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High pressure reactive distillation simulation and optimization for the esterification of pyrolysis bio-oil

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ABSTRACT

Reactive distillation (RD), which has tremendous advantages over traditional reaction and separation unit operations including handling of unfavorable chemical and phase interactions, enhancing conversion and selectivity, circumventing azeotropic mixtures and reducing capital and energy costs, has been utilized for the reactive separation of various equilibrium controlled chemical systems. Aspen simulation for RD of pyrolysis bio-oil esterification with n-butanol is carried out using UNIQUAC property method in RADFRAC module by minimizing Gibbs free energy at 10 bar. The presence and reactions of phenol, which represents phenolic compounds in bio-oil, are also considered. The binary and ternary interaction between phenol and the other components were studied for n-butanol/acetic acid esterification system to determine the azeotropes and the homogeneous region of mixtures, before carrying out RD operation. The conversions for the esterification reactions were found to be 88−99% for various simulated bio-oils with phenol composition 5−20% for n-butanol:acid ratio of 2.5, and water was almost completely separated from the ester products which should increase the fuel quality. Higher water percentage in bio-oil feed was found to reduce acid conversion and ester separation. The reaction of phenol with fatty acids was incorporated and phenol was found to react with formic acid entirely, which increases the reaction conversion up to a certain quantity due to its favorable effects. All the distillation column parameters such as condenser and reboiler heat duty, number of stages, reflux ratio, feed stages location and inlet conditions were optimized for a complex mixture of fatty acids and phenolics to develop a cost minimized RD unit. This study can serve as a simulation platform to design RD unit for pyrolysis bio-oil upgradation without any intermediate cooling unit between pyrolysis and upgradation units.

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1. Introduction

Sustainable energy source and management is a major issue in the modern societies and the safety, renewability, non-toxicity and biodegradability of bio-fuels make it one of the most attractive energy sources [1, 2]. More importantly, they can be obtained by thermal pyrolysis or hydrothermal liquefaction of virtually every waste material including agricultural and animal waste providing simultaneous energy production and waste treatment [3-5]. Biofuel has an overall life cycle energy balance of 3.2 units of fuel product energy per unit of energy consumed compared to 0.83 of the

petroleum fuels and can be blended together with petroleum diesel to upgrade the fuel efficiency, resulting in reduced CO, CO_2 and other undesirable emissions [6, 7], except NO_x. However, the results of our recent work have demonstrated the feasibility of some inexpensive technologies to reduce NO_x emission with/without SO_x present in the flue gas [8-11]. Crude bio-oil has very similar properties compared to petroleum fuel but it is highly viscous, corrosive and has high water content and high flash point [5, 12], and requires upgradation before its use as engine-fuel. Storage and stability of pyrolysis bio-oil is also a problem, and cooling after pyrolysis often leads to unintended polymerization [13-15]; and these necessitate immediate high-temperature upgradation. Bio-oil

upgradation is usually carried out by heterogeneous catalysis in transesterification or esterification reactions [16], and high temperature is also beneficial for increasing reaction conversion, as reported by Banchero and Gozzelino [17]. Heterogeneous catalysis provides tremendous advantages over traditional homogeneous catalysts, where costly separation of the catalysts from the product can affect economic viability of a project [6, 18]. Thermal and hydrothermal treatment of biomass to produces bio-oil is operated at high temperature and pressure [3, 4], thus the heterogeneous catalytic upgradation process at the same condition can avoid intermediate cooling. Although, ion exchange resins are widely used as low-temperature catalyst for esterification [19, 20], it can be very easily deactivated in RD process and thus not suitable for high temperature operation [21]. Single or mixed metal oxides catalyst with higher acid conversion has been recently developed which can withstand high temperature operations [7, 15, 22, 23]. Besides upgradation, esterification with an alcohol is also reported to be beneficial to pyrolysis oil stability [15, 21]. Although some studies reported upgradation of bio-oil with methanol at both low and high pressure [24, 25], it is highly expensive due to difficulties in methanol-water separation [25] and lower fuel quality of methanol compared to other alcohols [26]. On the other hand, pyrolysis of bio-oil upgradation in RD under reduced pressure (<0.1 bar) are carried out with n-butanol, ethylene glycol and 2-ethylhexanol, among which n-butanol was shown to have the most potential in utilizing solid acid catalysts [27]. Supercritical alcohol feeding directly to RD column is also another technique for bio-oil upgradation, which has shown some promise for n-butanol [28].

Pyrolysis bio-oil is a very complex mixture of different organic compounds, mainly fatty acids, aldehydes, ketones, phenolics and alcohols [15, 18], which makes separation and upgradation very difficult in traditional chemical operations. A complete reactive separation unit such as reactive distillation in presence of solid catalysts, which also facilitate the separation of water presents in bio-oil in a single operation unit, is of immense interest. In general, the organic compounds in bio-oil are sparingly soluble in water. Hence, the liquid mixture can split into two phases (aqueous and organic) in the reactive distillation column, which is detrimental to further reaction and separation as liquid phase splitting could stop proper mass transfer. Therefore, the molar feed ratio need to be properly chosen by carefully observing the chemical and phase equilibrium (CPE) diagram so that the mixture in the column always stays in the single liquid phase region [29]. The Aspen simulation in conjunction with economic analysis was performed for acetic acid/n-butanol esterification system with 35% water in feed for different hybrid systems, among which single column RD unit was found to be most economically suitable [30]. Regarding design and optimization, three kinds of design techniques were used in RD: topological, heuristics based and optimization based, for feasibility analysis, post design analysis and detailed design, respectively [31]. Two kinds of optimization techniques exist: deterministic and evolutionary, and for a multicomponent RD column design evolutionary approach is best suitable.

The Aspen simulation of RD column considering all the components present in bio-oil is a complex task. Our objective is to first carry out reactive distillation considering only one acid for the simulation and then expand the components to incorporate other short chain and long chain fatty acids, in an evolutionary approach.

In our previous work [32], we have modeled and optimized RD for the esterification of a complex fatty acid mixture. Effects of water percentage in bio-oil on reaction conversion and ester separation was discussed and stoichiometric n-butanol flow was found to be optimum. UNIQUAC property method was used as it is the most suitable for esterification of fatty acids [20, 33]. However, the presence and reaction of phenolic compounds (integral part of pyrolysis bio-oil) in the simulation was not considered. Here, modeling of RD for multicomponent simulated bio-oil esterification with n-butanol was carried out using Aspen PLUS V 8.0, where a complex mixture of fatty acids and phenol was considered the bio-oil. Since pyrolysis bio-oil also consists of alcohols and phenols, they were considered as part of bio-oil in appropriate amount and the n-butanol feed was reduced accordingly. Also, since bio-oil consists of water, it is considered in the bio-oil, which was separated from the esterification products. A typical analysis of pyrolysis bio-oil reveals several chemical compounds [34, 35], where water content varies typically 15% to 40% and a mid-range values of 30% is a good estimation for all the simulation, whereas phenolic composition varies 5−20% and thus inclusion of 10% phenol was considered as part of bio-oil. The simulation results were compared for complex fatty acids esterification with varying amount of phenol in order to understand the effects of phenolic compounds on reactive distillation. Evolutionary modeling and optimization technique was carried out from less complex (acetic acid as bio-oil) to highly complex (fatty acid mixture and phenol) systems, and the RD parameters were optimized using Aspen Sensitivity Analysis, where condenser and reboiler heat duty was minimized to reduce the energy costs by varying input parameters including number of rectifying, reactive and stripping stages, bio-oil and n-butanol feed stage locations, reflux ratio, distillate to feed ratio, and n-butanol to fatty acid feeding ratio, for optimum acid conversion and ester recovery.

2. Simulation frameworks and applied heuristics

2.1. Heuristics applied for preliminary designs

Heuristics are 'rules of thumb' that typically do not guarantee best or correct solution but can guide through and shorten the process of obtaining solution of a design problem by providing the short-cut design with reasonable estimates. Here, we applied several heuristics for selecting values of parameters in initial short-cut design. It is a reasonable practice to use a pressure between 1 to 10 bar and any pressure more than 10 bar will create high pressure concern and needs to be properly justified. Operating temperature in industrial processes are kept between 40−250 °C, so that cooling water and high pressure steam (hps) can be used as utilities in condenser and reboiler, respectively, in this range. Below 40°C, special refrigerant and above 250 °C, heating method other than steam increases the costs. It is generally assumed that high pressure will increase column, overhead and bottom temperatures. A pressure drop of 0.5 bar across the column can be safely assumed. Initial reflux ratio of 1.35 times R_{min} and initial number of stages, $N = 2.2 \times N_{min}$ can be selected before optimization, where R_{min} and N_{min} are minimum reflux ratio and number of stages, respectively, obtained from Fenske-Underwood equation. For a reacting system, stoichiometric feed is preferable as it reduces costly separation of

unreacted reactants, but a reactant that increases quality of product mixture is sometimes used in excess to drive the forward reactions [36]. Rectifying and stripping sections were fed with saturated liquid and saturated vapor, respectively, at the feed stage condition whenever possible.

2.2. Process simulation steps

The reaction is simulated in a Reactive Distillation unit (RADFRAC module) in Aspen PLUS. All the components were present in Aspen data-bank except phenyl formate, which was incorporated by "user defined" component option and the properties were estimated from molecular structure. The reaction is incorporated with the RADFRAC distillation unit in equilibrium form (where Aspen will calculate the equilibrium constant by minimizing the Gibbs free energy). In case of known reaction equilibrium constants, the known parameters can be also be provided as input to calculate the reaction products. Because of many complicated interactions between the components, the binary and ternary interactions between the components usually provide a simple guide-step for the initial clue. Aspen Property PLUS was used to observe the binary and ternary interactions between the two or three components, respectively. These interactive diagrams can provide the valuable insight into the possible azeotropes present in the reactive distillation operations. Also, chemical and phase equilibria could be observed to understand the liquid phase separation into two. The presence of a homogeneous region of mixture is vital to the healthy RD operations. This helps to prevent liquid phase splitting resulting in proper mass transfer, which is very important for both reaction and separation. For shortcut distillation column design without any reactions, a pressure was selected first and 0.5 bar column pressure drop was assumed. Then, the column top and bottom temperatures were determined from preliminary simulation and checked whether heat duties can be satisfied and feed stage conditions are close to that of bio-oil received from pyrolysis plant. After selecting best pressure, minimum reflux ratio and minimum number of stages were determined from Fenske-Underwood equation using DSTWU module. Based on the heuristics, actual initial reflux ratio and number of stages were selected and then feed location was optimized. Feed conditions (pressure and temperature) was selected as it entered the feed plate as saturated liquid by using FLASH2 separator module to find bubble point temperature at that pressure for every column simulation. The DSTWU results were used as the initial estimate for DISTL simulation to study the process parameters such as pressure, number of stages, reflux ratio, location of feed stage, distillate to feed ratio and water and n-butanol fraction in feed using Aspen 'Sensitivity analysis' under 'Model Analysis Tools'. Shortcut distillation column was simulated using NRTL as base method for simplicity. The flow diagram in Aspen for reactive distillation was drawn by using Aspen process flow sheet with the RADFRAC Module acting as column performing both reaction and separation. The reaction equilibrium was determined by specifying Aspen to calculate it by minimizing Gibbs free energy. For all the simulations using RADFRAC, UNIQUAC property method was used as the base method for property estimation and missing parameters were estimated by UNIFAC method whenever necessary. The process was further optimized using the 'Design Specification' and 'Sensitivity Analysis' tools by varying several parameters, which maximize the fractional conversion and separation efficiency. The temperature and composition profile was drawn along the column for different feed mixtures. Ester flow rate and fractional conversion were drawn with alcohol and water feed rates. All the distillation column parameters such as condenser and reboiler heat duty, number of stages, reflux ratio with different inlet condition were studied to develop a completely energy cost minimized RD unit.

3. Results and discussion

3.1. Analysis of the physical properties and interactions

Although pressure alone does have minimum effect on reaction conversion in esterification in a RD column, increase in pressure results in higher temperature, sometimes required for higher conversions. The relatively high temperature and pressure are also chosen to comply with the previous step pyrolysis and we expect the bio-oil entering the RD from pyrolysis unit will maintain high temperature and pressure, thus avoiding any intermediate cooling or heating operation. Since the reaction is equilibrium controlled, unreacted acid and alcohol are present in some amount with the product and the whole reaction and separation phenomena in RD unit is quite complex. Binary and Ternary interactions between the four components of acid/n-butanol/butyl ester/water system using Aspen Property Plus was previously reported at average column temperature and pressure of 200 °C and 10 bar, respectively [32], which showed the final two products water and ester form a binary azeotrope as well as two reactants acetic acid and n-butanol. Acids do not form any azeotrope with either water or ester and that is why it is easy to separate unreacted acid either from water and ester; n-butanol also forms a minimum boiling binary azeotrope with water. Here, since we are incorporating phenol as a component in our simulations, binary property analysis is performed between phenol (and product phenyl esters) with other components in the system. From the binary y-x diagram in Fig. 1, it can be seen that, phenol and phenyl formate do not create binary azeotrope with any of the components except water, thus they can be easily separated from other components in RD column.

The ternary interaction plots or the residue plots for acid/n-butanol/butyl ester/water systems were also provided previously [32], from where it was evident that no ternary azeotrope is present in this system. At 90 °C, a low-boiling ternary azeotrope was reported to be present in ester-acetic acid-water systems [30], which was eliminated at high pressure and temperature systems reported here. Fig. 2 represents the residue plots of phenol (plots for phenyl esters are similar and thus are not shown) with all components of acetic acid esterification system, which also shows absence of any ternary azeotrope. Residue curve with other acid systems are similar (not shown). Unfortunately, Aspen ternary (residue) plot does not provide arrows in the line for separation direction. But we can guess the direction of the lines from the relative volatility of the components and pure component/binary azeotrope boiling points; normally esters are the least volatile components in esterification systems and will be expected to be found at bottom of the column where temperature is the highest. Hence, phenol or phenolic esters

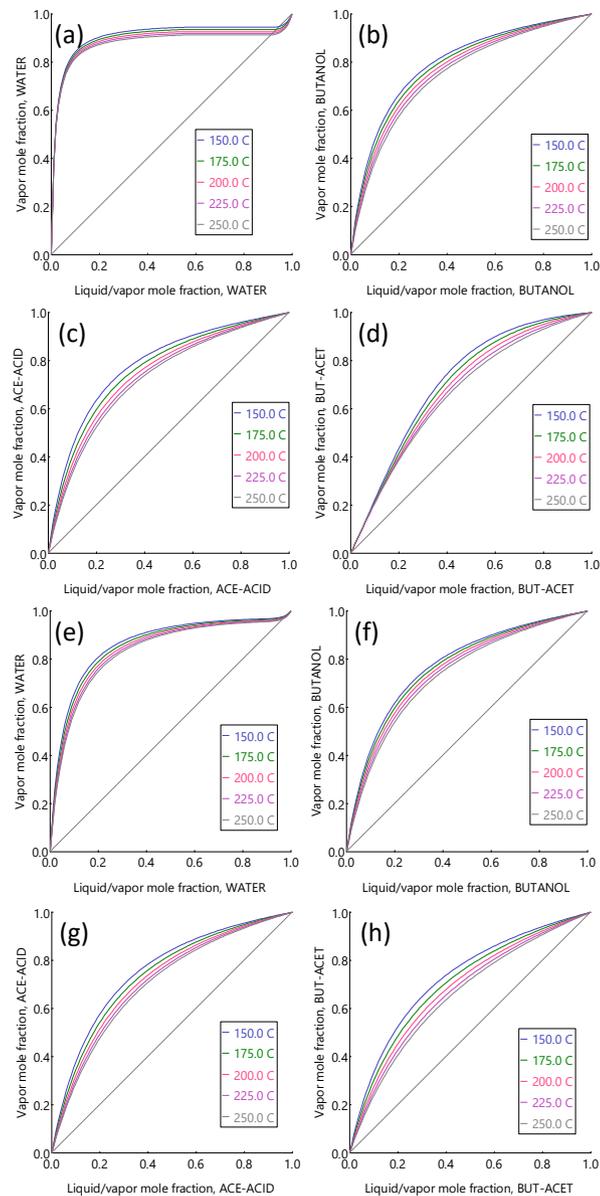with highest boiling point are the heaviest components expected to present at the bottom products.

Fig. 1 – Binary y-x diagram by UNIQUAC method using Aspen Properties PLUS at 10 bar and 150-250 °C for: (a) phenol-water, (b) phenol-butanol, (c) phenol-acetic acid, (d) phenol-butyl acetate, (e) phenyl formate-water, (f) phenyl formate-butanol, (g) phenyl formate-acetic acid and (h) phenyl formate-butyl acetate.

Ternary plots can be considered as four sides of a quaternary plots, where pure ester and butanol-acid binary azeotrope acts as stable nodes, and pure butanol behaves as saddle point in the presence of reaction [37]. Normally, in RD, the organic compounds are sparingly soluble in water and thus sometimes the liquid mixture can be split into two phases (aqueous and organic) in the reactive distillation column, which is detrimental to our objective

since the liquid phase splitting could stop further reaction and separation. Cho et al. reported that there is a high immiscibility region between water and ester at high water concentration [38]. Liquid-liquid equilibria exist for higher water composition [36, 39], thus continuous water removal by RD is beneficial. Residue curve map of lauric acid with methanol (highly soluble in water) or 2-ehylhexanol (sparingly soluble in water) reveals large immiscibility region regardless of alcohol solubility in water [29]. The molar feed ratio should be chosen by carefully observing the chemical and phase equilibrium (CPE) diagram so that the mixture in the column always stays in the single liquid phase region. From this diagram it was clear that bottom right part is the region where liquid-liquid equilibrium region occurs, where the liquid phase split into two and the system is operated in the single liquid phase region (left and upper region).

3.2. RD simulation for esterification of bio-oil consisting of fatty acid mixture and phenol

RD is carried out in the temperature and pressure where distillation is possible and a reasonable reaction conversion and selectivity is attainable [7]. The flow diagram in Fig. 3 for RD is drawn by using Aspen process flow sheet with the RADFRAC Module as the column simultaneously performing both reaction and separation operations. In the RADFRAC, besides conventional distillation input parameters, the reaction parameters can also be incorporated and the reactive stages can be specified. For the simulation, UNIQUAC property method is used as the base method for property estimation. The reaction equilibrium is determined by specifying Aspen to calculate it by minimizing Gibbs free energy.

As mentioned earlier, RD simulation of complex and multicomponent bio-oil is rigorous and we have previously reported simulations for multicomponent fatty acid mixtures as bio-oil, which was performed using evolutionary procedure from the simplest to more complex systems [32]. Briefly, at first 1 kmol/h of bio-oil is considered as 70% acetic acid and 30% water and the simulation was carried out with stoichiometric amount of n-butanol (0.7 kmol/h). The optimum distillate rate, reflux ratio, alcohol flow rate, percent of water and feed stage location were found by using Aspen 'Sensitivity Analysis' for the optimum overall conversion and separation. The simulation was optimized further for the condenser and reboiler heat duty, and number of stages (reactive, rectifying and stripping) and optimized RD unit for the esterification of acetic acid was achieved. To reduce the amount of unreacted acid with ester products, bio-oil (acid) was reported to be fed into the top section of the column in the literature [6]. We found the conversion to be higher when acid was fed in top reactive stages and n-butanol in middle reactive section, which is in agreement with other reports [20]. The conversion was 76.7% and all the water was separated from the ester product. But some ester was carried away with water due to the presence of azeotrope as well as the unreacted n-butanol with ester (bottom ester recovery was 85.1%) and unreacted acetic acid was found in the top and bottom products in almost equal quantity. The condenser heat duty was -19.32 kW and reboiler heat duty was 17.12 kW. This simulation can provide valuable insight in recovery of acetic acid from waste water when mixed with other components using RD without any pretreatment unit as proposed by Araromi et al. [40] and demonstrated to be most economically viable [30].
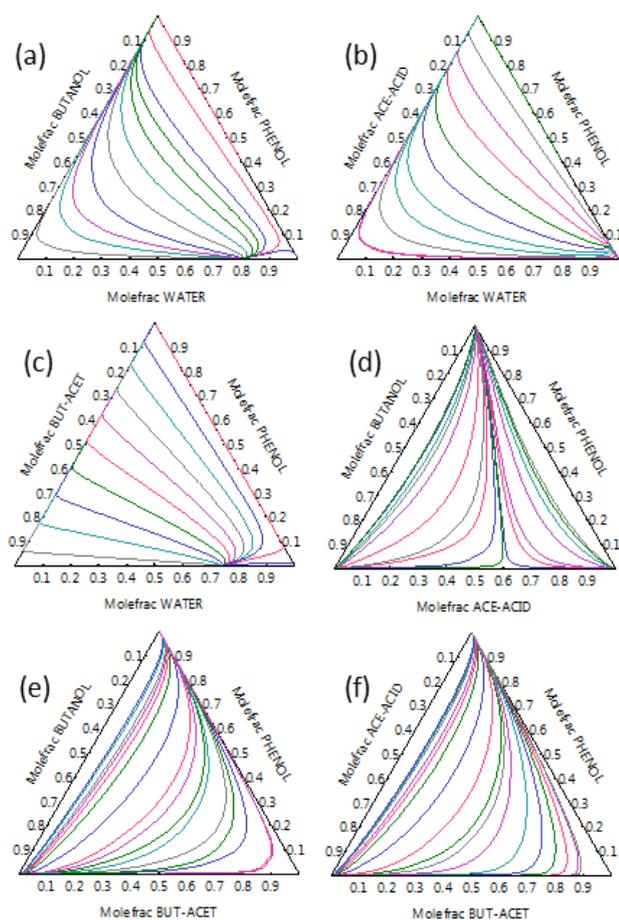
Fig. 2 – Ternary residue plots by UNIQUAC method using Aspen Properties PLUS at 10 bar: (a) phenol-water-butanol, (b) phenol-water-acetic acid, (c) phenol-water-butyl acetate, (d) phenol-acetic acid-butanol, (e) phenol-butanol-butyl acetate and (f) phenol-acetic acid-butyl acetate.

These optimized results were used for the simulation of bio-oil composed of 30% water, 30% acetic acid, 20% formic acid and 20% propionic acid with stoichiometric amount of n-butanol and further optimization was performed in terms of ester flow rate in bottom and top products, and conversion of acids. Overall conversion was 87.1% and the conversions of acetic, formic and propionic acid were 88.3%, 86.0% and 86.5%, respectively, whereas the ester recovery at bottom were 81.9%, 97.1% and 97.6% respectively. The conversion is higher than the previous simulation, which can be attributed to the higher reaction rates using acid mixtures. The conversion is also higher compared to liquid phase esterification of propionic acid with n-butanol, where the acid conversion was found to be 40−60% for different solid acid catalyst [41]; again validating the superiority of RD process for esterification reactions. Water was completely separated from the ester but the unreacted acids and tiny amount of ester left with water for the presence of binary azeotrope in water-ester mixture. The optimum reboiler and condenser heat duty were 23.18 and −24.90 kW respectively.

Finally here, the reactions of phenol with the acids to produce phenyl esters (formate, acetate and propanate) is incorporated to the simulations considering 10% phenol as part of feed stream since significant amount of phenol and phenolic compounds (lignin derived) are present in the pyrolysis bio-oil [3, 4, 42]. The amount of phenolic and other alcoholic compound typically varies 5−20% and 10% phenol in feed stream is a good approximation. Stream results indicate that almost all the phenol reacts with formic acid to form phenyl formate (Table 1). The reaction of acetic/propionic acid with phenol is very slow to be meaningful unlike formic acid, which due to its high reactivity can react with phenol to form phenyl formate [43, 44]. Since, phenol reacts the same way as butanol reacts with acids total n-butanol feed rate was reduced accordingly.
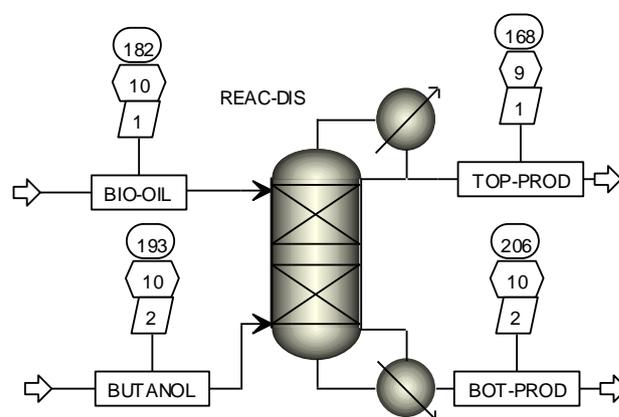

Fig. 3 – A typical Aspen PLUS flow diagram of reactive distillation for the esterification of bio-oil with RADFRAC module at pressure 10 bar (circle: temperature in °C, hexagon: pressure at bar and rhombus: total flow rate at kmol/h).

The simulation including acid mixture and phenol is optimized further in terms of the number of rectifying, reactive and stripping stages, feed stage location, bio-oil compositions and other RD parameters and optimized results are presented in Table 1 (see section 3.6 for a detail discussion). The feed pressure was selected based on their feeding location (9.72 bar and 9.96 bar for bio-oil and n-butanol, respectively) and feed temperature (182 °C and 193 °C for bio-oil and n-butanol, respectively) was calculated at feeding stage condition using Aspen FLASH2 separator module so that feeds are saturated liquid. The overall fractional conversion of the esterification reaction was 95% using 10% phenol, which substantiates the beneficial effects of phenolics in the system. The temperature and composition profile in the column is given in Fig. 4. Steam can be used at reboiler heating as bottom temperature is slightly above 200 °C. It can be seen that in the reactive stages (13−25) the composition of acids steadily decreases and ester composition increases. In the bottom section (stage 23−27) composition of water decreases to zero and above that amount of ester remains low. The abrupt change of composition in stage 13 is due to the introduction of bio-oil feed stream.

Table 1 – Optimized parameters for the reactive distillation of bio-oil with n-butanol with varying composition of phenol.

Parameters	Complex bio-oil (65% acid mixture + 30% water + 5% phenol) with n-butanol	Complex bio-oil (60% acid mixture + 30% water + 10% phenol) with n-butanol	Complex bio-oil (50% acid mixture + 30% water + 20% phenol) with n-butanol
Pressure, P (bar)	10	10	10
Column ΔP (bar)	0.5	0.5	0.5
Number of Stages, N	27	27	27
Rectifying stages	11	11	11
Reactive stages	13	13	13
Stripping stages	1	1	1
Feed stage	Bio-oil 13, Butanol 25	Bio-oil 13, Butanol 25	Bio-oil 13, Butanol 25
Reflux ratio, RR	1.5	1.5	1.5
Distillate:Feed ratio	0.38	0.38	0.38
Condenser type	Total	Total	Total
Condenser heat duty (kW)	−23.88	−24.15	−23.92
Reboiler type	Kettle	Kettle	Kettle
Reboiler heat duty (kW)	20.57	20.33	20.20
Feed pressure (bar)	Bio-oil 9.72, Butanol 9.96	Bio-oil 9.72, Butanol 9.96	Bio-oil 9.72, Butanol 9.96
Feed temperature (°C)	Bio-oil 182, Butanol 193	Bio-oil 182, Butanol 193	Bio-oil 182, Butanol 193
Feed flow rate (kmol/h)	Bio-oil 1.0, Butanol 1.5	Bio-oil 1.0, Butanol 1.5	Bio-oil 1.0, Butanol 1.5
Butanol (kmol/h)	1.5	1.5	1.5
Water (kmol/h)	0.3	0.3	0.3
Acetic acid (kmol/h)	0.3	0.3	0.3
Formic acid (kmol/h)	0.2	0.2	0.15
Propionic acid (kmol/h)	0.15	0.1	0.05
Phenol (kmol/h)	0.05	0.1	0.2
Top temperature (°C)	168.1	167.2	167.5
Top flow rate (kmol/h)	0.95	0.95	0.95
Butanol (kmol/h)	0.003	0.004	0.023
Water (kmol/h)	0.783	0.829	0.796
Acetic acid (kmol/h)	0.02	0.006	0
Butyl acetate (kmol/h)	0.086	0.081	0.111
Formic acid (kmol/h)	0.019	0.002	0
Butyl formate (kmol/h)	0.017	0.011	0
Propionic acid (kmol/h)	0.013	0.011	0.004
Butyl propionate (kmol/h)	0.008	0.005	0.003
Phenol (kmol/h)	0	0	0.003
Phenyl formate (kmol/h)	0	0	0
Phenyl acetate (kmol/h)	0	0	0.001
Phenyl propionate (kmol/h)	0	0	0.009
Bottom temperature (°C)	201.1	205.4	211.4
Bottom flow rate (kmol/h)	1.55	1.55	1.55
Butanol (kmol/h)	0.972	1.024	1.143
Water (kmol/h)	0.092	0.042	0
Acetic acid (kmol/h)	0.008	0.004	0
Butyl acetate (kmol/h)	0.186	0.209	0.187
Formic acid (kmol/h)	0.005	0.002	0
Butyl formate (kmol/h)	0.109	0.085	0
Propionic acid (kmol/h)	0.01	0.003	0
Butyl propionate (kmol/h)	0.118	0.08	0.033
Phenol (kmol/h)	0	0	0.035
Phenyl formate (kmol/h)	0.05	0.1	0.15
Phenyl acetate (kmol/h)	0	0	0
Phenyl propionate (kmol/h)	0	0	0.002

3.3. Optimization of non-reactive and reactive stages and the locations of feed stages

The number of rectifying, reactive and stripping stages (N_{rec}, N_{rea} and N_{str}, respectively) are optimized based on the effects on overall fatty acid conversion, ester recovery at bottom and heat duties at condenser and reboiler as shown in Fig. 5. It can be observed that conversion increases initially with N_{rec} and then the increment levels around 96%, whereas ester separation and heat duties remain constant (Fig. 5a). Higher N_{rec} produces better separation between water and unreacted acid/butanol and drives them downward, thus increasing the conversion. But increase in number of stages without much improvement in conversion or

separation will result in higher capital costs, and hence, 11 rectifying stages are selected as optimum. On the other hand, highest conversion of around 95.3% was found for N_{rea} = 11 to 13, which becomes steady after 13th stage but ester separation continues to increase with increasing N_{rea} (Fig. 5b), which prompted us to choose 13 reactive stages as optimum. Lastly, increase in N_{str} is found to be detrimental to reaction conversion (Fig. 5c), as opposed to the low pressure acetic acid esterification RD simulation [33, 45], where lower N_{rec} and higher N_{str} was mentioned to be needed. This is probably due to the fact that higher N_{str} separates butyl esters from phenyl esters and send them back to the reactive section, thus driving the reaction equilibrium backwards. It was also reported that higher N_{str} are required to costly ultra-purification of the ester products [20, 30]. With higher N_{rea}, more esters are produced and necessity for higher N_{str} reduces [30]. Thus only one stripping stage was considered, which makes N_{total} = 27 for optimum simulations. The fairly constant heat duties found for varying N_{rec}, N_{rea} and N_{str} is also in contrast with the study of low temperature n-butyl acetate RD process, where heat duties were found to increase with increasing number of any of the stages [45].
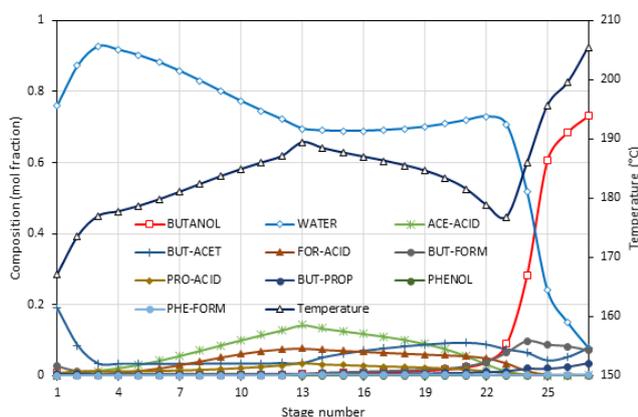

Fig. 4 – Composition and temperature profiles of the constituents in the reactive distillation column for the esterification of complex bio-oil consisting of fatty acid mixture, phenol and water (30% acetic acid, 20% formic acid, 10% propionic acid, 10% phenol and 30% water).

Another important parameter is the respective feed stage location of bio-oil and alcohol, as concentration of reactants changes based on feed stage location, the highest concentration of reactants should be ensured in the reactive section for higher conversion [45]. Although pure acetic acid (no water) and n-butanol was fed together based on their relative boiling points for high conversion [38]; since bio-oil consists of 30% water in our case, it was fed in upper stage above butanol. Optimum bio-oil and alcohol feed stage locations just above and below the reactive zone, respectively, are considered best for bio-oil esterification [21], contrariwise to the RD for acetalization of aldehydes, where both aldehyde and alcohol were fed in upper section [46].

Fig. 6a shows the effect of bio-oil feeding location on overall acid conversion, bottom ester recovery and heat duties. When bio-oil is fed into 11th stage (rectifying section), the conversion and ester recovery were 92% and 83%, respectively. Acid conversion increased when bio-oil was fed into any of the stages below (about 96% when bio-oil fed into 15th stage) but ester separation decreased slightly to 82.4%. Therefore, first reactive stage (13th) was considered optimum for bio-oil feed location. Similarly, optimum acid conversion (95.2%) and ester separation (83%) were obtained when n-butanol was fed into 25th stage (Fig. 6b). For the stages above that, although acid conversion was little higher (for example 95.3% at 23rd stage), ester separation was lower (82.3%). Optimum n-butanol stage location is unlike low pressure (1 bar) n-butyl acetate synthesis by esterification, where acetic acid and n-butanol was fed together above the reactive section as optimum configuration [20]. Thus, first and last reactive stages (13th and 25th, respectively) were selected to be optimum location for bio-oil and n-butanol feeds, respectively.
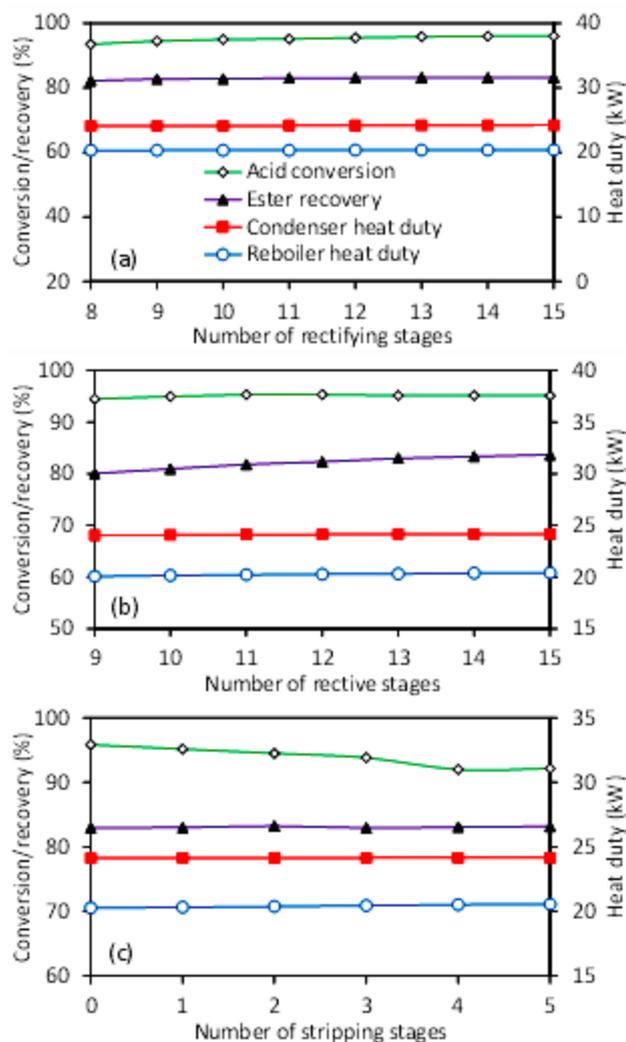

Fig. 5 – Effects of the number of (a) rectifying, (b) reactive and (c) stripping stages on overall acid conversion, bottom ester recovery and heat duties for reflux ratio (RR) and distillate to feed ratio (D:F) of 1.5 and 0.38, respectively
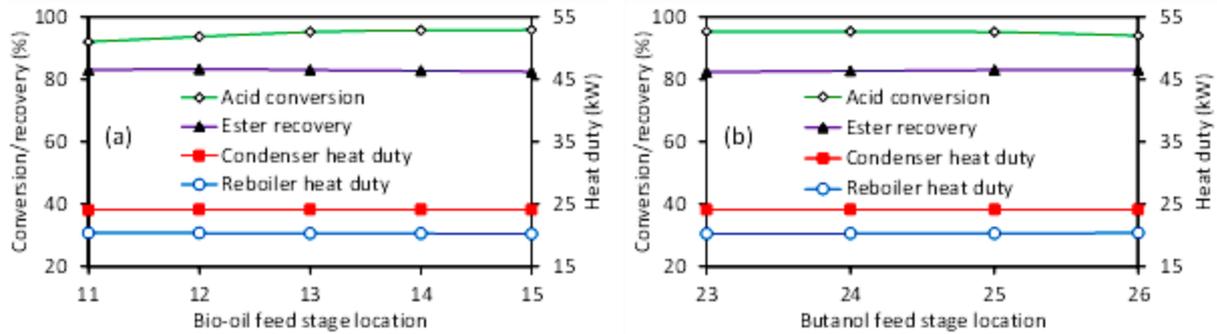
Fig. 6 – Effects of (a) bio-oil and (b) n-butanol feed stage location on conversion of acid, ester recovery and heat duties for the reactive distillation of bio-oil (11 rectifying stages, 13 reactive stages and 1 stripping stage).
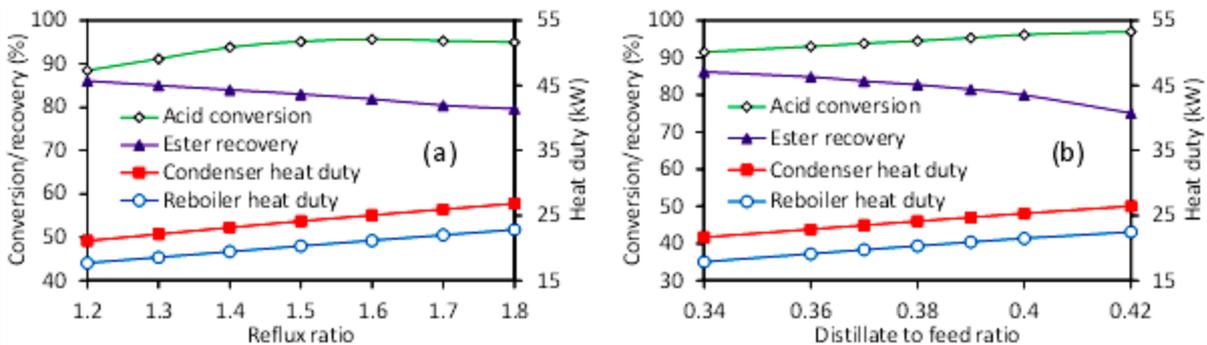

Fig. 7 – Effects of (a) Reflux ratio (RR) and (b) distillate to feed ratio (D:F) on conversion of acid, ester recovery and heat duties for the reactive distillation of bio-oil with 27 total stages.

3.4. Optimization of reflux ratio (RR) and distillate to feed ratio (D:F)

In RD column, high reflux ratio (RR) produces high conversion but it reduces separation efficiency as well as increasing energy costs [46]. In contrast, although low RR is favorable for separation efficiency and energy demand it reduces reaction conversion [17] and optimization of RR is required. High number of stages and RR of 1.8 to 2.2 is found to be suitable for RD of transesterification reaction [47]. Effects of varying RR is provided in Fig. 7a, which shows an increase of conversion from 88.5% (for RR = 1.2) to about 95.7% (for RR = 1.6) and reduction in ester separation with increase in RR. Condenser and reboiler heat duties are highly sensitive to RR, as they increase almost linearly with increasing RR because higher RR allows high amount of liquid back into the RD column. It should also be noted that water percent at bottom product increases with higher RR (6% of total water at RR = 1.8). Increase in conversion and energy requirements with higher RR is in accordance to literature study involving oleic acid esterification [33]. The increase in conversion with increasing RR up to an optimum point (95.7% at RR = 1.6) and the slight decrease afterwards (95.3% at RR 1.7 and 95% at RR = 1.8) is in accordance with propyl-propionate esterification

reported by Altman et al. [48]. Thus, optimization in RR is a tradeoff between conversion and separation/energy requirement and hence, a mid-range value of 1.5 was selected as optimum.

Fig. 7b is shows the effects of distillate to feed ratio (D:F) on acid conversion, ester recovery and heat duties for the optimization of D:F. Although acid conversion continues to increase with increasing D:F (91.5% for D:F of 0.34 to 97% for D:F of 0.42), ester recovery at bottom feed decreases dramatically (86.2% to 75.1%). At higher D:F (>0.38), as distillate flow rate increases, more esters can be driven towards the top product by the phenolics due to the volatility differences. Percent of water in bottom product was high for lower D:F (5% of total water for D:F= 0.34), which reduces with higher D:F as higher distillate rate creates more leverage for the water to go to the top product. Observation regarding ester recovery is in line with literature that D:F has tremendous influence on product purity for esterification RD [29]. Higher D:F also increases energy requirements at both reboiler and condenser by putting back more liquid into the column which needs to be re-separated. Thus, a middle value of 0.38 was selected as optimum D:F, which optimizes between acid conversion and ester recovery/heat duties. This lower optimum D:F is very different from RD simulation without phenol (D:F ~ 0.6) reported earlier [32] or other literature reports (D:F ~ 0.5) without phenol [36].
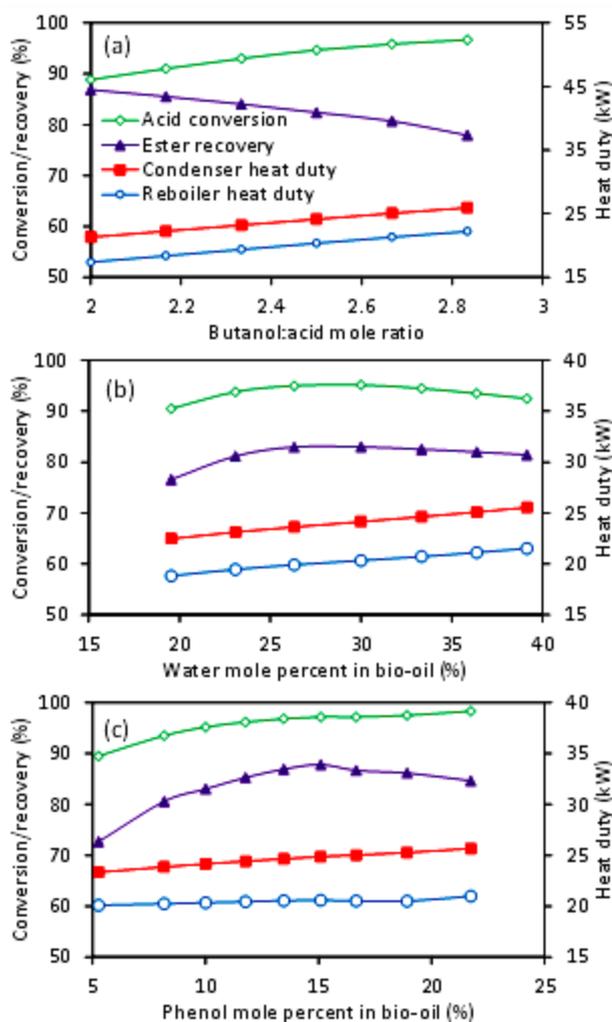
Fig. 8 – Effects of (a) molar ratio of butanol used and total fatty acid, (b) water mole percent in bio-oil, and (c) phenol mole percent in bio-oil on overall acid conversion, bottom ester recovery and heat duties for RD of bio-oil consisting of 0.3 kmol/h acetic acid, 0.2 kmol/h formic acid and 0.1 kmol/h propionic acid.

3.5. Effects of butanol to acid feeding ratio (B:A) and bio-oil composition

Amount of n-butanol and feeding ratio of butanol to acid (B:A) is an important factor for acid conversion and ester recovery, which should be optimized in RD process design. High amount of alcohol is said to be necessary in breaking azeotrope [49] that also drives up the conversions [33, 36]. To investigate this possibility, the effects of B:A is presented in Fig. 8a, where acid conversion was found to increase with increasing butanol flow rate (or B:A). Conversely, ester separation decreases dramatically with increasing butanol flow (87% to 78% for B:A = 2.0 to 2.8, respectively), due to fact that increasing butanol in the column which primarily separated at bottom product drives some esters toward the top product and reduces ester separation at bottom. Heat duties also increases steadily with increasing B:A as more butanol flow rate drives up the separation energy requirements. Negligible amount of n-butanol

(~0.4% of unreacted) was at the top product with water, which is desirable and the presence of esters (by acting as internal entrainers [38]) is probably responsible for this high separation of n-butanol. It should be noted that butanol is a high value fuel [26] and its presence in high quantity (unreacted due to use in excess) in the bottom will not affect fuel quality of bottom products.
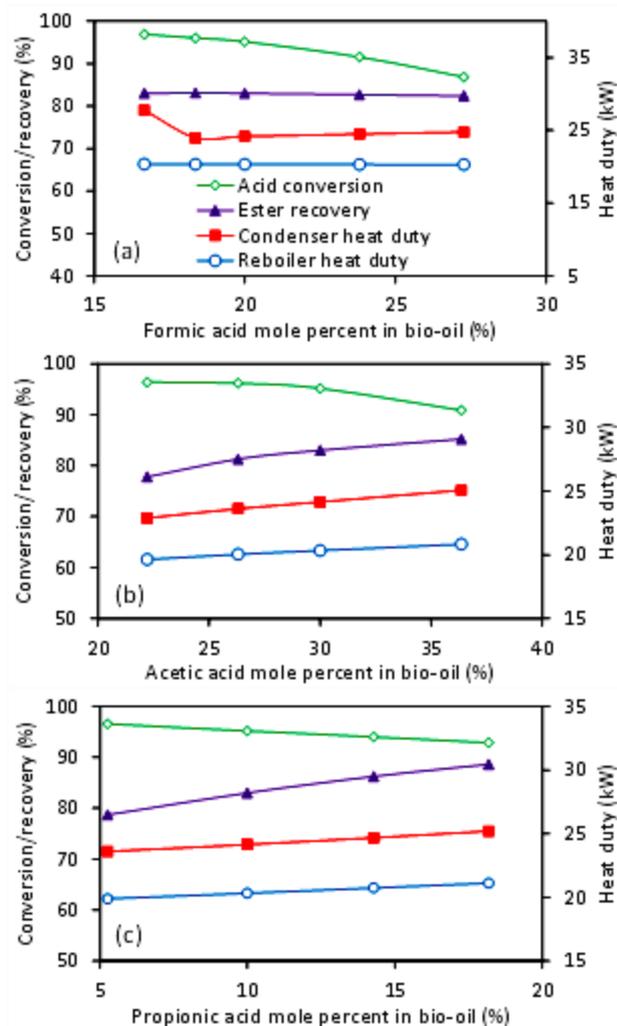

Fig. 9 – Effects of constituent fatty acid mole percent on overall acid conversion, bottom ester recovery and heat duties: (a) formic acid, (b) acetic acid and (c) propionic acid (n-butanol 1.5 kmol/h, water 0.3 kmol/h and phenol 0.1 kmol/h).

It has also been reported that the higher reaction conversion in RD is due to continuous product removal and higher water percent in bio-oil which makes RD process more expensive [30]. To investigate the effects of water percent in bio-oil, acid conversion, ester separation and heat duties are plotted with varying water percent in Fig. 8b, by keeping all other RD and feed conditions constant. The conversion and separation both exhibit a maximum value (95.2% conversion and 83% recovery) when bio-oil constitutes around 30% water, which is similar to our previous observation without the inclusion of phenolics [32]. Higher amount of water drives up the backward reaction and hence, can reduce the conversion. The reason behind the lower conversion with lower

water percent (<30%) is quite surprising, but can be explained by the fact that other parameters were optimized based on 30% water content and a water content other than 30% is not optimized. Both condenser and reboiler heat duties increase with increasing water percent as more water needs to be separated in RD column, which increases the energy requirements.

Additionally, since we are using phenol for the first time for bio-oil esterification, an understanding of the effects of phenol composition is certainly a necessity. When acid conversion, ester recovery and heat duties are plotted against varying phenol concentration by keeping the amounts of acids and RD parameters the same, we found that acid conversion continues to increase with increasing phenol from 89.5% for 5% phenol to 98.3% for 22% phenol (Fig. 8c). This is probably due to the fact that the presence of phenol and phenolic products breaks or diminishes the azeotropes in butanol/acid/ester/water systems by acting as entrainers; and phenol reacts with formic acid primarily to drive up the conversions. Ester separation at the bottom shows an interesting trend as it increases to 87.8% (for 15% phenol) but decreases again for more than 15% phenol. The reduction in ester recovery after 15% phenol can be ascribed to the volatility difference between phenolics and other components that drives other esters toward the top products (Table 1). Relation between condenser heat duty and phenol concentration is straightforward as it increases almost linearly with increasing phenol concentration whereas reboiler heat duty is less affected by the phenol concentration.

Effects of different fatty acid (formic, acetic and propionic) composition is presented in Fig. 9a-c, where acid percentage in the feed was varied by keeping water and phenol feeding rate and all other distillation parameters constant. Overall acid conversions tend to decrease when any of the constituent acid in bio-oil percent is higher (96.6% to 86.8% for 16.7% to 27.3% formic acid, 96.9% to 90.9% for 22.2% to 36.4% acetic acid, and 96.6% to 92.9% for 5.3% to 18.2% propionic acid). This is understandable as higher amount of acid find same amount of n-butanol to react with and B:A reduces, resulting in lower conversions. Thus n-butanol molar flow in reactive distillation should be increased accordingly to drive up the conversion again. Ester separation increases with increasing amount of acetic (77.8% to 85.2% for 22.2% to 36.4% acetic acid) and propionic acid (78.7% to 88.6% for 5.3% to 18.2% propionic acid) but the effect of formic acid composition on ester separation is less pronounced (constant around 82.5−83%). This is because formic acid reacts primarily with phenol to produce phenyl formate, which ends up as bottom product very easily, whereas acetic and propionic acid produces butyl acetate and propionate, respectively, which have effects on overall ester separation. Energy requirements at condenser and reboiler increases linearly with increasing acid compositions as more acid needs to be separated, which drives up the energy requirement. Condenser heat duty change from 16.7% to 18.4% of formic acid (−27.8 kW to 24.0 kW) is surprising but may be due to competing reaction between formic acid/n-butanol and formic acid/phenol systems.

3.6. Optimized simulation results with different bio-oil compositions

Since, for the first time, we are including phenol as part of bio-oil in RD simulation, a detail understanding of the effects of phenol

concentration is required. In Table 1, RD simulation results were presented for 5, 10 and 20 mol% of phenol, using the previously optimized RD column and feed conditions. The optimized N_{rec}, N_{rra} and N_{str} were 11, 13 and 1, respectively (N_{total} = 27) and optimized location were 13th and 25th stage for bio-oil and n-butanol feed, respectively. Total condenser and kettle reboiler were used for all the simulations. Optimum RR and D:F were 1.5 and 0.38, respectively, as described earlier. When 5% phenol was used (along with 30% water, 30% acetic acid, 20% formic acid and 15% propionic acid), overall acid conversion was 88.5% and ester separation was 80.5%. Individual acid conversions were 90.7%, 88% and 84.7% for acetic, formic and propionic acid, respectively. Phenol exclusively reacted with formic acid with 100% conversion to produce phenyl formate and all the phenyl formate was separated as a bottom product. Regarding n-butanol and water, only 0.3% n-butanol was found in the top product whereas almost 10% of total water (5.9 mol% of bottom product) was present in the bottom product. Top product and bottom product temperatures were 168.1 °C and 201.1°C, respectively, which correspond to higher amount of water (82.4% of top products) present in the top product. The condenser and reboiler heat duties were −23.88 kW and 20.57 kW, respectively. It is very interesting to note that, higher feed bio-oil temperature reduces the reboiler heat duties, similar to high molecular weight fatty acid esterification with methanol [17]. Hence, high pressure reactive distillation allows reduction in total energy requirements, which should negate the higher costs of high-pressure column.

When 10% phenol was used with 30% water, 30% acetic acid, 20% formic acid and 10% propionic acid, total acid conversion and ester recovery increased to 95.2% and 83%, respectively. This observation is in agreement with Fig. 8c, where it was shown that both conversion and ester recovery increase with phenol composition up to 15% phenol. The individual acid conversion was 96.7%, 98% and 95% for acetic acid, formic acid and propionic acid, respectively. Higher conversion for formic acid indicates it has a very high reactivity towards phenol (100% phenol conversion). Like 5% phenol simulation, negligible amount (0.4%) of unreacted n-butanol was lost with water in top product but less water was found in the bottom (4.8% of total water or 2.7% of bottom product), which should increase the fuel quality of the upgraded bio-oil. Lesser amount of water also resulted in higher bottom temperature (205.4°C). Although, condenser heat duty increased to −24.15 kW for 10% phenol, reboiler heat duty reduced slightly to 20.33 kW. But, these trends changed drastically when 20% phenol (30% water, 20% acetic acid, 15% formic acid and 5% propionic acid) was used, for which although overall conversion increased to 99.2%, ester separation decreased to 74.6%, similarly as shown in Fig 8c. Individual acid conversion was 100%, 100% and 92% for acetic acid, formic acid and propionic acid, respectively. Although, water in bottom reduced to zero, 2% unreacted n-butanol went into top water-rich product. Higher amount of butyl-acetate also went towards the top product, which is the main reason behind lower ester recovery at bottom. Bottom feed temperature was 211.4 °C, suggesting absolute absence of water that drives up the temperature. Heat duties were −23.92 kW and 20.20 kW for condenser and reboiler, respectively. It is also evident that phenol is not reactive towards acetic and propionic acid, as unreacted phenol is found primarily at the bottom product when molar ratio of phenol to formic acid is more than one (20% phenol to 15% formic acid).

Higher amount of phenolics as well as binary azeotrope between water-butyl acetate system [32] drives the acidic esters toward the top, which in this case is responsible for less ester at bottom.

Finally, it should be noted that four steps (feasibility, synthesis, design and economic/energetic optimization) required to fulfill a RD unit operation described by Thery et al. [50], have been demonstrated for a complex bio-oil system consisting of fatty acid mixtures, phenolics and alcohols using common process design and optimization (AspenTech™) software tools. This should provide a robust background for the simulation of more complex multicomponent upgradation processes involving other bio-oil components including glycerol, aldehydes, ketons, other phenolics and sugars. Additionally, aldehydes/ketones and phenolics present in bio-oil can undergo acetylation/ketalization and alkylation types of reaction, respectively, with n-butanol to produce high value chemicals and fuel additives [21, 51-54], and should be incorporated with esterification reactions. There are rooms for further process intensification such as heat integration, external and internal recycling and internal product recovery. Butyl acetate present at top product (0.08−0.11 kmol/h) can be separated from water using another extractive/azeotropic distillation unit (to break the water-ester azeotrope) and can be mixed with ester product. Also, there are possibilities of several side reactions at high temperature including ether formation and decompositions [36], which should be incorporated for a more comprehensive process design. However, these are beyond the scope of the current investigation and will be the subject of future studies.

4. Conclusion

The Aspen simulation for reactive distillation (RD) of complex bio-oil esterification with n-butanol was carried out for the upgradation of pyrolysis bio-oil. The binary and ternary interaction between the components of n-butanol/acetic acid/n-butyl acetate/water system with phenolic compounds were studied by using Aspen Property PLUS at 10 bar pressure to observe the phase equilibrium behavior of this complex mixture, liquid-liquid phase splitting and possible location of azeotropes. Aspen 'Design Specification' and 'Sensitivity Analysis' tools were used to optimize the RD unit and to establish the effect of various parameters and to optimize the RD process, respectively, when 1 kmol/h of complex fatty acid mixture and phenol was considered as bio-oil. The simulation should advance the existing knowledge of single ester synthesis which has been previously done mostly at low pressure to more complex systems, and provide a framework for extending column simulation to complex RD.

When 10% phenol was added to the bio-oil as a constituent, overall reaction conversion was 95% and the alcohol feed requirement reduced considerably due to the acid-phenol reaction (primarily with formic acid). The produced fatty acid esters were in a mixture and this high degree of conversion and separation was attributed to internal entrainer effects of esters and phenolics. Phenol was found to be highly reactive to formic acid and all the phenol reacted to formic acid exclusively to produce phenyl formate. Optimum total number of stages was found to be 27 where optimized number of rectifying, reactive and stripping stages were 11, 13 and 1, respectively. Optimum bio-oil and n-butanol feed stages were 13th and 25th, respectively, for the simulation. The

temperature and composition profiles for each of the simulation are drawn along the column length. Sensitivity analysis was done to optimize various input parameters including reflux ratio, distillate to feed ratio and butanol flow-rate to achieve higher acid conversion, ester separation and lower energy requirements. Optimum reflux ratio, distillate to feed ratio and n-butanol:acid molar feed ratio was 1.5, 0.38 and 2.5, respectively. The effects of varying amount of water, phenol and acids (acetic, formic and propionic) were also demonstrated. The inclusion of phenolic reaction will open a new dimension, where phenolic compounds (a major portion of bio-oil) can be incorporated in bio-oil RD design. The Aspen based simulation performed in this work could also provide valuable insight into lab-scale and industrial reactive distillation column design and the parameters calculated could play a vital role in catalyst design for RD of pyrolysis bio-oil.

Acknowledgements

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