaOH	H ₂ SO ₄	SnO	N/A
Reactor type	CSTR ^a /CSTR	CSTR	Multiphase	CSTR
Temperature (°C)	70 ^a /60	80	60	350
Pressure (kPa)	400 ^a /400	400	101.3	20 × 10 ³
Alcohol-to-oil ratio	6:1 ^a /6:1	50:1	4.5:1	42:1
Residence time (h)	1 ^a /4	4	3	0.333
Conversion (%)	100 ^a /95	97	94	98
<i>Methanol recovery</i>				
Reflux ratio	5 ^a /2	2	3.99	3.42
Number of stages	5 ^a /6	6	14	12
Condenser/reboiler pressure (kPa)	20 ^a /30	101.3/111	40/50	101.3/105.3
%Recovery	94 ^a /94	99.2	99.9	99.3
Distillate flowrate (kg/h)	201 ^a /119.3	1687	66.33	1239.7
Distillate purity (%)	99.5 ^a /100	100	99.9	99.99
<i>Catalyst removal</i>				
	Glycerol wash ^a /N/A	N/A	hydrocyclone	N/A
<i>Glycerol separation</i>				
	Water washing	Water washing	Gravity	Gravity
Water flowrate	11 kg/h	46 kg/h	–	–
<i>Catalyst neutralization</i>				
Neutralizing agent	H ₃ PO ₄	CaSO ₄	N/A	N/A
<i>Biodiesel recovery</i>				
Reflux ratio	2	2	2	2
Number of stages	5	10	8	8
Condenser/reboiler pressure (kPa)	10/15	10/15	101.3/111.3	101.3/111.3
%Recovery	99.9	98.65	99.9	99.9
Final purity	99.97	99.65	99.9	99.65

3.2 Equipment Information

Equipment such as pump, mixer, reactor vessels, columns, gravity separator and hydrocyclone have been used in this project.

Reactor vessels: The size of the reactor is obtained by dividing residence time by the flowrate of feed. Vessels have a 3:1 aspect ratio.

Columns: Columns with diameters higher than 0.90 meter are known as tray tower while columns with diameters less than 0.90 m are packed tower. Flooding velocity showed each packs' diameter. The height of tray tower is obtained by multiplying the actual stages by tray spacing. The height of reboiler and condenser is obtained by increasing the tray tower height by 20%. By multiplying the height equivalent of a theoretical plate by the number of stages, packed tower height can be obtained.

Gravity separators: Gravity separator is used for impurity separation. It was placed in heterogeneous acid-catalyzed and supercritical processes vertically with a ratio of 2.

Hydrocyclone: Hydrocyclone separates or cuts solid parts of a stream based on their size and density. Initial dimensions of hydrocyclone were obtained from HYSYS unit block [36].

3.3 Process Description

Simulation results

In the simulation performed, according to all the issues raised in the original source, it was necessary to choose some parameters hypothetically. It caused the results of the simulation to be slightly different from the results mentioned in the source. Another part of the difference is related to the software version and its activation type. Therefore, according to these cases, some results obtained from the simulation that was used with the software Case Study tool are presented.

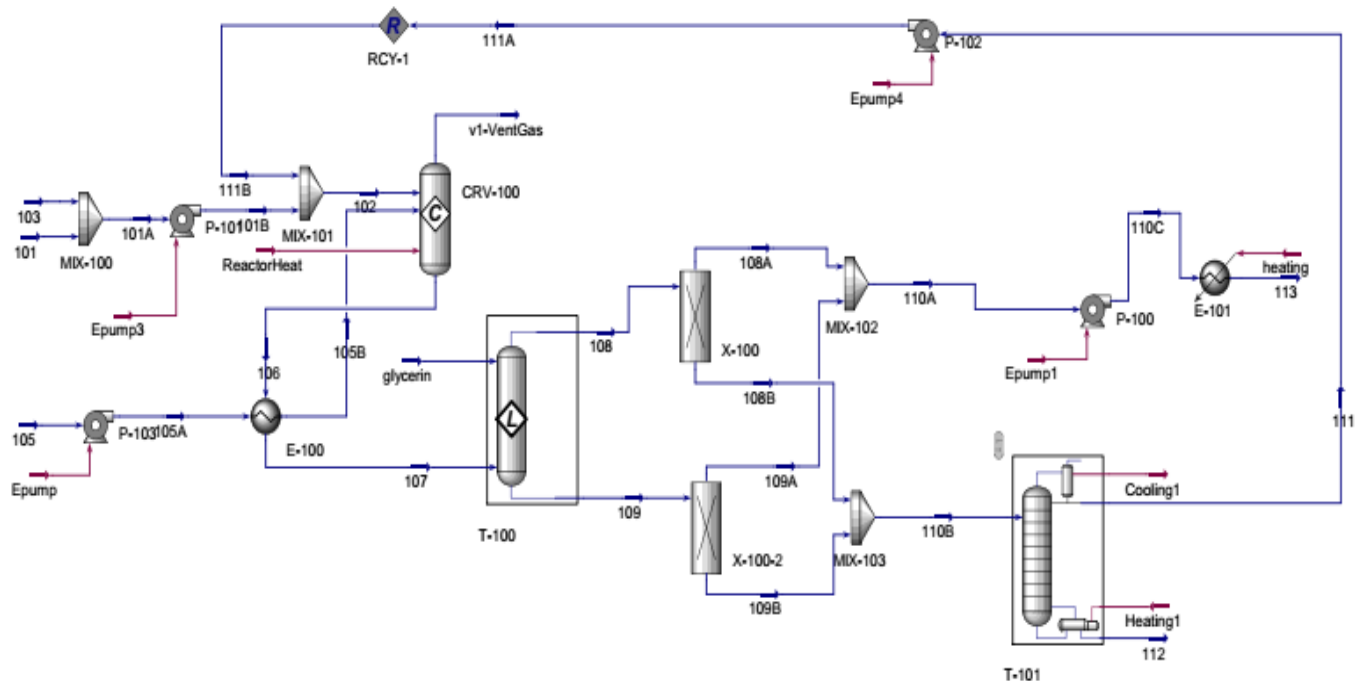


Figure 52-Process flow diagram.

3.4 Case Study

3.4.1 Case Study1: Effect of temperature on product amount

In this study, the temperature of the reactor was changed in the range of 75 to 112°C according to the flow of energy input to it, and the effect of temperature change on the mole fraction of the product was calculated by the software, which is shown in Figure 53.

Case Study 1

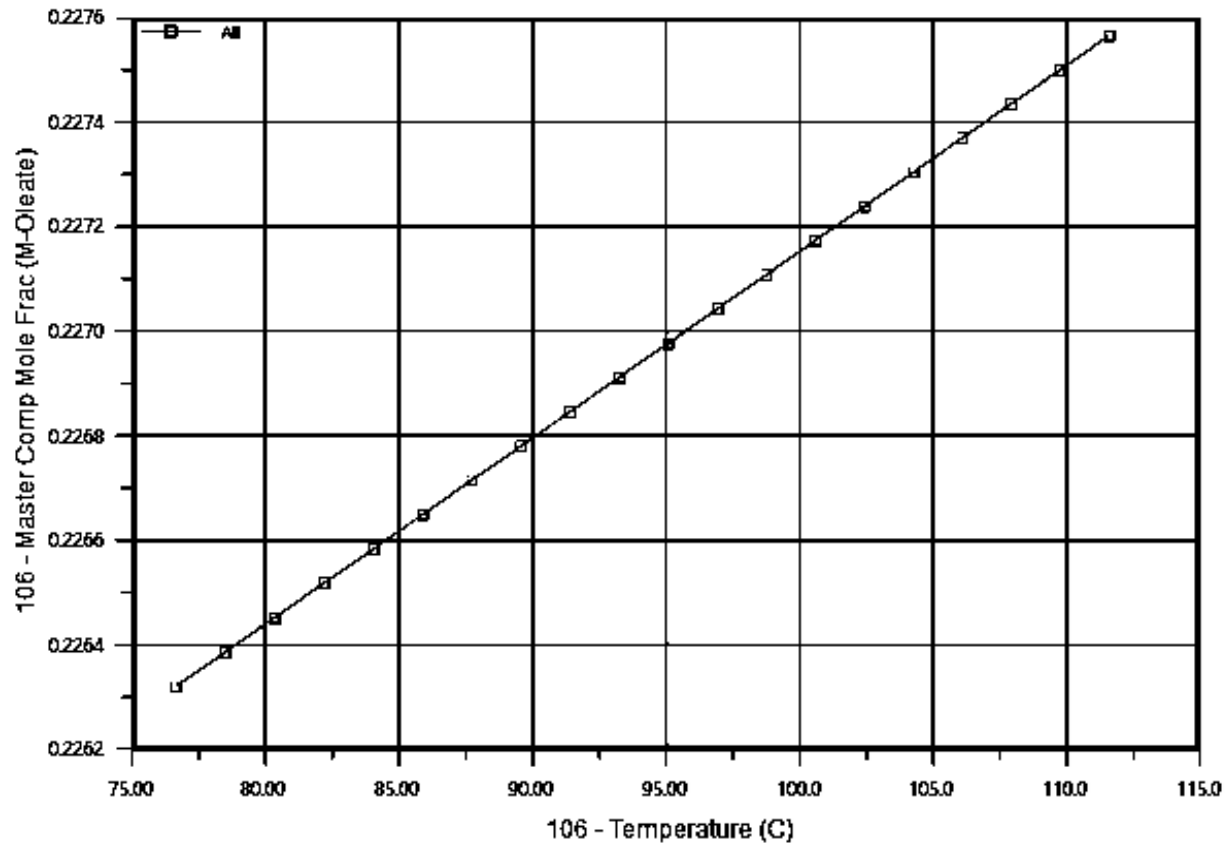


Figure 53- The effect of changing the reactor temperature on the molar fraction of the product in the output stream.

As it is shown in this figure, the molar fraction of the product increases by about 55% with the change of temperature from 75 to 112 °C, which is due to the endothermic nature of the biodiesel production reaction.

3.4.2 Case study 2: The effect of glycerin flow intensity in the product extraction process

In the extraction process that leads to product purification, determining the optimal amount of extractant is very important. According to the simulation, this issue was investigated in the liquid-liquid extraction tower.

As it is shown in figure 54, according to the three-phase equilibria related to the discussion of extraction, it shows that in different intervals in terms of flow intensity, the amount of extraction within the interval has a decreasing trend with increasing flow intensity, but each interval compared to its previous interval in total increases extraction.

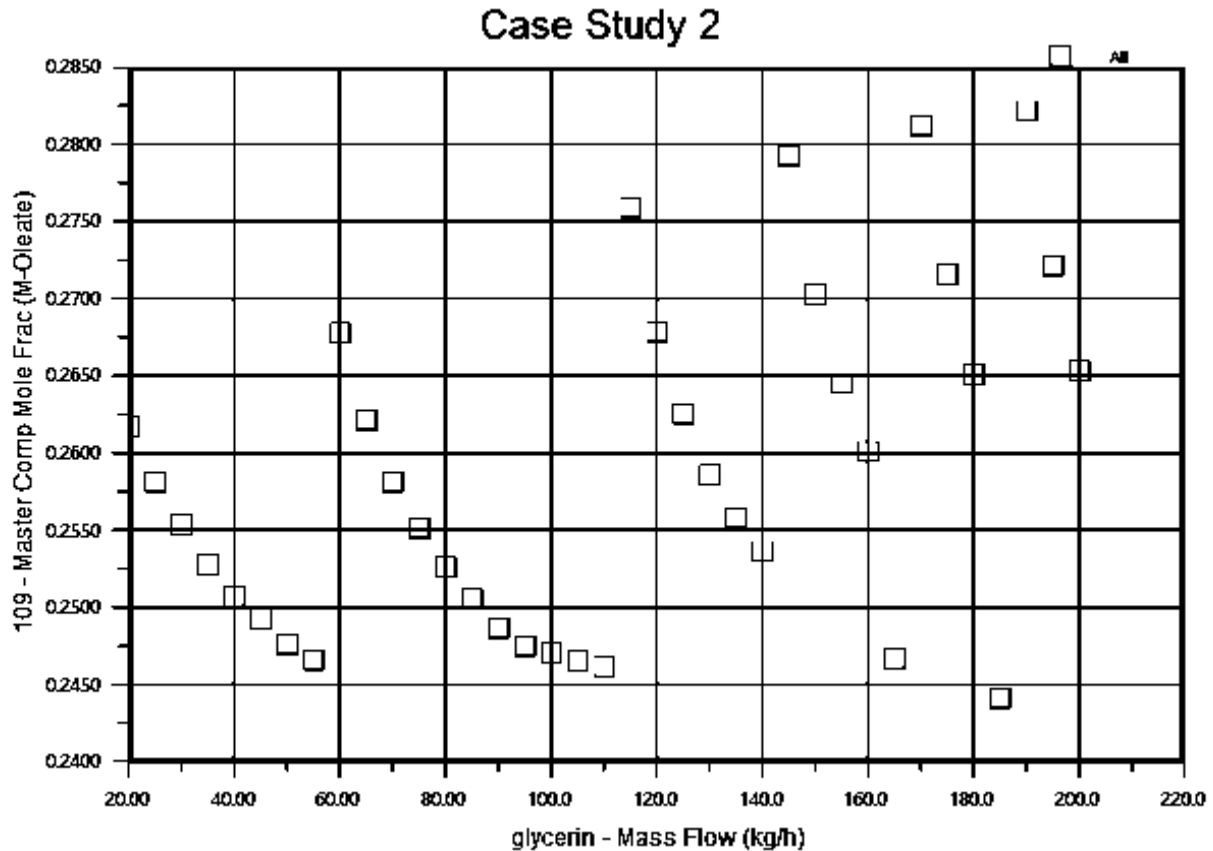


Figure 54-The influence of the flow intensity of the extraction material in the extraction process.

3.4.3 Case Study 3: The effect of temperature on the extraction process

Another factor that was investigated in the extraction process is the flow temperature of glycerin as an extractant. In this study, the temperature of this stream was changed from 5 to 100 °C. The results are shown in Figure 55.

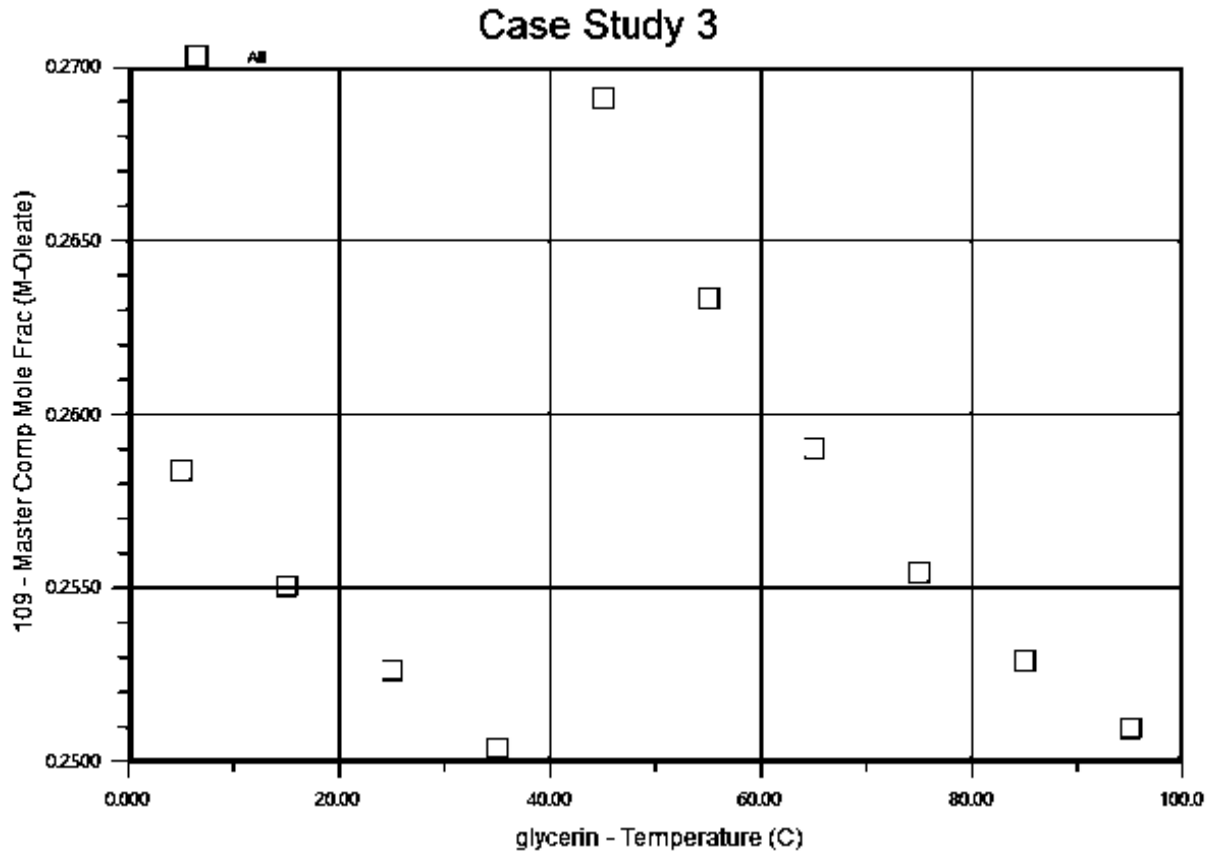


Figure 55- The influence of the temperature of the extractant flow in the extraction process.

As it is visible in this figure, it decreases with increasing temperature in the temperature range of 5 to 35 mole parts, but with increasing temperature from 35 to 40 we face an increase in mole parts, and it decreases again in the temperature range of 40 to 100 mole parts. This behavior is due to the three-phase equilibria of these materials in the vicinity of each other and under the influence of temperature.

3.4.4 Case Study 4: Effect of inlet temperature to methanol purification tower

Another investigated case is the influence of the temperature of the inlet stream to the methanol purification tower. This case, which was investigated separately, showed that with the increase in temperature from 20 to 150 °C the amount of methanol mixture in the upper flow of the tower decreases. This decrease will be around 14%. The results of this study are shown in Figure 56.

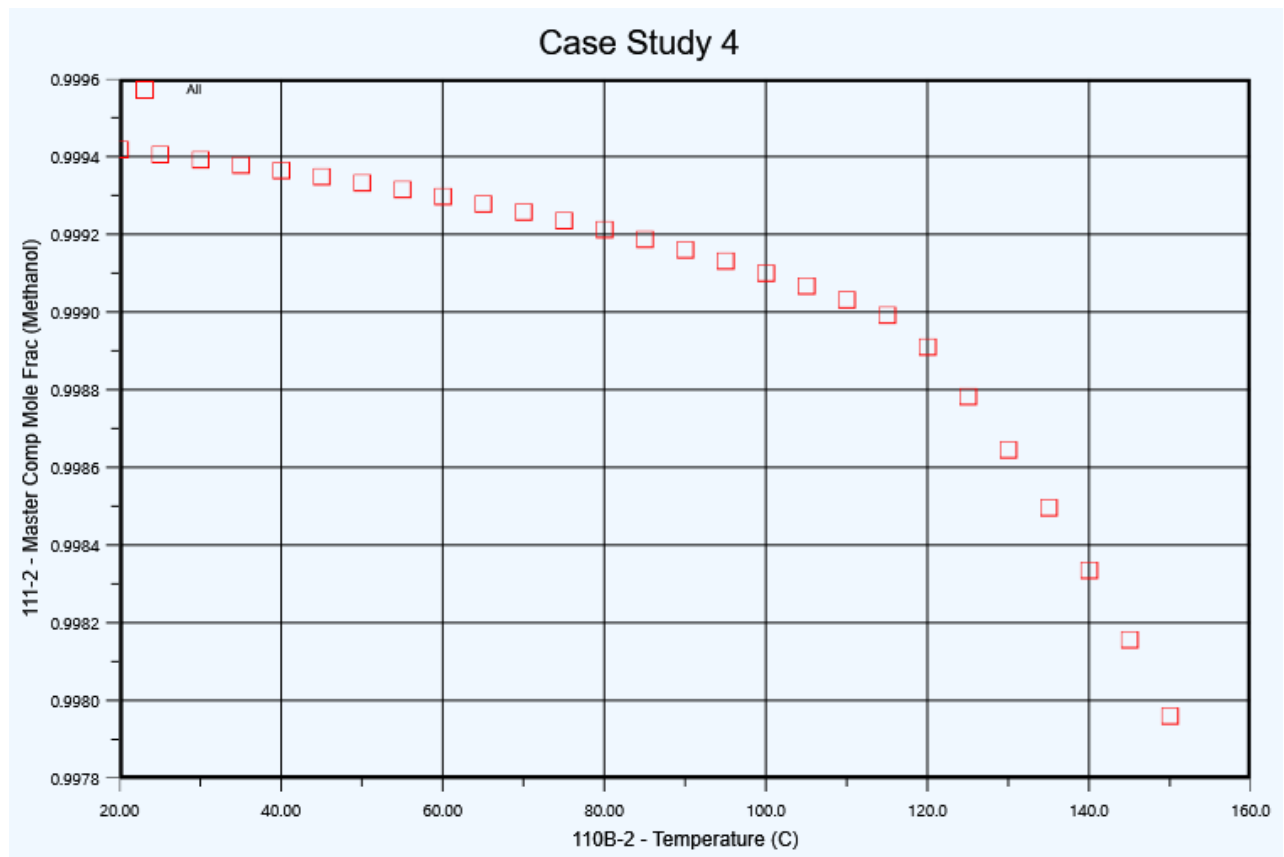


Figure 56-The effect of the temperature of the inlet flow to the methanol purification tower.

Chapter 4

Conclusion

Conclusion

The biodiesel production process is an effective process to provide energy from natural sources, which, in addition to environmental benefits, can be a sustainable and clean method for fuel production. The study conducted according to the simulation showed that this process, like most chemical, refinery and petrochemical processes, is influenced by process factors such as temperature, pressure, current intensity, etc. Although in this study, due to the fact that most of the materials in the process were in the liquid phase and the vapor and gas phases were created in the distillation process, the effect of pressure was not investigated. Simulation and case study results show that:

1-If the reactor temperature changes from 75°C to 30°C, the mole fraction changes from 0.2263 to 0.2275, which is equivalent to 0.57%.

2-If the mass flow of glycerin changes from 20 kg/h to 200 kg/h, the mole fraction changes from 0.2625 to 0.2650, which is equivalent to 0.95%.

3-If the flow temperature changes from 5°C to 100°C, the mole fraction changes from 0.2585 to 0.2700, which is equivalent to 4.44%.

4-If the inlet stream temperature changes from 20°C to 150°C, the mole fraction changes from 0.9994 to 0.9997, which is equivalent to 0.03%.

Suggestions

Due to the time constraints during this project, the following suggestions are provided to complete and continue this project:

Simulation and investigation of other biodiesel production methods

Simulating and checking other clean fuels such as biogas

References

- [1 N. G. Society, "National Geographic," 20 May 2022. [Online]. Available:
] <https://www.nationalgeographic.org/encyclopedia/fossil-fuels/> .
- [2 30 August 2018. [Online]. Available: https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Glossary:Petroleum_products.
- [3 A. Turgeon and E. Morse, "National Geographic," 28 July 2022. [Online]. Available:
] <https://education.nationalgeographic.org/resource/petroleum/>.
- [4 "Worldometers," [Online]. Available:
] <https://www.worldometers.info/oil/#:~:text=World%20Oil%20Reserves&text=The%20world%20has%20proven%20reserves,levels%20and%20excluding%20unproven%20reserves>.
- [5 A. Augustyn. [Online]. Available: <https://www.britannica.com/technology/gasoline-fuel>.
]
- [6 "HSA," [Online]. Available: https://www.hsa.ie/eng/about_us/.
]
- [7 "akpsho," [Online]. Available: <https://www.akpsho.com/en/single/10398/Mazut> .
]
- [8 "Energy Education," [Online]. Available: https://energyeducation.ca/encyclopedia/Natural_gas .
]
- [9 "worldometer," [Online]. Available: <https://www.worldometers.info/gas/gas-consumption-by-country/>.
]
- [1 "Office of Fossil Energy and Carbon Management," [Online]. Available:
0] <https://www.energy.gov/fecm/liquefied-natural-gas-lng>.
- [1 "shell," [Online]. Available: <https://www.shell.com/energy-and-innovation/natural-gas/liquefied-natural-gas-lng.html>.
1]
- [1 E. Koons, "energy tracker Asia," 31 March 2022. [Online]. Available: <https://energytracker.asia/is-lng-the-fuel-of-the-future/> .
2]
- [1 "java T point," [Online]. Available: <https://www.javatpoint.com/advantages-and-disadvantages-of-coal>.
3]
- [1 "Energy Education," [Online]. Available: <https://energyeducation.ca/encyclopedia/Coal> .
4]
- [1 "United Nations," [Online]. Available: <https://www.un.org/en/climatechange/what-is-renewable-energy#:~:text=Renewable%20energy%20is%20energy%20derived,plentiful%20and%20all%20around%20us> .
5]

- [1 "Solar Energy Industries Association," [Online]. Available: <https://www.seia.org/initiatives/about-solar-6> energy.
- [1 "National Renewable Energy Laboratory," [Online]. Available: <https://www.nrel.gov/research/re-7> solar.html.
- [1 "WINDExchange," U.S Department of Energy's Wind Energy Technologies Office, [Online]. Available: <https://windexchange.energy.gov/what-is-wind.8>
- [1 "EPA," [Online]. Available: <https://www.epa.gov/rhc/geothermal-heating-and-cooling-9> technologies#:~:text=Geothermal%20comes%20from%20the%20Greek,the%20ambient%20air%20above%20ground..
- [2 "Energy Education," [Online]. Available: https://energyeducation.ca/encyclopedia/Geothermal_power_plants.0
- [2 "energy.gov," Water Power Technologies Office, [Online]. Available: <https://www.energy.gov/eere/water/how-hydropower-works.1>
- [2 "energy.gov," Water Power Technologies Office, [Online]. Available: <https://www.energy.gov/eere/water/types-hydropower-plants#:~:text=There%20are%20three%20types%20of,renewable%20energy%20to%20the%20grid..2>
- [2 "ARENA," 8 August 2022. [Online]. Available: <https://arena.gov.au/renewable-energy/ocean/.3>
- [2 A. Turgeon and E. Morse, "National Geographic," 20 May 2022. [Online]. Available: <https://education.nationalgeographic.org/resource/biomass-energy.4>
- [2 "eia," [Online]. Available: <https://www.eia.gov/energyexplained/biomass/.5>
- [2 "SYNTECH BIOENERGY LLC," [Online]. Available: <https://www.syntechbioenergy.com/blog/biomass-6> advantages-disadvantages.
- [2 "britannica," [Online]. Available: <https://www.britannica.com/technology/fuel-oil.7>
- [2 "National Grid," [Online]. Available: <https://www.nationalgrid.com/stories/energy-explained/what-is-8> biogas.
- [2 "HomeBiogas," [Online]. Available: <https://www.homebiogas.com/blog/what-is-biogas-a-beginners-9> guide/.
- [3 J. F. Peters, D. Iribarren and J. D. Dufour, "Simulation and life cycle assessment of biofuel production via 0] fast pyrolysis and hydrouprgrading," *Fuel*, vol. 139, pp. 441-456, 2015.
- [3 V. F. Marulanda, "Biodiesel production by supercritical methanol transesterification: process simulation 1] and potential environmental impact assessment," *Cleaner Production*, vol. 33, pp. 109-116, 2012.

- [3 D. Pashchenko, M. Gnutikova and I. Karpilov, "Comparison study of thermochemical waste-heat
2] recuperation by steam reforming of liquid biofuels," *International Journal of Hydrogen Energy*, vol. 45, no. 7, pp. 4174-4181, 2020.
- [3 W.-R. Chang, J.-J. Hwang and W. Wu, "Environmental impact and sustainability study on biofuels for
3] transportation applications," *Renewable and Sustainable Energy Reviews*, vol. 67, pp. 277-288, 2017.
- [3 T. P. Souza, L. Stragevitch, A. Knoechelmann, J. G. Pacheco and J. M. Silva, "Simulation and preliminary
4] economic assessment of a biodiesel plant and comparison with reactive distillation," *Fuel Processing Technology*, vol. 123, pp. 75-81, 2014.
- [3 S. Morais, T. M. Mata, A. A. Martins, G. A. Pinto and C. A. Costa, "Simulation and life cycle assessment of
5] process design alternatives for biodiesel production from waste vegetable oils," *Journal of Cleaner Production*, vol. 18, no. 13, pp. 1251-1259, 2010.
- [3 A. H. West, D. Posarac and N. Ellis, "Assessment of four biodiesel production processes using
6] HYSYS.Plant," *Plant Bioresource technology*, vol. 99, pp. 6587-6601, 2008.
- [3 "National Grid," [Online]. Available: [https://www.nationalgrid.com/stories/energy-explained/what-is-](https://www.nationalgrid.com/stories/energy-explained/what-is-biogas)
7] biogas.
- [3 "AKY Technology," [Online]. Available: [akytechnology.com/en/specs/241/gravity-separators/gravity-](https://akytechnology.com/en/specs/241/gravity-separators/gravity-separator-machine)
8] separator-machine.
- [3 "WEIR," [Online]. Available: [https://www.global.weir/newsroom/global-news/news-articles/what-is-a-](https://www.global.weir/newsroom/global-news/news-articles/what-is-a-hydrocyclone-used-for-and-how-does-it-work#:~:text=A%20hydrocyclone%20is%20a%20simple,stream%20by%20size%20and%20density..)
9] hydrocyclone-used-for-and-how-does-it-
work#:~:text=A%20hydrocyclone%20is%20a%20simple,stream%20by%20size%20and%20density..

● 48% Overall Similarity

Top sources found in the following databases:

- 30% Internet database
- Crossref database
- 22% Submitted Works database
- 41% Publications database
- Crossref Posted Content database

TOP SOURCES

The sources with the highest number of matches within the submission. Overlapping sources will not be displayed.

1	coek.info Internet	12%
2	mafiadoc.com Internet	7%
3	Víctor Fernando Marulanda. "Biodiesel production by supercritical met..." Crossref	7%
4	Jens F. Peters, Diego Iribarren, Javier Dufour. "Simulation and life cycl..." Crossref	4%
5	Sérgio Morais, Teresa M. Mata, António A. Martins, Gilberto A. Pinto, C... Crossref	3%
6	Thibério P.C. Souza, Luiz Stragevitch, Augusto Knoechelmann, Jose G.... Crossref	1%
7	Dmitry Pashchenko, Mariya Gnutikova, Igor Karpilov. "Comparison stud..." Crossref	<1%
8	University of Western Ontario on 2022-11-20 Submitted works	<1%

9	Wei-Ru Chang, Jenn-Jiang Hwang, Wei Wu. "Environmental impact and..."	<1%
	Crossref	
10	University of Malaya on 2016-01-12	<1%
	Submitted works	
11	allaboutchemistry.net	<1%
	Internet	
12	researchgate.net	<1%
	Internet	
13	autodocbox.com	<1%
	Internet	
14	afdc.energy.gov	<1%
	Internet	
15	jotscroll.com	<1%
	Internet	
16	Eastern Institute of Technology on 2023-03-24	<1%
	Submitted works	
17	RMIT University on 2022-10-03	<1%
	Submitted works	
18	University of Sheffield on 2022-05-12	<1%
	Submitted works	
19	Vincenzo Palma, Daniela Barba, Eugenio Meloni, Simona Renda, Conce...	<1%
	Crossref	
20	mdpi-res.com	<1%
	Internet	

21	mobt3ath.com	Internet	<1%
22	ethesis.nitrkl.ac.in	Internet	<1%
23	Universiti Malaysia Perlis on 2020-01-14	Submitted works	<1%
24	fultonschools on 2022-01-27	Submitted works	<1%
25	authenticus.pt	Internet	<1%
26	hl-128-171-57-22.library.manoa.hawaii.edu	Internet	<1%
27	irep.iium.edu.my	Internet	<1%
28	worldwidescience.org	Internet	<1%
29	ciencia.lasalle.edu.co	Internet	<1%
30	"Carbon Footprints and Greenhouse Gas Emission Savings of Alternati...	Crossref	<1%
31	sigarra.up.pt	Internet	<1%
32	"Abstracts", Fuel and Energy Abstracts, 2015.	Crossref	<1%

33	Beijing City International School on 2019-12-02	<1%
	Submitted works	
34	CSU, San Jose State University on 2020-05-15	<1%
	Submitted works	
35	Kralisch, Dana, Denise Ott, and Doerthe Gericke. "Rules and benefits of ...	<1%
	Crossref	
36	Massey University on 2020-04-24	<1%
	Submitted works	
37	Plaza Vista School on 2011-11-23	<1%
	Submitted works	
38	The University of Manchester on 2015-04-27	<1%
	Submitted works	
39	University of Johannesburg on 2021-08-15	<1%
	Submitted works	
40	University of Wollongong on 2021-12-05	<1%
	Submitted works	
41	Kingston University on 2020-11-05	<1%
	Submitted works	
42	"Biorefineries", Springer Science and Business Media LLC, 2017	<1%
	Crossref	
43	American Public University System on 2020-11-22	<1%
	Submitted works	
44	greenmountainpower.com	<1%
	Internet	

45	aidic.it Internet	<1%
46	Brisbane Catholic Education on 2023-08-11 Submitted works	<1%
47	Jens F. Peters, Diego Iribarren, Javier Dufour. "Life cycle assessment o... Crossref	<1%
48	Lycoming College on 2021-11-29 Submitted works	<1%
49	Marulanda, V.F.. "Investigations on supercritical transesterification of ... Crossref	<1%
50	Monash University on 2015-12-16 Submitted works	<1%
51	Nottingham Trent University on 2022-05-30 Submitted works	<1%
52	The University of Manchester on 2013-04-22 Submitted works	<1%
53	Thibério P. C. Souza, Ronaldy J. M. C. L. Silva, James C. Melo, Isabelle ... Crossref	<1%
54	Whitsunday Anglican School on 2023-08-17 Submitted works	<1%
55	goingsolar.com Internet	<1%
56	A WEST, D POSARAC, N ELLIS. "Assessment of four biodiesel producti... Crossref	<1%

57	De Montfort University on 2022-03-27	<1%
	Submitted works	
58	University College London on 2011-09-05	<1%
	Submitted works	
59	scribd.com	<1%
	Internet	
60	Hingham High School on 2022-01-20	<1%
	Submitted works	
61	Solihull College, West Midlands on 2023-03-30	<1%
	Submitted works	
62	University College London on 2012-11-09	<1%
	Submitted works	
63	ecplaza.net	<1%
	Internet	
64	Engineers Australia on 2023-08-15	<1%
	Submitted works	
65	Hungarian University of Agriculture and Life Sciences on 2023-08-21	<1%
	Submitted works	
66	Southampton Solent University on 2013-12-08	<1%
	Submitted works	
67	Universiti Brunei Darussalam on 2022-09-27	<1%
	Submitted works	
68	University of Witwatersrand on 2022-06-07	<1%
	Submitted works	

69	docplayer.net	Internet	<1%
70	scilit.net	Internet	<1%
71	Anitescu, G.. "Fluid properties needed in supercritical transesterificatio...	Crossref	<1%
72	Antonio J. Yuste, M. Pilar Dorado. "A Neural Network Approach to Sim...	Crossref	<1%
73	Avondale College on 2023-03-17	Submitted works	<1%
74	Loughborough University on 2010-05-20	Submitted works	<1%
75	University of Malaya on 2010-05-18	Submitted works	<1%
76	University of Warwick on 2012-04-27	Submitted works	<1%
77	dokumen.pub	Internet	<1%
78	"Encyclopedia of Thermal Stresses", Springer Nature, 2014	Crossref	<1%
79	Brisbane Catholic Education on 2022-08-19	Submitted works	<1%
80	Coventry University on 2017-03-03	Submitted works	<1%

81	Coventry University on 2020-04-15	<1%
	Submitted works	
82	Griffth University on 2020-05-29	<1%
	Submitted works	
83	José A. León, Gisela Montero, Marcos A. Coronado, José R. Ayala et al...	<1%
	Crossref	
84	Konstadinos Abeliotis, Katia Lasaridi, Christina Chroni. "Life cycle asse...	<1%
	Crossref	
85	Moustapha Ouédraogo, Rasmané Semdé, Issa Toudoridomou Somé, R...	<1%
	Crossref	
86	Pennsylvania State System of Higher Education on 2020-02-10	<1%
	Submitted works	
87	Universiti Putra Malaysia on 2010-01-05	<1%
	Submitted works	
88	Universiti Sains Malaysia on 2010-11-22	<1%
	Submitted works	
89	academicrepository.khas.edu.tr	<1%
	Internet	
90	engj.org	<1%
	Internet	
91	coursehero.com	<1%
	Internet	
92	scielo.br	<1%
	Internet	

93	Columbus State University on 2020-10-09	<1%
	Submitted works	
94	Dmitry Pashchenko. "How to choose endothermic process for thermoc...	<1%
	Crossref	
95	East Allen County Schools on 2019-03-29	<1%
	Submitted works	
96	Gemma Vicente, Mercedes Martínez, José Aracil, Alfredo Esteban. "Kin...	<1%
	Crossref	
97	InSite Institution Placeholder on 2017-03-11	<1%
	Submitted works	
98	KDU College Sdn Bhd on 2021-04-15	<1%
	Submitted works	
99	Mariano Martín, Ignacio E. Grossmann. "Simultaneous Optimization an...	<1%
	Crossref	
100	Marulanda, VÃctor Fernando. "Biodiesel production by supercritical me...	<1%
	Crossref	
101	Peters, Jens F., Fontina Petrakopoulou, and Javier Dufour. "Exergy anal...	<1%
	Crossref	
102	Sawangkeaw, R.. "A review of laboratory-scale research on lipid conver...	<1%
	Crossref	
103	Tanawan Pinnarat, Phillip E. Savage. "Assessment of Noncatalytic Biod...	<1%
	Crossref	
104	Texas State University- San Marcos on 2021-10-26	<1%
	Submitted works	

105	The University of Manchester on 2014-04-04	<1%
	Submitted works	
106	Universiti Sains Malaysia on 2014-06-17	<1%
	Submitted works	
107	University of Strathclyde on 2013-04-25	<1%
	Submitted works	
108	University of West London on 2020-12-18	<1%
	Submitted works	
109	Youngsub Lim, Hong-shik Lee, Youn-Woo Lee, Chonghun Han. "Design ...	<1%
	Crossref	
110	alsf.academy	<1%
	Internet	
111	cdxapps.epa.gov	<1%
	Internet	
112	es.scribd.com	<1%
	Internet	
113	honors.libraries.psu.edu	<1%
	Internet	
114	uwspace.uwaterloo.ca	<1%
	Internet	
115	aimspress.com	<1%
	Internet	
116	hindawi.com	<1%
	Internet	

117	omicsonline.org	Internet	<1%
118	Dmitry Pashchenko. "A heat recovery rate of the thermochemical wast...	Crossref	<1%
119	Dmitry Pashchenko. "Industrial furnaces with thermochemical waste-h...	Crossref	<1%
120	Rochester Community and Technical College on 2020-11-30	Submitted works	<1%
121	University of Bath on 2015-12-25	Submitted works	<1%
122	"AI-Powered IoT in the Energy Industry", Springer Science and Busines...	Crossref	<1%
123	"Chapter 4 Biorenewable Liquid Fuels", Springer Science and Business ...	Crossref	<1%
124	Higher Education Commission Pakistan on 2009-08-19	Submitted works	<1%
125	Mohsen Rezaei, Mehdi Mehrpooya. "Investigation of a new integrated ...	Crossref	<1%
126	North West University on 2011-10-31	Submitted works	<1%
127	The University of Manchester on 2014-04-04	Submitted works	<1%
128	Zaimes, George Gregory, Kullapa Soratana, Cheyenne L. Harden, Amy E...	Crossref	<1%