Design and Optimization of the Process of Preparing Biofuel Ethanol from Lignocellulose

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Fossil resources are increasingly exhausted and energy problems are facing severe challenges. The synthesis of ethanol from abundant lignocellulose is conducive to alleviating energy shortage, reducing environmental pollution, and achieving sustainable development. In this paper, compared with the traditional process, the whole process simulation of lignocellulose to biofuel ethanol is established, and a deep-eutectic solvents (DES) pretreatment process for Lignocellulose is proposed. Firstly, to verify the feasibility of the process, the steady-state simulation of the biofuel ethanol production process is carried out using Aspen Plus. Secondly, based on the steady-state simulation, the process is optimised to obtain the optimal operating parameters. Finally, DES is used as an entrainer to increase the concentration of ethanol, and its mechanism is investigated by molecular dynamics simulation (MD). The simulation results show that the DES has good effect in pretreatment and extractive distillation. The final yield of ethanol is 16.8 kg/h and the purity is 99 %. The results of molecular dynamics simulation show that the interaction between DES and water is much larger than that between DES and ethanol. The results are consistent with the process simulation results.

1. Introduction

Environmental problems and dwindling fossil fuels exacerbated the world's energy crisis, creating an urgent need for a clean, renewable and sustainable fuel (Wang et al., 2019). Biofuel ethanol has the advantages of being cheap, environmentally friendly, clean, safe, and renewable, and is considered as the best fuel to save and replace gasoline. Since the traditional method of producing biofuel ethanol is based on sugar or starch, large-scale production will obviously affect human food sources. Rijn et al. (2018) established a model for converting raw materials such as sugarcane and sweet sorghum into biofuels. The results show that the cost of converting sugar crops into biofuels is too high. Lignocellulose is an attractive renewable resource that can be obtained in large quantities at relatively low cost. Because of the complex structure of lignocellulosic biomass, a pretreatment stage is required by destroying the lignin structure, which is the main protective barrier for lignocellulose, thereby improving the efficiency of sugar recovery. Ionic liquid (IL) pretreatment of biomass has attracted extensive scientific attention, but its high cost and potential toxicity have not been widely used (Vigier et al., 2015). Fortunately, as an alternative to ionic liquids, deep eutectic solvents (DESs) with similar physicochemical properties to ionic liquids are emerging rapidly, which is both cheap and environmentally friendly. Carlos Alvarez-Vasco et al. (2016) evaluated the treatment effects of four choline chloride (ChCl) - based DES on hardwood (poplar) and softwood (cedar). It was found that these DES treatments can selectively extract a large amount of lignin from high-yielding wood, and the purity of the extracted lignin is as high as 95 %.The results from these studies show that DES is a promising wood delignification solvent. Compared with the traditional process, the whole process of converting lignocellulose into biofuel ethanol was simulated in this paper, including raw material pretreatment, enzymatic hydrolysis and saccharification, fermentation, product refining and by-product recovery. The pretreatment of lignocellulose with DES is emphasised. In addition, molecular dynamics simulation (MD) is used to explain the excellent effect of DES as extractant in extractive distillation of ethanol-water system.

2. Process simulation

The proposed new process flowsheet is described in this section. A DES method for pretreatment of lignocellulose to produce biofuel ethanol is proposed in this paper. The model is based on information about the process of producing fuel ethanol from cornstalk by NREL. The proposed new process of producing ethanol from lignocellulose by DES as a pretreatment solvent is shown in Figure 1. The specific process is as follows.

2.1 Process description

Firstly, lignin and ash are separated by breaking lignocellulosic materials and combining them with the pretreatment solvent. Cellulose and hemicellulose then enter the saccharification and fermentation stage to produce fuel ethanol. Finally, DES is used as an entrainer for the extractive distillation of the ethanol-water system. The pretreatment process is conducted at 120 °C and 0.1 MPa, and a solid-liquid separator is used to separate the slurry after treatment. The liquid components are mainly pretreatment solvent and lignin. The solid is formed into monosaccharides by enzymatic hydrolysis and then ethanol by fermentation. At the same time, the traditional ethanol production process using sodium hydroxide as the pretreatment solvent is established and compared with the former, and the operating conditions and feed amount are the same as the former. As ethanol contains a large amount of water and a part of unconverted sugar, the strict distillation module is used to separate sugar and ethanol, and then extractive distillation module is used to separate ethanol and water with cheap and environmentally friendly DES as entrainment agent. Sensitivity analysis is used to find the optimal parameters of the two towers. The related parameters of the two towers are shown in Table 1.

This process is simulated using Aspen Plus. Since there are no related thermophysical properties of DES in the database. Therefore, we need to determine the following parameters of DES: Liquid Molar Volume, Heat Capacities, Viscosity, Surface Tension, Liquid-Vapor Pressure, Binary Interaction Parameter. The related parameters of DES are listed in Table 2.
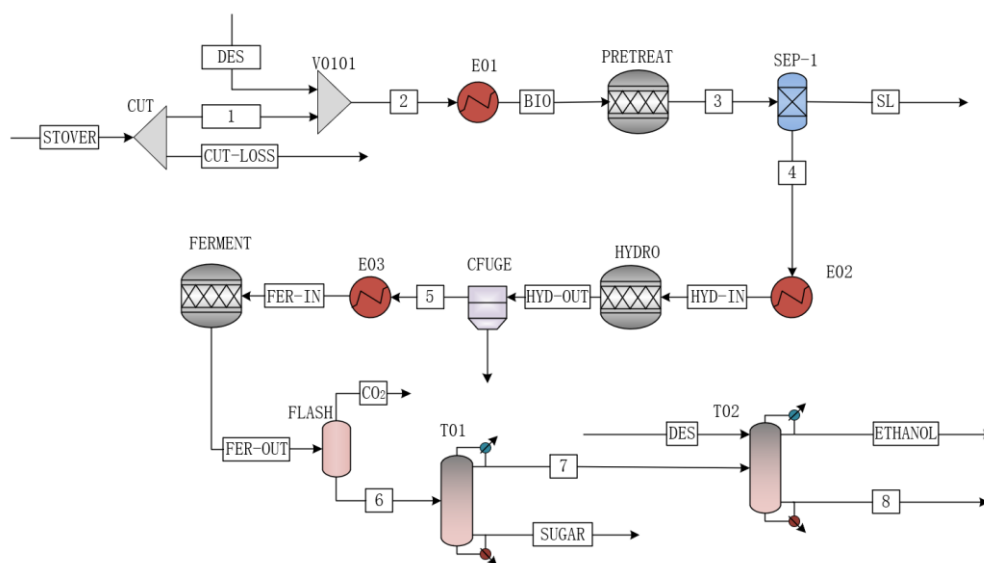

Figure 1: Flowsheet of DES pretreatment lignocellulose to produce biofuel ethanol

Table 1: The common operation parameters of two columns

Operation parameters	T01	T02
Number of Stages	10	30
Feed Stages	5	14(DES), 3
Column Top Temperature, °C	25.06	-18.14
Column Top Pressure, MPa	0.1	0.1
Column Top Heat duty, kW	-52.75	-18.61
Column Bottom Heat duty, kW	53.46	23.51
Column Bottom Temperature, °C	350.94	138.04
Reflux Ratio (mole)	2.96	4

2.2 Process simulation results

The simulation results of the DES pretreatment lignocellulose process are shown in Table 3. Compared with the traditional solvent (NaOH) pretreatment, the amount of ethanol obtained by DES pretreatment increased from 9.9 kg/h to 16.8 kg/h. The reason is that DES will destroy the lignin and cellulose bonding in lignocellulose, leaving more cellulose and hemicellulose exposed (Xu et al., 2016) indirectly increasing the sugar conversion rate, and ultimately increasing the production of ethanol. Meanwhile, the distillation process of ethanol and water system with DES (dosage of 0.4 kmol/h) as entrainment agent also achieved excellent results, and the final purity of ethanol reached 99 %.

Table 2: Related parameters of DES

Properties	Equations	Units	Parameters C_1	C_2	C_3
Liquid Molar Volume	$V_m = C_1 + C_2 T + C_3 \mathrm{T}^2$	T/K, V_m/cum·kmol^{-1}	0.0635	2.427×10^{-5}	1.62×10^{-8}
Heat Capacities	$C_P = C_1 + C_2 T + C_3 \mathrm{T}^2$	T/K, C_p/kJ·kmol^{-1}·K^{-1}	117.3	0.2085	1.68×10^{-12}
Viscosity	$\ln \eta = C_1 + \dfrac{C_2}{T} + C_3 \ln T$	T/K, η/Pa-sec	-443.7	26,670	62.14
Surface Tension	$\sigma = C_1 \left(1 - T_r\right)^{(C_2 + C_3 T_r)}$, $T_r = T / T_C$	T/°C, σ/dyne·cm^{-1}	101.635	1.222	-8.40×10^{-10}
Liquid Vapor Pressure	$\ln P = C_1 + \dfrac{C_2}{T + C_3}$	T/°C, P/bar	77.474	-9,895.03	0

Component i	Component j	Binary Interaction Parameters a_{ij}	a_{ji}	b_{ij}	b_{ji}	c_{ij}
Ethanol	Water	0	0	-29.23	613.42	0.3
Water	DES	0	0	145.898	-672.841	0.3
Ethanol	DES	0	0	7,698.22	502.646	0.3

3. Molecular dynamics simulation

ChCl-based DESs are extremely promising in the extraction process of alcohol, but the mechanism of extraction by these DESs remains unknown. Understanding the molecular interactions between molecular structures and components is crucial to the development of suitable and efficient solvents.

3.1 Molecular dynamics simulation details

The Gaussview (Tian et al., 2015) software builds the initial structure of the molecule being studied. Based on the B3LYP theory and the 6-31 g* level basis set, Gaussian09 D01 optimised the geometry of all molecules. The charge distribution of all molecules is obtained by the restrained electrostatic potential (RESP) charge derivation method (Bayly et al., 1993). Figure 2 shows the molecular structure and atomic markers of all the optimised compounds in this study. Combined with the ANTECHAMBER module, the generalised AMBER force field (GAFF) functional form is used to generate the force field parameters of the compound.

For this work, GROMACS 2018.4 (Pronk et al., 2013) package is used for all atom molecular dynamics (MD) simulations. Firstly, the molecules studied were added to a box of size 6.0 × 6.0 × 10.0 nm^3 under a ratio of DES: H_2O: ethanol to 10: 6: 9. All of the initial simulation boxes are generated by Packmol (Martínez et al., 2009) software. Periodic boundary conditions (PBCs) apply in three directions, ensuring a constant number of particles inside the box. Secondly, use the Langevin thermostat and Nose-Hoover Langevin barostat to stabilise the temperature (303.15 K) and pressure (1 atm), respectively. Long-range electrostatic interactions with 0.16 grid spacing and fourth-order interpolation are calculated by using Particle Mesh Ewald (PME). Verlet cutoff-scheme is used for short-range interactions with 1.0 nm electrostatic and van der Waals cutoff lines. Solute - solvent interaction is described by the total atomic force field of gromos54a7. Finally, at 298.15 K and 1 bar, the system energy is minimised by 50,000 steps of simulation, and then the system is gradually heated to 303.15 K. The balancing system continues for 3 ns in the NVT ensemble. After reaching the expected temperature, the NPT ensemble is further balanced under the condition of isothermal and isobaric and lasts for 30 ns. Visual molecular dynamics (VMD) software (Humphrey et al., 1996) is used to analyse the trajectory data.

Table 3: Simulation results of lignocellulosic ethanol production process

| Data Items	BIO	HYDRO-IN	HYDRO-OUT	FER-IN	FER-OUT (DES)	ETHANOL	FER-OUT (NaOH)
Temperature, °C	140	48	48	35	32	-18.1	32
Pressure, MPa	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Vapor Fraction	0.9	0	0	0	0.2	0	0.3
Mass Flows, kg/h	520.1	37.1	46.14	41.0	35.5	15.2	27.7
H_2O	391.9	0	4.9	4.9	4.9	3.63×10^{-3}	6.47
ETHANOL	0	0	0	0	16.8	15.01	9.90
GLUCOSE	0	2.5	23.1	23.1	1.15	0	0.656
XYLOSE	0	1.45	11.6	11.6	1.7	0	1.06
ARABINOS	0	0.2	1.4	1.4	0.2	0	0.152
EXTRACT	16.5	0	0	0	0	0	0
CO_2	0	0	0	0	10.7	0.13	9.46
CELLULOSE	22.8	20.2	1.7	0	0	0	0
XYLAN	12.9	9.0	0.04	0	0	0	0
ARABINAN	1.4	1.3	0.1	0	0	0	0
LIGNIN	11.0	2.4	2.4	0	0	0	0
ASH	5.0	0	0	0	0	0	0
ENZYME	0	0	0.9	0	0	0	0
DES	58.6	0	0	0	0	3.89×10^{-2}	0
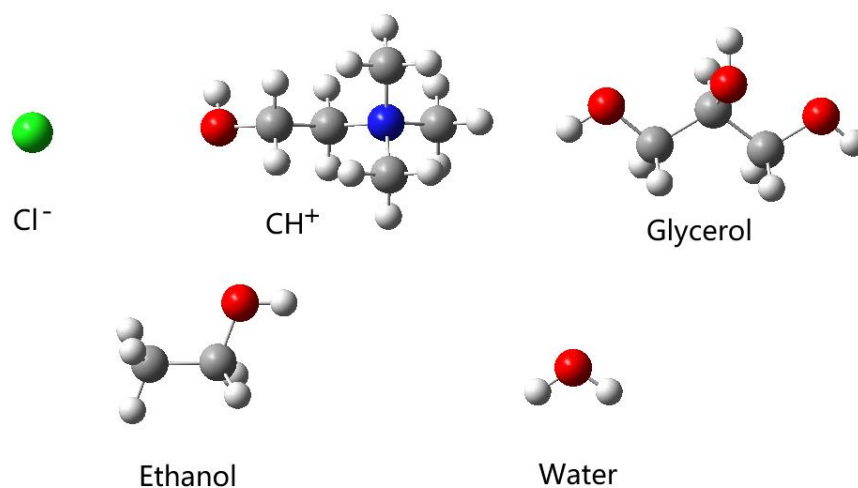
Figure 2: Optimised molecular structure

3.2 Molecular dynamics simulation results

The simulated snapshot is shown in Figure 3, where the hydrogen bond donor is ChCl and the hydrogen bond acceptor is glycerol. The water molecules are distributed in DES, while most of the ethanol molecules are excluded, indicating that the interaction force between DES-H_2O is higher than that between DES- ethanol. In the RDFs of hydrogen bond donor (HBD) -H_2O and hydrogen bond acceptor (HBA) -H_2O, as shown in Figure 4a, the magnitude of the interaction force is determined by the peak value of the first peak. The first peak of both is greater than 1, and the maximum peaks are 1.86 and 1.22, indicating that DES has a good dissolution effect on H_2O, and the interaction force of HBD-H_2O is large, indicating that HBD in DES plays a role in dissolved water Leading role. As shown in Figure 4b, there is no significant peak in both HBD-ethanol and HBA-ethanol, indicating that the interaction force between ethanol and DES is poor. When DES is used to separate ethanol and water in the extractive distillation process, the interaction force between DES-H_2O is much higher than that of DES-ethanol, so ethanol will flow out from the top of the tower, and water and DES will flow out of the tower kettle. In line with the results of process simulation.
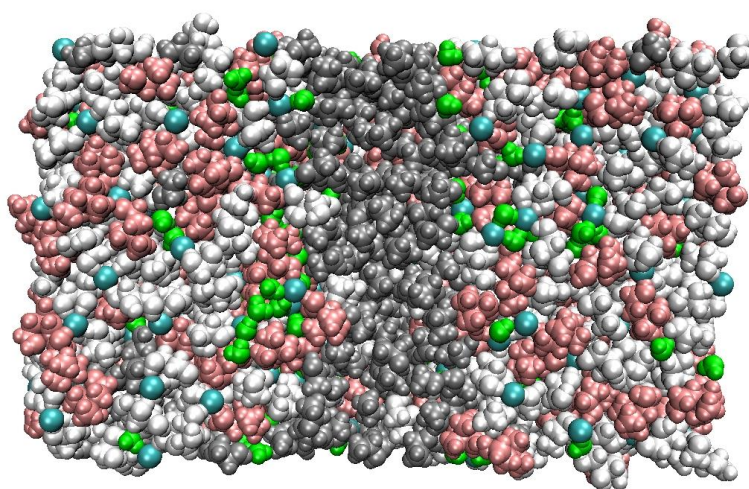

Figure 3: A snapshot from the simulations for DES + H_2O + ethanol. Cl^- is shown in biue , Ch^+ in red, glycerol in write, ethanol in black and H_2O in green. The specific ratio is Cl^-: Ch^+: glycerol: ethanol: H_2O=400: 400: 800: 360: 240

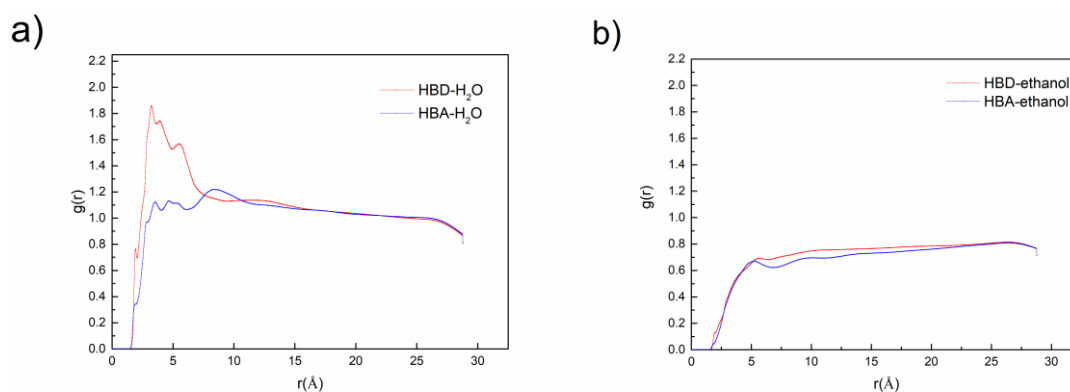
Figure 4: Radial distribution function of a) DES-H2O and b) DES-ethanol

4. Conclusions

In this paper, Aspen Plus software is used to simulate the whole process of lignocellulosic ethanol. After comparing the pretreatment effect of two different solvents (NaOH, DES), it is found that DES has excellent pretreatment effect, indirectly increasing the hydrolysis conversion rate of polysaccharides to 80 % - 90 %, and the final yield of ethanol is 16.8 kg/h, which is 1.7 times of the traditional pretreatment method. In the process

of refining ethanol, using environmentally friendly DES as an entraining agent, the water in ethanol is removed by extractive distillation to obtain ethanol with a purity of 99 %. According to the results of molecular dynamics simulation, the interaction mechanism between DES and water-ethanol system is analysed, indicating that the interaction force between DES and water is far greater than that between DES and ethanol. Therefore, the solubility of water is higher than that of ethanol in DES, thus changing the relative volatility of the ethanol-water system to achieve the effect of ethanol dehydration. The results of molecular dynamics are consistent with those of process simulation. In the RDFs diagram of the simulation results, it is also found that the hydrogen bond donor in DES plays a leading role in the extractive distillation process. In the future work, the reflux of DES in the process will be considered and the effect and mechanism of various DES in extractive distillation will be studied.

Acknowledgements

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