Process Modeling and Simulation of Levulinate Esters Production Using Commercial Software

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Abstract: This paper presents the conceptual design and simulation of a biofuels (Levulinic esters) synthesizing process by esterification of Levulinic acid with lower alcohols using H2SO4 as catalyst. Levulinic esters are used as valuable fuels and fuel additives due to their high octane number, low water solubility, and high content of oxygen. Furthermore, they have less negative environmental impacts compared to the base fossil fuels. The Levulinic esters production process was simulated using HYSYS V8.8 software. The thermodynamic properties and kinetic data are obtained from open literature and used in the Aspen HYSYS model. The process simulation method involved selecting thermodynamic model, defining chemical components, selecting suitable operating units and identifying operating conditions. A detailed process flow sheet for production of Levulinate esters was developed. Effects of pressure, temperature and type of alcohol on biofuel yield were investigated and optimum values of temperature, pressure and types of alcohol were obtained. The optimum conversion was achieved when the conversion reactor operates at a pressure and temperature of 5 bar and 150°C respectively. Maximum conversion was obtained using methanol compared to other considered types of alcohols.

1 Introduction

1.1 Background

Biomass is a biological material derived from living organisms relevant to plants or animals. However, biomass for energy production includes dedicated energy corps, agriculture wastes, aquatic plants, like algae, wood and wood residues, and animal waste. The increase consumption of biomass for producing non-food products has raised investigations and improvement activities around the world toward better market introduction. In this regard, bio-refining as a novel concept was introduced. Bio-refinery is a facility that combines biomass conversion processes and equipment to produce power, and biomass-based fuels and chemicals [1-3]. Both bio-refinery and conventional petroleum refinery have identical objectives such as, large scale operability. However, the bio-refinery processes that related to biomass production has potential improvement where more energy and cost effective novel processes can be established. Based on these principles, lignocellulosic biomass derived from Levulinic acid as one of the top-twelve sugar-
based building blocks was found as an excellent feedstock for additional alteration and utilization in bio-
refinery processes [4].

Levulinic acid (LA) is an organic compound with the formula CH3C(O)CH2CH2CO2H, density: 1.14 g/cm3, and molar mass: 116.11 g/mol. It has high solubility in water and organic solvents including acetone, diethyl ether and lower alcohols. The first study on the preparation of LA was conducted by heating sucrose with mineral acids at high temperature as shown in Figure 1.

Figure 1: Chemical equation for acid catalyzed production of LA

Conversion of lignocellulosic biomass to LA has been widely studied. The acid technology is vital for the commercial manufacture of LA. The conversion process of a typical biomass to LA is shown in Figure 2.

Figure 2: Reaction scheme for the conversion process of lignocellulosic biomass into LA [5]

Acidic hydrolysis of lignocellulose is a simple thermochemical process causes the break of polymer sugars to both C5 and C6 sugars. A degradation product of C6 sugar is 5-hydroxymethylfurfural (HMF); a furan compound that can be changed (through hydration) to Levulinic acid and formic acid in equimolar quantities. LA is a maintainable platform molecule that can be promoted to valued chemicals and fuel additives [6]. For higher scale applications of LA, continuous process for the production is advantageous [5].

1.2 Levulinate esters as biofuels

Biofuels are types of fuels that derived from natural sources. Biofuels could be produced from organic materials in a short period of time in contrasts with fossil fuels, which take millions of years to form. Generally, the feedstocks of biofuels are biomass including vegetable oils or animal fats [7].

A new process to produce a levulinic acid from lignocellulose consists of four steps was introduced by Shell Company in 2010 [8]. The four steps of the process are the acid hydrolysis of lignocellulosic materials to LA, the hydrogenation of the acid to GVL (gamma-Valerolactone) and valeric acid (VA), and finally esterification of the intermediates to alkyl (mono/di) valerate esters. Figure 3 shows the pathway for the conversion of lignocellulosic biomass to chemicals and fuels including LA and derivatives.
Figure 3. Pathway for the conversion of lignocellulosic biomass (rectangular) to chemicals (ovals) and fuels (pentagons), via intermediate formation of C5 and C6 sugars (GVL: gamma-Valerolactone) [9].

Since valerates (Levulinate esters) exhibit properties similar to those of engine fuels, they have been studied in order to assess their capacity as potential fuels for car engines or blends with gasoline or diesel. In general, Levulinate esters can in particular be used as plasticizers and fuel additives to modify the fossil fuel properties. Levulinate esters from low boiling alcohols like Ethyl levulinate, can be used as oxygenate additive. Also, it can be used as octane booster for gasoline [10, 11] and fuel extender for diesel and biodiesel [12]. However, other higher alkyl levulinates like butyl levulinate are also found to be good quality improvers for diesel, biodiesel and gasoline [11]. Also, levulinate esters could interchange kerosene as a fuel for the direct firing of gas turbines [5, 13]. Additional potential applications of Levulinate esters are in the fragrance and flavoring industries, and as plasticizer for cellulose plastics [14].

On the other hand, transesterification reaction has been indicated as the simplest and the most effective path for biofuels production in great quantities, in contrast to less friendly to the environment, costly and eventually low yield methods of pyrolysis and micro-emulsification. Hence, transesterification has become more common and the chosen method of biofuels production.

One of the typical organic esterification reactions to produce different esters of LA is the gradual reversible reaction of Levulinic acid with an alcohol. For the purpose of achieving high yields of levulinate esters, the reaction is usually carried out in the existence of a catalyst. Sulfuric acid (H2SO4) is a strong homogenous acid catalyst has been used widely to catalyze the esterification reaction and speed up the reaction [15, 16]. Heterogeneous metal catalysts [47, 48, 49] and solid acid catalysts such as acidic zeolites [17-22], Heteropolyacid [23-26] and acid supported catalysts [27,28] have been widely used in industry to overcome the drawbacks of homogeneous catalyst such as strong acids and peroxides in terms of non-environmentally friendly, separation, recycling and equipment corrosion. Alcohol has been used in excess to shift the equilibrium towards the formation of esters, to have complete reaction. Alcohols has frequently been used for transesterification are methanol, ethanol, propanol, and butanol, where methanol is the most widely used in transesterification process due to its low cost compared to other alcohols [7], and it’s petrochemical origin [29]. Novel methods to produce levulinate esters included the reaction of LA with an organic alcohol in a reactive-extraction mode. Here, the organic alcohol phase actions both as the esterifying agent and the extractant phase [30]. Figure 4 shows a typical chemical pathway for Levulinate esters.
Figure 4: Typical Chemical reaction for Methyl Levulinate synthesis

The physical properties of the four first members of Levulinate esters were identified by Lange and co-workers [8]. The properties are listed in Table1.

Table1. Properties of Velurinate fuels based on [9] with some modifications

| Fuel         | Structure          | M.Wt. g/mole | Blending Research Octane No. | IIIH | IVH | T | BRON | â-H exp. (kcal/mol) at 298K | Density kg/l |
|--------------|--------------------|--------------|------------------------------|------|-----|---|------|-----------------------------|--------------|
| Methyl Valerate | ![Methyl Valerate](image1) | 116          | 27.5                         | 28.5 | 410 | 115 | 371 | 0.875                      |
| Ethyl Valerate | ![Ethyl Valerate](image2) | 130          | 24.6                         | 30.3 | 415 | 100 | 361 | 0.874                      |
| Propyl Valerate | ![Propyl Valerate](image3) | 144          | 22.2                         | 31.5 | 446 | 90  | 277 | 0.870                      |
| Butyl Valerate | ![Butyl Valerate](image4) | 158          | 20.2                         | 32.6 | 466 | n.a. | 335 | 0.868                      |

BRON: Blending Research Octane No.

On the other hand, simulation is an effective tool used for design, control, and optimize of production processes. Simulations give a pre-assessment for the investigated processes. Hence, lot of time and money can be saved. Moreover, simulation technologies are much faster than running series of experiments [31]. Levulinate esters manufacturing processes have taken considerable attention from laboratories and bench scale production point of view. However, and to the best of our knowledge, rare information are available in the literature regarding the simulation of Levulinate esters production plant, design and operations. Hence, the aim of this study is to simulate and model a Levulinate esters production process on industrial scale.

Levulinic acid have been selected as the renewable feedstock for a strong homogenous acid catalyzed esterification reaction to produce different Levulinate esters. The oxygenated fuels highly contribute in the reduction of particulate matter and carbon monoxide formation. In addition, the oxygenated fuels improve the physical properties of the blended fuels such as lubricity and viscosity compared to the base fuel.

Flowsheet and simulation process have been developed to model the biofuels production process. A plant was designed for the esterification process. Moreover, effects of different parameters on conversion of the fuels produced were studied and optimized. These are types of alcohol, reactor temperature, and pressure. The analysis of the process was carried out based on the material and energy balance reported by Aspen-HYSYS software.
2 Methodology

2.1 Aspen-HYSYS simulation

Aspen-HYSYS is widely used as a powerful tool for simulation different chemical processes. In the current work, Aspen-HYSYS version 8.8 is used to simulate the biofuel production. Aspen-HYSYS simulator can be used to investigate operability and efficiency of the process. It offers reliable information on the operation of the process due to its comprehensive thermodynamic packages along with huge component libraries and progressive calculation techniques [32]. Further advantages of Aspen Hysys are its wide simulation capabilities and ability to easily include sizing and economic calculation within spreadsheet tool [33-35].

2.2 Design and Simulate the industrial plant using Aspin HYSYS

An industrial plant for esterification of Levulinic acid to the biofuel Levulinate esters as biofuel and fossil fuel modifiers had been designed and optimized. Most of the biofuel yield formulation was derived from literature data based on laboratory scale experiments on the kinetics and yield of transesterfication reactions [36]. The flow sheet for biofuels production is developed in Aspen HYSYS version 8.8 using Lee-Kesler-Plocker fluid package. Table 2 shows a summary for the operating conditions of the plant.

Table 2. Summary of unit operating conditions for the process

| Process               | Parameters                              | values |  
|-----------------------|-----------------------------------------|--------|
| Esterification        | Reactor type (Conversion Reactor)       |        |
|                       | Temperature (°C)                        | 150    |
|                       | Pressure (atm)                          | 5      |
|                       | LA:Methanol                             | 05:01  |
|                       | LA molar flow rate (kg mol/h)           | 165    |
|                       | Conversion %                            | 99     |
|                       | Residence time (h)                      | 3      |
|                       | Catalyst (H₂SO₄) flow volume (m³/h)     | 4,144  |
| Seperator             | Temperature (°C)                        | 260    |
|                       | Pressure (bar)                          | 5      |
|                       | Flow rate (kg mol/h)                    | 369.9  |
|                       | % Recovery                              | 99.1   |
|                       | Reflux ratio                            | 1.2    |
|                       | No. of stages                           | 10     |
|                       | condenser/reboiler pressure (atm)       | 20/30  |
|                       | % recovery                              | 99     |
|                       | Distillate purity                       | 99     |

Designing the plant using Aspin HYSYS was carried out by starting a new case, followed by entering the properties environment, selecting the components that to be used in the model and setting the calculation methods for physical properties (fluid package). For building the model a component list has been created which contain the entire components that are used in the process. The components are Levulinic acid, Methanol and H₂SO₄. The next step was selection of the fluid package where Lee-Kesler-Plocker was used. Once the property packages specified, the simulation environment is selected for building the flow sheet by adding either the unit operation or a material stream from the palette, then flow sheet objects will be added.

For simulation establishment, both the operating variables (input specifications) and the definition of the mixture (characterization) have to be specified. The operating variables of the material streams (H₂SO₄, Methanol and Levulinic acid) are temperature (150 °C), pressure (5 atm) and LA molar flow rate (156 kg mol/hr). The compositions of the materials are specified manually by adding the mole fraction of each component, after which the streams were specified and calculated. Then, unit operations are specified and connections be added for output and input on the design and connections tab. The unit operations include a
mixer, reactor, chiller, separators and a distillation column. The basic pressure profile used in the column are, for reboiler (30 kPa), condenser (20 kPa), and reflux ratio (1.2). Finally, the created biofuel model was simulated. Figures 5 and 6 show typical Hysys windows for the distillation column and the complete specifications of the distillation column respectively.

Figure 5. Distillation Column

Figure 6. Complete Distillation Column Specification

2.3 Simulation parameters
For the conventional esterification of Levulinic acid to Levulinate esters, the effect of pressure, temperature and alcohol type on the production process was investigated and optimized. The applied operating condition were: operating pressure ranged (2-7 atm), temperature ranged (120-160°C), and alcohol types (methanol, ethanol, propanol, butanol, and pentanol). The plant operations were simulated following the same sequence for the simulation steps.

3 Results and Discussion
3.1 Simulation of Plant design and operation
Aspen HYSYS simulation for biofuels had been conducted by many research groups [35,37,38]. The typical sequence of the production and separation process of the biofuels investigated in the current work using Methanol is shown in Figure 7.
Levulinic acid is esterified in the reactor, followed by downstream purification, which consisted of: methanol recovery by distillation, by product separation; and Levulinic-ester purification by distillation.

The Levulinic acid esterification initially started with raw material transport and handling. Methanol and the homogeneous catalyst H$_2$SO$_4$ are set at pressure 5 atm and 150 $^\circ$C then mixed together in a mixer. After that the mixture of methanol and catalyst (stream 3) with the recycle stream of methanol is fed into the trans-esterification reactor (conversion reactor). The Levulinic acid (Stream 4) is also fed to the same reactor after its setting at the same operating conditions.

The product of esterification of Levulinic acid with methanol in presence of H$_2$SO$_4$ is methyl levulinate ester. The product in stream 7 is then cooled for a better separation of the catalyst then fed into a simple vertical separator where the catalyst solution is separated, while the product which is free of catalyst in stream 6 is fed to a distillation column where the unreacted amount of methanol is separated from the product stream and recycled back into the feed stream through methanol stream. The biofuel product with small amount of methanol leaving the distillation column in the ester stream is separated to purity in another separation unit, to remove any remaining methanol from the biofuel product. All the described units and parameters are provided in a biofuel simulation plant by Aspen HYSYS. The final purity of the biofuel was quantified by reporting the product stream composition, which was determined by thermodynamic calculations in ASPEN. The designed plant comprises the following main processes:

**3.1.1 Esterification by Conversion Reactor**

A conversion reactor was used in Aspen HYSYS to operate at 150$^\circ$C and 5atm. The conversion of Levulinic acid to ester was specified as a 99 % conversion. The feed stream of Levulinic acid to the reactor was specified at 150 $^\circ$C and fed to the reactor at a rate of 165 kg mol/hr. To keep the appropriate molar ratio, the fresh methanol was mixed together in a mixer with the recycle methanol such as for every one mole of Levulinic acid 5 moles of methanol were being fed to the reactor. Hence the total flow of methanol being combined and fed to the reactor was 178 kg/hr. The H$_2$SO$_4$ catalyst was added and mixed with fresh methanol in a mixer. Next, the mixture of the resulted products from the convertor is fed to the first separation operation by which a gravity separation is conducted in order to obtain satisfactory separation of the catalyst solution, and then the separator upper stream 6 is fed into the distillation column.

**3.1.2 Methanol Separation**

Methanol is a toxic and highly flammable solvent. The recovery of residual alcohol and its recycling back into the process is essential for minimizing the environmental impacts and operating costs [39]. A distillation column was used to model the vacuum separation of excess methanol from the ester product in Aspen HYSYS. The operating parameters for this column were 20 kPa for the condenser pressure, 30 kPa for the reboiler pressure, with 10 theoretical stages for separation and an operating reflux of 1.2. The reflux ratio is to ensure that every 1 mole of distillate produced, 1.2 mole from the splitting point will returned and recycled back to the distillation column. Hence this reflux ratio is to provide the desirable purity of methanol in the distillate, however the operating cost should be considered as well so the column will not be too offensive. The principle reason for conducting the column under vacuum condition is to avoid the degradation of ester product, where any degradation of ester products will lead to difficulties in subsequent separation operating. The recovery of methanol in methanol stream was specified to be 88% of the total methanol in stream 8. Methanol stream which
is the recovered methanol is recycled and mixed with the fresh methanol so it can be used as feedstock for the esterification reaction again. The upper stream of the distillation column composed of the ester and small amount of methanol will be sent to another separator for further separation to purify the biofuel.

3.1.3 Biofuel Purification
The contamination of biofuel with methanol may result in lowering the flash point of the fuel [40], accelerating the corrosion of aluminums and zinc parts, and deterioration of rubber seals and gaskets of fuel engines [41]. The ultimate purification stage for methanol remaining in ester stream is carried out in gravity separation unit to obtain satisfactory purification. The final biofuel product purity obtained in this study was in agreement with those reported by other researchers [35, 37] relevant to using a commercial process simulators to develop a detailed simulation of biodiesel production process.

3.2 Effect of temperature on biofuel yield
The effect of temperature on percent yield of biofuel from Levulinic acid was investigated. The investigations were carried out at pressur (5 atm), 5:1 methanol to acid ratio at different temperatures (120, 140, 150 and 160°C). The impact of temperature on biofuel % yield at various temperatures is shown in Figure 8. The results indicate that the % yield of the biofuel produced at temperatures (120 to 140°C) were in the range 99.73 – 99.77 %. Moreover, by increasing the temperature of the reactor from 150 to 160°C, the conversion increases significantly from 99.8 – 100 %. Based on these results, we can confirm that there is a positive increase of methyl levuliniate ester yield % with the temperature increasing.

Effect of temperature on reaction yield can be explained through the theory of chemical reaction kinetics. An increase in temperature will result in increasing the mean kinetic energy of the particles; increase the collision energy, thus, the fraction colliding particles increases leading to increase the biofuel yield. The findings of the current work are in agreement with others published in literature [42, 43].

![Figure 8: Effect of temperature on percent yield of biofuel](image)

3.3 Effect of pressure on biofuel yield
In general, high equipment costs and precise safety management policy are required for implantation processes operate at high pressures. The effect of the reaction pressure on the biofuel yield of Levulinic acid esterification is shown in Figure 9. The converter reactor was operated at different pressures, (2-7) atm at constant temperature (150°C), and LA to methanol ratio 1:5.

The results shown in Figure 9 indicated that the yield of the biofuel produced at reactor temperature 150°C increases with increasing the applied pressure. At a pressure range (2 to 3 atm), the yield of the biofuel was in the range (9.54 – 11.77) %. Apparently, by increasing the pressure from 4 to 5 atm., the conversion increases significantly (13.12 to 99.17) respectively. Further increase in reactor pressure (5 to 6 atm.) resulted in the highest conversion yield of biofuel (99.82 – 99.88%). Increasing the pressure to 7 atm resulted in small change
in percent conversion of biofuel (99.89 %). The increasing of biofuel yield with pressure might be due to the increase in solvent power of alcohol with increasing pressure. In brief, 5 atm. seemed the optimum value of the reactor pressure for Levulinic acid esterification for achieving 99.82 % yield of biofuel. The findings are in line with other results reported in the literature [43]. However, positive effects of pressure with higher ranges were observed for continuous transesterification processes for biodiesel production from bean oils using supercritical fluids as solvents [44,45].

Figure 9: Effect of pressure on the percent yield of biofuel

3.4 Effect of alcohol type on biofuel yield
The effect of various alcohol types on biofuel yield derived from Levulinic acid esterification was investigated. The conversion reactions were carried out at constant operating conditions, pressure (5 atm), temperature (150°C), and 1:5 LA to methanol ratio in presence of acid catalyst (H2SO4). Five lower alcohol members were investigated, they are methanol, ethanol, propanol, butanol and pentanol. The results obtained are illustrated in Figure 10.

The results show that the percent yield of the biofuel produced using methanol, ethanol, propanol, butanol and pentanol were 99.76, 99.68, 99.18, 98.7 and 98.37 respectively. Based on the result obtained, the yield of biofuel produced by using different types of alcohol decreased in the following order: Methanol > Ethanol > Propanol > Butanol > Pentanol.

The estimated results indicated that methanol in addition to its low cost, was the alcohol that gives the highest yield of biofuel, followed by ethanol, propanol, butanol and pentanol respectively. The reason may be attributed to the stability of the emulsion formed during alcoholysis that increases with increasing the size of the non-polar group in alcohols making the separation and purification of the biofuel more difficult with high alcohols. Similar findings were reported for biodiesel produced from waste canola oil using methanol in alkali-catalyzed transesterification; biofuel yield using Methanol was higher than that using ethanol [46]. Similar results were also documented by other researchers [43].
4 Conclusions
In a world like today, we are getting closer to the peak oil point where petroleum reserves are getting limited, depleted, and will ultimately end. On the other hand, the environmental consequences associated with the consumption of fossil fuel are getting worse. All these factors have generated increasing pressure on researchers to find new substitutes and alternatives to fossil fuels. Biofuels, have drawn more attention as alternatives to fossil fuels due to its renewable resources and its environmental benefits. Various innovative technologies have been developed to promote and improve the efficiency and quality of biofuel production. Nevertheless, in spite of the moving to renewable fuels is growing significantly, it represents only a small fraction of the current fuel demands.

Levuinate esters produced from renewable feedstocks like Levulinic acid via esterification is considered as a promising renewable biofuels and fossil fuels blending agent. On the other hand, current engineering simulation programs are behind the successful planning, optimization and implementation of new production technologies of industrial plants. Moreover, the development of existing production technologies and the recent innovations in the advanced emerging technologies are getting great help from the engineering Computer Aided Designs software like Aspen HYSYS which enables most profitable designs for greater margins.

In the current work, a production process of biofuels (Levulinat Esters) was designed and simulated using Aspen Hysys software. Optimum biofuel yield investigated using different operating conditions such as temperature, pressure and different types of alcohol. Optimum Levulinate esters yield was achieved when the conversion reactor operates at a pressure and temperature of 5 bar and 150 oC respectively, using Methanol as solvent.

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