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Development of an estimation model for the evaluation of the energy requirement of dilute acid pretreatments of biomass☆

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ARTICLE INFO

ABSTRACT

This study aims to develop a mathematical model to evaluate the energy required by pretreatment processes used in the production of second generation ethanol. A dilute acid pretreatment process reported by National Renewable Energy Laboratory (NREL) was selected as an example for the model's development. The energy demand of the pretreatment process was evaluated by considering the change of internal energy of the substances, the reaction energy, the heat lost and the work done to/by the system based on a number of simplifying assumptions. Sensitivity analyses were performed on the solid loading rate, temperature, acid concentration and water evaporation rate. The results from the sensitivity analyses established that the solids loading rate had the most significant impact on the energy demand. The model was then verified with data from the NREL benchmark process. Application of this model on other dilute acid pretreatment processes reported in the literature illustrated that although similar sugar yields were reported by several studies, the energy required by the different pretreatments varied significantly.

1. Introduction

The world population is expected to reach 9.6 billion by 2050 and will demand a large amount of energy to allow these people to fulfil their daily lives. In approximately 20% of the world's population (predominantly in the under-developed nations), continuous and reliable supply of energy is not easily accessible [1]. These under-developed nations seek to improve their standard of living by tapping into the existing energy resources. This in combination with the ever-increasing population puts a tremendous strain on the finite fossil fuel resources.

Lignocellulosic materials including for example agricultural residues such as bagasse [2], corn stover [3] and wheat straw [4]; forest residues [5]; energy crops [6] and waste paper [7] provide a renewable and potentially inexpensive source of raw material for the production of liquid fuels such as ethanol. However, to effectively gain access to the sugars in the lignocellulose structure, a pretreatment process is required to weaken the naturally recalcitrant structure of lignocellulosic materials [8–13]. Pretreatment processes are currently essential for the conversion of lignocellulosic materials into ethanol using biocatalyst such as enzymes and fermentative microorganisms. Pretreatments are recognised as a large

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contributor to the cost of cellulosic ethanol production. In some processes, pretreatment is responsible for up to 14% of the total fixed capital [14] while Yang and Wyman proposed that pretreatment accounted for 20% of the total cost of production [8].

Several studies have been carried out on the economic performance [15–17], the life cycle assessment [18], and the minimum selling price of the ethanol [16,17] of the various pretreatments but very few have considered the evaluation of the energy consumption in the pretreatment process. Conde-Mejia et al. [19], using ASPEN software compared the energy consumption and associated cost of several pretreatment processes with and without direct recycle streams implemented into the design and concluded that steam explosion and dilute sulphuric acid pretreatments were the most energy efficient pretreatments in terms of the energy cost (dollars per tonne of dry biomass). Kumar and Murthy [20] used the simulation software SuperPro Designer to explore the energy balance of the production of cellulosic ethanol and also found steam explosion to be the most energy efficient pretreatment; its ethanol yield however was the lowest of the pretreatment processes examined. These studies however contain insufficient information on the key influences of the rate of energy consumption during the pretreatment process, which is a key factor in evaluating the economic performance of the process. These studies focussed more on the types of processing technique used, processing equipment used, operating conditions and the price of ethanol (15–19).

This paper therefore aims at presenting an effective energy estimation model developed from a fundamental level to clearly identify the energy consumption factors of a pretreatment process. In this case, the dilute acid pretreatment process was used as an example.

2. Model development and results

2.1. Process description of the base case

The pretreatment design basis for the energy estimation model was taken from the National Renewable Energy Laboratory (NREL) dilute acid process [21]. The process was built upon the evaluation of previous models designed by NREL. It should be noted that the original operating conditions of 190 °C for 2 min with a sulphuric acid mass fraction of 1.1% was deemed too harsh and resulted in a significant number of degradation products. NREL subsequently revised the process to reduce the pretreatment severity without generating high amounts of the degradation products. This included a two-stage pretreatment process. Stage 1 uses a sulphuric acid content per dry g of biomass of 18 mg at 158 °C and 557 kPa (5.5 atm) for a period of 5 min with a solids fraction of 30% (defined as the amount of dry biomass divided by the total mass of the biomass and liquid added). Under these conditions a considerable amount of oligomers is formed from the glucan, xylan, arabinan, mannan and galactan from the plant cell wall hemicelluloses. The second stage of the pretreatment hydrolysis is operated at 130 °C for 20 min–30 min with the addition of a further 4.1 mg of sulphuric acid. This hydrolyses the oligomers released in the first stage into their respective monomers (glucose, xylose, arabinose, mannose and galactose).

During this process, there are several chemical reactions that occur [21]. Table 1 lists the chemical reactions that were considered for the model in this paper. Arabinan, mannan, and galactan were assumed to have the same reactions and conversion pathways as xylan. The reactions involving the

Table 1 – Pretreatment hydrolysis reactions of the NREL dilute acid pretreatment process with the compositions of the reactants, the reactions' assumed conversions and the calculated heats of formation values.

No.	Reactions[a]	Composition[b]	Conversions[a]	Heats of Formation/cal mol^{-1c}
1	$(Glucan)_n + nH_2O \rightarrow nGlucose$	31.9%	9.90%	1004
2	$(Glucan)_n + nH_2O \rightarrow nGlucose\ Oligomer$	31.9%	0.30%	68 232
3	$(Glucan)_n \rightarrow nHMF + 2nH_2O$	31.9%	0.30%	−2941
4	$Sucrose \rightarrow HMF + Glucose + 2H_2O$	3.6%	100%	−55,669
5	$(Xylan)_n + nH_2O \rightarrow nXylose$	18.9%	90.0%	892
6	$(Xylan)_n + mH_2O \rightarrow mXylose\ Oligomer$	18.9%	2.40%	0
7	$(Xylan)_n \rightarrow nFurfural + 2nH_2O$	18.9%	5.00%	−2102
8	$Acetate \rightarrow Acetic\ Acid$	2.2%	100%	26
9	$(Lignin)_n \rightarrow nSoluble\ Lignin$	13.3%	5.00%	0
10	$(Arabinan)_n + nH_2O \rightarrow nArabinose$	2.8%	90.0%	892
11	$(Arabinan)_n + mH_2O \rightarrow mArabinose\ Oligomer$	2.8%	2.40%	0
12	$(Arabinan)_n \rightarrow nFurfural + 2nH_2O$	2.8%	5.00%	−2102
13	$(Mannan)_n + nH_2O \rightarrow Mannose$	0.3%	90.0%	1004
14	$(Mannan)_n + mH_2O \rightarrow mMannose\ Oligomer$	0.3%	2.40%	0
15	$(Mannan)_n \rightarrow nHMF + 2nH_2O$	0.3%	5.00%	−2941
16	$(Galactan)_n + nH_2O \rightarrow nGalactose$	1.5%	90.0%	1004
17	$(Galactan)_n + mH_2O \rightarrow mGalactose\ Oligomer$	1.5%	2.40%	0
18	$(Galactan)_n \rightarrow nHMF + 2nH_2O$	1.5%	5.00%	−2941

Note: Because minor components are not listed, the composition percentages do not sum to 100%.
[a] From Table 6 in Ref. [21].
[b] Data from Table 3 in Ref. [21].
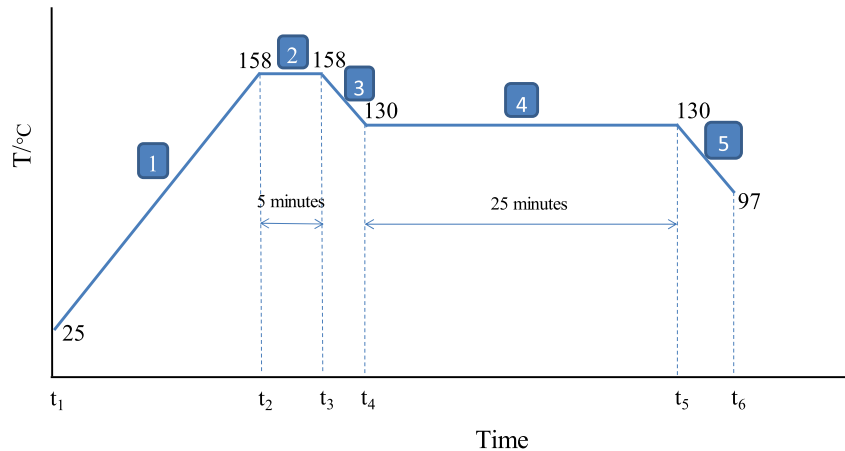[c] From calculations based on data in Appendix D in Ref. [21].

Fig. 1 – Temperature profile of the NREL dilute acid pretreatment process.

formation of inhibitory compounds from mannan and galactan were assumed to form 5-hydroxymethylfurfural (HMF) as in the case of glucan.

2.2. Process model development and calculations

In this study, an energy model was developed to simulate the NREL pretreatment process. It contained five stages according to temperature changes as shown in Fig. 1 and Table 2. These five stages are outlined as follows; Stage 1, the supply of steam to the pretreatment reactor in order to attain the desired reaction temperature of 158 °C; Stage 2, the supply of energy to maintain this temperature for the specified residence time of 5 min during which the oligomers are formed; Stage 3, the release of energy in order to cool the contents of the outlet stream down to 130 °C, the temperature required for the conversion of the oligomers; Stage 4, the supply of energy to maintain the reactor at 130 °C and allow the conversion of oligomers to monomers and Stage 5, the release of energy in order to cool the products down to 97 °C; the temperature suited for the next stage of the ethanol production process.

The energy estimation model created is an intricate version of the net energy balance Equation for a closed system;

$$\Delta E = Q - W \tag{1}$$

where ΔE is the change of the internal energy of the system, Q is the heat added to the system and W is the work done by the system. Equation (1) can be developed to incorporate the 5 stages outlined earlier as:

$$\Delta E = Q_{Stage1} + Q_{Stage2} + Q_{Stage3} + Q_{Stage4} + Q_{Stage5} - W_T \tag{2}$$

where W_T represents the total work done over the whole system.

Stage 1 is otherwise known as the heating stage while both Stage 2 and Stage 4 represent the period in which the hydrolysis reactions occur. In addition, Stages 3 and 5 are the cooling stages. It is obvious that energy could be recovered from Stages 3 and 5. As the paper aims to estimate the theoretical energy requirement for the pretreatment process, and Stages 3 and 5 do not require an input of energy but rather a release, these two-stages were not modelled. Equation (2) is therefore further simplified to Equation (3):

$$\Delta E = Q_{heating} + Q_{reaction} - W_T \tag{3}$$

There is no work done by this pretreatment system and the agitation energy input into the system was ignored for simplicity purposes. The W_T term was not considered in the following estimation.

It is inevitable that there will be some form of heat loss but in order to simplify the development of the model, this was set to zero. Its impact was however analysed during the model improvement stage.

The $Q_{heating}$ term in Equation (3) can be further broken down to Equation (4).

$$Q_{heating} = m_w \int_{T_0}^{T_H} C_{p_w} dT + m_b \int_{T_0}^{T_H} C_{p_b} dT + m_a \overline{C_{p_a}}(T_H - T_0) \tag{4}$$

Table 2 – Operating conditions of the pretreatment process.					
	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
T/°C	25 up to 158	158	158 down to 130	130	130 down to 97
Residence time/min	unknown	5	Unknown	25[a]	unknown
p/kPa	—	557	—	—	101
Acid loading/mg g^{-1b}	none	18	None	4.1	none

^a 25 min was selected as the mean value from the range of (20–30) minutes.
^b mg g^{-1}: sulphuric acid in mg, dry corn stover in g.

C_p represents the specific heat capacity in kJ kg^{-1} °C^{-1}; m is mass in kg with the subscripts w, b and a representing the water, biomass (corn stover) and sulphuric acid, respectively. T is the temperature in which T_H is the hydrolysis temperature in °C; and T_0 the environmental temperature set at 25 °C.

3. Application of the model to the dilute acid pretreatment process

To model the stages considered, three key components were specified; corn stover, sulphuric acid and process water as denoted in Equation (4). Some assumptions were also established to aid the development process and for the heating stage which include:

1. The model was created on a one-kilogram (1 kg) basis of dry corn stover at a solids mass fraction of 30%.
2. The environmental temperature of the pretreatment process was assumed to be 25 °C.
3. It was speculated that none of the chemical reactions outlined in Table 1 occurred during this stage.
4. It was also decided upon that the heating energy of the 3 components would be calculated individually and the sum used to simulate the total heating for this stage as depicted in Equation (4). The impact of mixing sulphuric acid with water on the heating energy was analysed in the model improvement section.
5. For the sulphuric acid heating energy, an average C_p value was used.

3.1. Heating energy calculation

The water heating energy was calculated using the first term in Equation (4) in which the specific heat capacity value used was obtained from the second order of the polynomial plot of varying water specific heat capacities against their corresponding temperature values as shown in Equation (5) (the specific heat capacity values were collected in the temperature range of 0.01 °C–200 °C from Engineering Toolbox [22])

$$C_{p_w} = 0.00001T^2 - 0.0013T + 4.2085 \qquad (5)$$

As the energy required for heating the water from 25 °C to 158 °C was to be calculated, it was determined that at a pressure of 557 kPa (5.5 atm), water boils at 155 °C. As a result, the latent heat of vaporisation of water at 155 °C was adopted into the model. This revelation also introduced an expression for the heating of the water vapour from 155 °C to 158 °C. At this stage in the model however, the total percentage of water presumed to evaporate at 155 °C was 5% (this was later confirmed to be 4%). Consequently, the assumption introduces another expression for the heating of the remaining 95% of water from 155 °C to 158 °C. For the heating energy of the water vapour, its specific heat capacity was calculated using Equation (6), which was created on the manipulation of specific heat values obtained from Engineering Toolbox [23].

$$C_p = 0.0000008T^2 + 0.0002T + 1.8572 \qquad (6)$$

Factoring in all these aspects, the term for the water heating energy is therefore modified to:

$$m_w \int_{25}^{155} (0.00001T^2 - 0.0013T + 4.2085)dT + 0.05m_w H_L$$

$$+ (m_w - 0.05m_w) \int_{155}^{158} (0.00001T^2 - 0.0013T + 4.2085)dT$$

$$+ 0.05m_w \int_{155}^{158} (0.0000008T^2 + 0.0002T + 1.8572)dT \qquad (7)$$

As a result, the total heating energy for 2.315 kg of water (m_w) was found to be 1531 kJ kg^{-1}.

For the corn stover heating energy, Differential Scanning Calorimetry (DSC) experiments were carried out in triplicate to obtain a dataset of specific heat capacity values which were plotted against their corresponding temperature values to produce Equation (8). The corn stover analysed was obtained on August 12 2013 from a local corn farm in Loughborough (United Kingdom); all the parts of the corn plant minus the roots and the ears were collected. The corn stover was approximately 3 months old with an initial moisture content of 11.6% and average cross-section diameter of around 18 mm. The corn stover sample was stored in a dark room at room temperature and inert conditions until use. The sample was washed and oven-dried overnight before being pulverised in a Fritsch P5 Planetary Ball Mill to an almost homogenized sample. The milling process was carried out at 10 repetitions of 5 min milling and 5 min pausing after which the sample was sealed in an aluminium tray at ambient temperature until further use in the DSC (Perkin Elmer DSC7 – ZAAA0495). For the DSC experiments, a known mass of the sample was pelleted in aluminium pans and analysed to temperatures of 160 °C. Triplicate runs of the sample were performed from which heat flow curves were obtained and manipulated to give the specific heat capacity curves and hence equation for the locally grown corn stover:

$$C_p = 0.00004T^2 - 0.0015T + 0.9325 \qquad (8)$$

The corn stover heating energy was therefore calculated using Equation (9) which was developed from the substitution of Equation (8) into the second term in Equation (4). The result of which was 158 kJ kg^{-1} at $m_b = 1$ kg.

$$m_b \int_{25}^{158} (0.00004T^2 - 0.0015T + 0.9325)dT \qquad (9)$$

Alternatively, the energy required for heating the sulphuric acid was calculated using the last term in Equation (4) with an average specific heat capacity value of 1.34 kJ kg^{-1} °C^{-1} [24] and a sulphuric acid mass (m_a) of 0.018 kg. The outcome of this calculation was 3 kJ kg^{-1}; thus making the total heating energy of the dilute acid pretreatment process 1692 kJ kg^{-1}. Fig. 2 shows the distribution of this energy in relation to the three key components.

From Fig. 2 it is clear that the main component responsible for the magnitude of the heating energy is water. This suggests that the solid loading rate is one of the determining factors that govern the amount of energy consumed in the
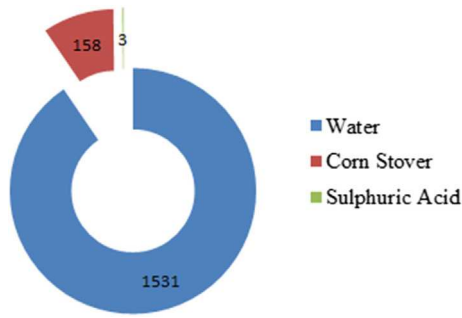
Fig. 2 – Illustration of the total pretreatment heating energy (kJ kg^{-1}).

heating stage of the pretreatment process. On the other hand, the amount of energy required to heat the acid up is negligible, indicating that in theory the sugar yield can be improved by the addition of acid without a notable increase in the energy consumed – presumably an advantage of the dilute acid pretreatment over other pretreatment processes like the hydrothermal.

3.2. Reaction energy calculation

For the reaction stage, three assumptions were made:

1. The reaction energy covered both stage 2 and stage 4 shown in Fig. 1.
2. All the reactions specified in Table 1 occurred in this stage.

The reaction energy was therefore calculated using the information in Table 1 together with Equation (10):

$$Q_{reaction} = \sum \left(m_b \times c_r \times x_r \times \Delta H_f / M_w \right) \tag{10}$$

where c_r and x_r are the composition of the reactant in the biomass and the conversion rate of the reactant to the product respectively and M_w the molecular weight of the reactant.

The equation was applied to the reactions and the overall net energy for the pretreatment process was found to be -17 kJ kg^{-1}. The negative energy value implies that the overall reaction process is exothermic and therefore in theory, results in a release of energy.

The total energy demand for the NREL dilute acid pretreatment process on a 1-kg basis according to the energy model is therefore only the heating energy of 1692 kJ kg^{-1}. In practice, a certain amount of energy could be recovered from the cooling stages. The net energy requirement will be lower than this value.

4. Model improvement

Some adaptations were made to look at the effect of calculating the heating energy of the sulphuric acid and water combined together on the total heating energy and to model the heat loss component that was initially ignored.

4.1. Sulphuric acid-water heating energy

In the model developed, an individual component heating method was implemented for ease of calculation. It was thought that the results from this method would not be far off from the results that would have been obtained if the heating energy for water and sulphuric acid were calculated together. In order to validate this assumption, the heating energy for the sulphuric acid and water combined together was calculated using a specific heat capacity graph for the sulphuric acid-water system obtained from a sulphuric acid bulletin [25].

A slightly modified version of Equations (4) and (11) was used in working out the heating energy involving the sulphuric acid-water system and is a modification of Equation (4), incorporating the combined mass of water and sulphuric acid and specific heat capacity of water and sulphuric acid:

$$Q_{heating} = m_b \int_{T_0}^{T_H} C_{p_b} dT + m_{a-w} \cdot \overline{C_{p_{a-w(T_H,T_0)}}} \cdot (T_H - T_0) \tag{11}$$

where subscript a–w represents the sulphuric acid-water system and the biomass heating term is kept constant.

In the heating stage of the pretreatment process (Stage 1), the acid loading rate per gram of dry corn stover is 18 mg, which is equivalent to a concentration of 0.7%; the boiling point of the sulphuric acid-water system was therefore assumed to be the same as pure water at 557 kPa (5.5 atm) (155 °C) due to the small concentration of acid and just as in the case of the individual heating energy of water there are four heating parts to the sulphuric acid-water heating energy; the heating of the system to its boiling point, the latent heat energy, the heating of the vapour to the reaction temperature and the heating of the remaining liquid to the reaction temperature. The expression for the sulphuric acid-water heating energy therefore becomes:

$$m_{a-w} \cdot \overline{C_{p_{a-w(155,25)}}} \cdot (155 - 25) + 0.05 m_{a-w} \times H_L$$
$$+ (m_{a-w} - 0.05 m_{a-w}) \cdot \overline{C_{p_{a-w(158,155)}}} \cdot (158 - 155) \tag{12}$$
$$+ 0.05 m_{a-w} \cdot \overline{C_{p_{a-w(158,155)}}} \cdot (158 - 155)$$

The sulphuric acid-water system graph used was assumed to represent both liquid and vapour form of the sulphuric acid-water mixture at a mass fraction of 0.7%, simplifying the above heating energy equation to:

$$m_{a-w} \cdot \overline{C_{p_{a-w(155,25)}}} \cdot (155 - 25) + 0.05 m_{a-w} \times H_L$$
$$+ m_{a-w} \cdot \overline{C_{p_{a-w(158-155)}}} \cdot (158 - 155) \tag{13}$$

The outcome of these calculations was 1541 kJ kg^{-1}, which is close to the 1534 kJ kg^{-1} calculated in the individual heating method; thereby justifying the assumption made about the method of calculation chosen in the model. It should be noted however that the same latent heat of vaporisation of water at 155 °C was used.

4.2. Heat loss

To model the heat loss during the pretreatment process, three different methods were used. In the first approach, the

amount of heat lost was evaluated from an experimental procedure using a Genesis Benchtop Autoclave by Rodwell Scientific Instruments to simulate the pretreatment process. The autoclave was run at 123 °C for 18 min. The entire experiment ran for approximately 115 min with the power readings taken with a plug-in mains power and energy monitor from Maplin Electronics (L61AQ) every 5 min for the heating and cooling stages which lasted 40 and 55 min respectively and every minute for the 'hydrolysis' stage. During the heating up period, the power readings remained relatively constant at 2.4 kW while during the 'hydrolysis' stage, the power readings fluctuated approximately every 6 s between high (2.4 kW) and low (0.013 kW) readings. Therefore, the power requirement for the maintenance was estimated to be 50% of that of the heating stage. Given that the residence time for the maintenance stage in the model is 5 min and assuming a heating up time of 15 min, the heat loss during the hydrolysis stage in this approach was calculated using Equation (14):

$$Q_{lost} = 0.5 \times \left(\frac{\tau_{maintenance}}{\tau_{heating}} \right) \times Q_{heating} \qquad (14)$$

This resulted in a heat loss value of 282 kJ kg^{-1}.

In the second approach, the pretreatment reactor was assumed to be of an insulated cylindrical nature and as a result, the amount of heat lost during the pretreatment process was likened to that of a pipe where the heat loss is represented as:

$$Q_{lost} = UA\Delta T \qquad (15)$$

As the heat transfer is considered to be through the wall of an insulated pipe, the overall heat transfer coefficient, U, is defined as:

$$U = 1/[(R_3/R_1 h_{in}) + (R_2 \ln(R_2/R_1)/k_{pipe}) \\ + (R_3 \ln(R_3/R_2)/k_{insulation}) + 1/h_{out}] \qquad (16)$$

Generally, the first two terms of the denominator in Equation (16) are a lot smaller than the other two terms and so their influence on the result of the final calculation of overall heat transfer coefficient would be insignificant. The equation is therefore simplified to:

$$U = 1/[(R_3 \ln(R_3/R_2)/k_{insulation}) + 1/h_{out}] \qquad (17)$$

where R_3 is the outside radius of the pipe + insulation, R_2 the outside radius of the pipe, $k_{insulation}$ the thermal conductivity of the insulation and h_{out} the heat transfer coefficient at the outside insulation surface.

The NREL pretreatment process employs 3 screw-feed reactors each with a volumetric flow-rate of approximately 3.43×10^6 Lh^{-1} and an inside radius of 1.3 m. The thickness and insulation of the vessel were assumed to be 0.015 m and 0.1 m respectively resulting in1.315 m as the R_2 value and 1.415 m as R_3. The cladding material used for the reactor is Incoloy-825 and this at 158 °C, has a thermal conductivity value of about 13.8 Wm^{-1} °C^{-1} while the heat transfer coefficient of ambient air (h_{out}) is typically between 40 and 50 Wm^{-2} °C^{-1} depending on the climate and wind speed outside the vessel. Deciding on an average value of 45 Wm^{-2} °C^{-1} for h_{out}, the value of U was calculated to be

34 Wm^{-2} °C^{-1} and with a reactor length of 9 m, the heat loss per reactor was approximately 100 MJ. Taking into account the residence time of 5 min and assuming a heating up time of 15 min, the theoretical heat loss per kilogram at a mass fraction of 30% and an assumed bulk density of 0.08 kg L^{-1} was found to be 3.63 kJ kg^{-1}.

The third approach exploited a heat loss model developed by Briggs of Burton. In this model, various parameters such as the reactor diameter, temperature difference, insulation thermal conductivity and other factors had to be quantified; most of which were specified as the same values in the previous approach. The outcome of this approach resulted in a heat loss of 4.17 kJ kg^{-1} (See Appendix A for the description of the calculation method and a calculation example of one of the heat loss components along with the parameters used in calculating the other components). This value is comparable to the result obtained from the second approach (3.63 kJ kg^{-1}), indicating that the heat loss in this process is approximately 4 kJ kg^{-1}. The heat loss calculated in the first approach was significantly over estimated. However, compared to the 'heating' energy of the process, the amount of heat lost is of little significance.

4.3. Heat recovery

In the development of the above energy consumption model, the theoretical energy required to hydrolyse each unit of biomass into hydrolysate was examined. On a commercial scale pretreatment process however, there is energy that can and should be recovered in order to reduce the net energy input. In this case, the energy that potentially could be recovered in Stages 3 and 5 (Fig. 1) was estimated by calculating the enthalpy changes of the components at each stage. Based on the corn stover composition, the percentage of glucose, xylose and other component in the hydrolysate at Stages 3 and 5 were modelled as 35.5%, 20.0% and 44.5%, respectively. And as 5% of the total water was assumed to have evaporated in stage 1, the amount of water at Stages 3 and 5 was modelled as 95% of the total inlet water mass − 2.20 kg kg^{-1} dry corn stover. The heat content for stages 3 and 5 was calculated using Equation (18);

$$\Delta E = \Delta E_{glucose} + \Delta E_{xylose} + \Delta E_{rem.substrate} + \Delta E_{water} \qquad (18)$$

where the change in enthalpy for glucose and xylose was calculated using average values of their specific heat capacity values while that of the remaining substrate was calculated using Equation (9) and the change in enthalpy for water using the C_p equation in Equation (5). The average molar specific heat capacity values for glucose and xylose were found to be 224 J mol^{-1} K^{-1} and 184 J mol^{-1} K^{-1} respectively [26]. Equation (18) can therefore be re-written as;

$$\Delta E = \left(n_{glucose} \times C_{p_{glucose}} \times \Delta T \right) + \left(n_{xylose} \times C_{p_{xylose}} \times \Delta T \right) \\ + m_{rem.substrate} \int_{T_1}^{T_2} (0.00004T^2 - 0.0015T + 0.9325) dT \\ + m_{H_2O} \int_{T_1}^{T_2} (0.00001T^2 - 0.0013T + 4.2085) dT \qquad (19)$$

where the specific heat capacity of the hydrolysate was worked out within the temperature limits of the system 130 °C and 158 °C for stage 3. The result of the calculations was approximately 299.0 kJ kg^{-1}. The same approach was used for Stage 5 from 97 °C to 130 °C and the outcome was 345.7 kJ kg^{-1}. The total amount of energy that could be given off was therefore found to be 644.7 kJ kg^{-1}.

Of this amount, the total amount that a heat exchanger is capable of recovering is between 60% and 70% [27]. Assuming 65%, the total energy recovered from the process is therefore estimated to be 419.1 kJ kg^{-1}.

The heat that potentially can be recovered from the cooling stages in the pretreatment process is about 25% of the calculated energy required. The heat recovered is believed to be of a lower quality than that of the steam injected into the system. However, the recovered heat can be used to heat the reactants up as far as is possible or to heat the enzyme hydrolysis tank. Nevertheless, the exact amount of energy that could be recovered depends on the efficiency of heat exchange system, the pretreatment operating parameters and the degree of process integration.

5.   Sensitivity analysis

Five key variables were considered for the sensitivity analysis; the percentage of water evaporated, the solids loading rate, the acid loading, the operating temperature and the reaction conversion percentages. Reasonable ranges for the variables were selected based on estimates of the most probable ranges obtained from literature, with the baseline values for the variables set as the figures used in developing the model as depicted in Table 3.

Fig. 3a shows that the solids loading rate is the most sensitive variable to the model followed by the percentage of water evaporated while the operating temperature has a moderate impact and the acid loading together with the reaction yield the least impact.

The solids loading rate and the percentage of water evaporated were particularly sensitive, for example, when the percentage of water evaporated was increased from 5% (base case) to 100% (see Fig. 3a[i]) and the solids loading rate decreased from 30% (base case) to 5% (see Fig. 3a[ii]), the total pretreatment energy per kilogram increased by approximately 274% and 658%, respectively. This further reiterates the conclusion made about the solids loading rate and as such, optimization should be on achieving a pretreatment reactor that can accommodate high solids loading in order to

minimize the amount of water used and hence the energy consumed. Second generation ethanol pretreatment facilities operating at higher solids will require less energy in the form of heat to raise the temperature of the feedstock for pretreatment. However, increasing the total solids of the feedstock will affect the size of the motor required to mix and transport the feedstock. There are limited papers however citing solid loading rates greater than 30%, as above 30% solids loading rate, the wet material is likely to be un-pumpable in practice. On the other hand, most pretreatment processes reported in literature are carried out at a solids loading rate of 10% which coincides with the inflexion point in Fig. 3a(ii). These research works are however laboratory studies carried out for the purpose of investigating the impact of different conditions where low solids loading rate help to provide the greater mass and energy transfers needed for high hydrolysis yields. Miscibility is another factor as mixing in the laboratory is a lot more efficient at lower solids loading rates. The amount of energy consumed during pretreatment is of little or no concern in such studies. Chen et al. [28] has however quoted a solids loading rate of 45% for a dilute acid pretreatment process using corn stover at a temperature of 150 °C (for 5, 10 and 20 min) and an acid loading per gram of biomass of about 8 mg.

The effect of the acid concentration on the total energy consumed shows that it was not a major contributor to the energy efficiency of the pretreatment process (Fig. 3a[iii]). Varying the acid concentration per gram of dry biomass from 10 mg to 28 mg (18 mg being the base case) showed only a marginal decrease in the energy consumed from 1698 kJ kg^{-1} to 1686 kJ kg^{-1}. It will be interesting however to examine the effect of acid concentration on the sugar yield.

In the case of the operating temperature, the range of 120 °C–190 °C was chosen based on a range of maxima and minima values obtained from several papers on dilute acid pretreatment processes [8,20,29–32]. Fig. 3a[iv] shows that an increase in the operating temperature results in an increase in the total pretreatment energy.

Analyses of the chemical reaction conversion rates (Table 1) were conducted to assess its effects on the reaction energy; a constituent of the total pretreatment energy. 19 dilute acid pretreatment reaction conversions other than the NREL report were obtained from literature [20,33] (See Appendix B). In incidences where reaction conversions were not specified they were assumed to be the same as the base case scenario. Fig. 3b shows a variation in the reaction energy outcome from negative to positive values proving that the reaction conversions significantly impact the reaction energy. However, as

Table 3 – Raw data of the dilute acid pretreatment energy sensitivity analysis.		
Variables	Value	Range
Water evaporated/%	5	0–100 (increments of 5)
Solids loading rate/%	30	5–30 (increments of 5)
Acid loading/mg g^{-1}	18	10–28 (increments of 1)
T/°C	158	120–190 (increments of 5)
Reaction conversions	NREL conversion values for the 18 reactions displayed in Tables 1 and 3	20 different conditions for the reactions were obtained from literature. (see Appendix B)

the overall reaction energy was still insignificant compared to the heating energy and thus the total energy, the reaction conversions factor was not considered to be an important one for the optimization of the pretreatment energy efficiency.

6. Model verification

6.1. Verification approach 1

The mathematical model proposed for the energy estimation of dilute acid pretreatment processes was tested against the data provided by the NREL dilute acid pretreatment process. The process had a daily capacity of 2000 t with an expected up time of 96%. The numerical results of the model were compared to the NREL benchmark figures in order to verify the

model's accurate representation of the pretreatment process description and solutions.

The NREL pretreatment process description provides a comprehensive review with all the flow-rates and temperature values and was used in the verification process. In the NREL's Process Flow Diagram (PFD) [21], there are five input streams to the pretreatment vessel; the milled corn stover stream, the process water stream, the sulphuric acid stream and the two high pressure steam streams. The high pressure steam is injected into the vessel to obtain and maintain the reaction temperature and as such, the amount of energy carried by these streams was calculated using a generic form of the model developed, and represented in Equation (20). Furthermore, the amount of energy required by the corn stover, sulphuric acid and process water were calculated.
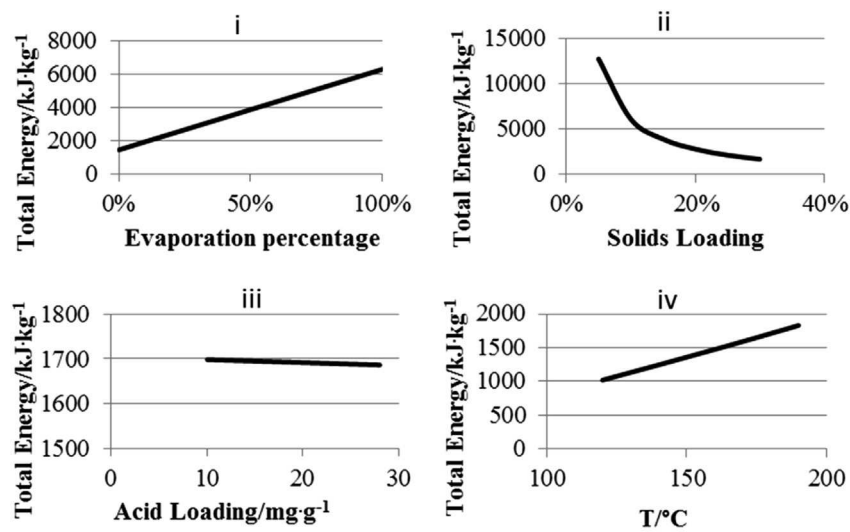
(a)
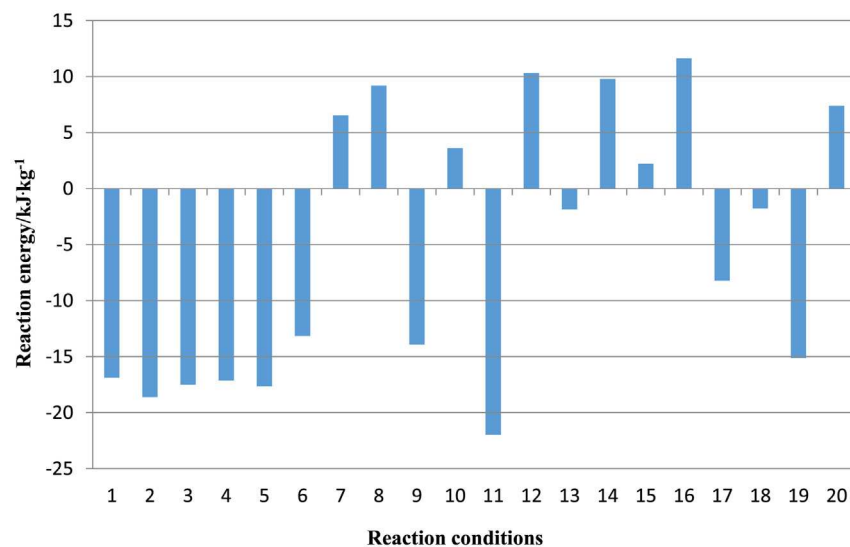
(b)

Fig. 3 — a: Effect of the percentage of water evaporated (i), solids loading rate (ii), acid loading (iii) and operating temperature (iv) on the total pretreatment energy (kJ). b: Effect of various reaction yields on the reaction energy.

$$\Delta E = m \overline{C_p} \Delta T \qquad (20)$$

In these calculations however, the initial temperature of the components were those specified in the NREL report as well as the mass flow-rates. The flow-rates and temperature values for each stream can be found in Table 4a. The model includes the following average specific heat capacities: corn stover (1.03 kJ kg^{-1} °C^{-1}), process water (4.2 kJ kg^{-1} °C^{-1}), high pressure steam (2.8 kJ kg^{-1} °C^{-1}) and sulphuric acid (1.34 kJ kg^{-1} °C^{-1}).

Both the corn stover and sulphuric acid streams contain water and as a consequence were calculated separately from the corn stover and sulphuric acid components. The energy required per kilogram of dry corn stover was calculated to be approximately 809 kJ.

Similarly, the amount of energy per kilogram of dry corn stover carried and supplied by the two steam streams with flowrates of 3490 kg h^{-1} and 24 534 kg h^{-1} were calculated from 268 °C to 158 °C; taking into account also the latent heat energy. The finding of these calculations was approximately 808 kJ. This is similar to the results obtained by the energy required, suggesting that the model is reliable with the data used in construction.

6.2. Verification approach 2

In another approach, the numerical results of the model the total pretreatment energy on a kilogram basis (kJ kg^{-1}) was multiplied by the mass flow-rate of the dry corn stover to attain the total pretreatment energy for the NREL pretreatment process. This calculation was executed a number of times using a range of pretreatment energies (kJ kg^{-1}) obtained from the sensitivity analysis of the percentage of water evaporated. The pretreatment energy ranged from 0% to 25% of water evaporated in increments of 1%.

The energy supplied to the process was gathered from various high energy content streams, such as high temperature process water and the water in the acid stream in addition to the two high pressure steams. This amount of energy was calculated and then subsequently used to determine at which water evaporation rate the energy supplied would meet the energy required As the results from the energy estimation model were used in determining the total energy required, the calculations of the total energy supplied were based on having the assumed initial temperature value of 25 °C as the final temperature and the stream temperatures as the initial temperature values.

A simplified form of Equation (7) was used in the steam calculations using average specific heat capacity values of 4.2 kJ kg^{-1} °C^{-1} and 2.8 kJ kg^{-1} °C^{-1} for water and steam, respectively. The calculations produced a total supplied energy of 138 GJ h^{-1} corresponding with the energy required by the pretreatment process using a water evaporation rate of 4% as shown in Table 4b.

Both verification approaches confirm that the majority of assumptions used to form the model can be validated.

7. Application of the model to other dilute acid pretreatment processes

The developed energy estimation model was applied to several other dilute acid pretreatment processes with varying temperatures, pressures, solids loading rates, residence times, and acid concentrations. The biomasses used in the processes comprised of tall fescue, corn stover, switchgrass, rye straw, bermudagrass and wheat straw [20,21,29–32].

The total pretreatment energies of these processes were obtained using similar assumptions as applied in the original model together with new assumptions e.g. the selection of specific heat capacity values for the various biomasses. These energy values were then plotted with their respective glucose and xylose yields as presented in Fig. 4a and b respectively. Out of the 80+ dilute acid pretreatment conditions modelled, roughly only 40 reported the glucose sugar yields directly after the pretreatment process. Nonetheless, the scatter of the glucose and xylose yield data points in relation to the pretreatment energy suggests that there is no direct link between the percentage of glucose and xylose sugars released and the

Table 4 − a: Conditions of the NREL pretreatment process used in the verification process. b: Range of pretreatment energies at varying water evaporation rates.

a)

Component	Units	Corn stover	Process water	Sulphuric acid	H.P Steam	H.P Steam
Total flow rate	kg h^{-1}	104,167	140,850	38,801	3490	24,534
Insoluble solids	%	67.7	0	0	0	0
Soluble solids	%	12.3	0	0	0	0
Temperature	°C	25	95	113	268	268
Pressure	kPa	101	476	618	1317	1317
Water mass flow rate	kg h^{-1}	20 833	140 850	36 767	3490	24 534

b)

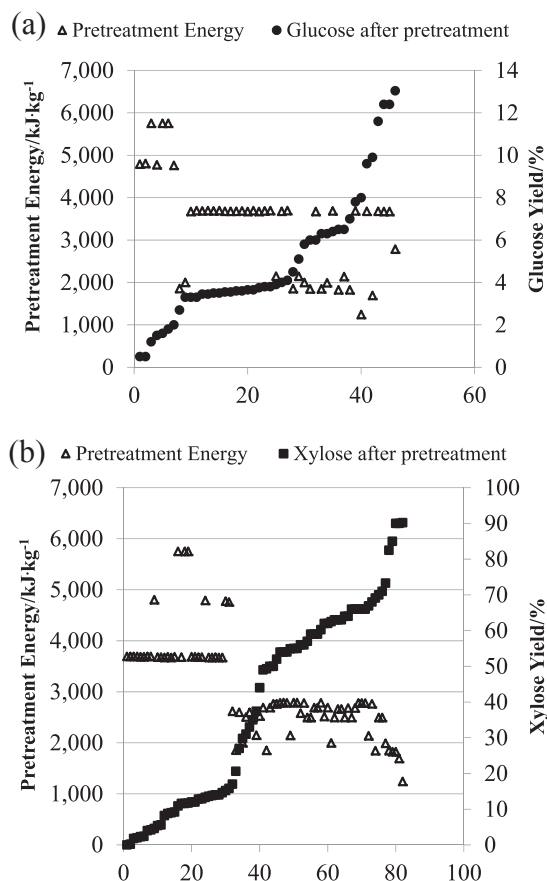|	Units	Water evaporation rate					
		0%	1%	2%	3%	4%	5%
Model pretreatment energy	kJ kg^{-1}	1434	1482	1531	1579	1628	1676
Dry corn stover mass flow rate	kg h^{-1}	83,334	83,334	83,334	83,334	83,334	83,334
Total pretreatment energy	GJ h^{-1}	120	124	128	132	136	140

Fig. 4 – a: Relationship between various dilute acid pretreatment energies and their glucose yields. b: Relationship between various dilute acid pretreatment energies and their xylose yields.

total pretreatment energy required for dilute acid pretreatment processes. Such plots can therefore be used to eliminate processes that are not economically viable. Nevertheless, the lack of correlation of the sugar yield and pretreatment energy could be attributed to a number of factors that were not taken into account such as; the type of biomass used and its state, that is, whether it was dried and/or milled, the way the sugars are structured in the biomass and how accessible they are. The lignin percentage in the raw material may also be a factor to consider in the pretreatment –glucose/xylose yield relationship.

8.   Conclusions

An energy estimation model was developed to evaluate the energy demand in dilute acid pretreatment processes. The majority of the energy required was found to be from the heating stage of biomass for the pretreatment reaction. In comparison the reaction energy and maintenance energy were insignificant. For the process reported by NREL, 1692 kJ kg^{-1} was required to pretreat the material. Solid loading rate was found to be a key factor in influencing the

energy requirements during pretreatment. Reducing the amount of process water increases the concentration of material in the process, which could potentially increase both the concentration of sugars liberated and reduce the energy required to heat the water to the reaction temperature. The heat recovery in the cooling steps could reduce the net energy requirement significantly. This model could be used as a decision-making tool for pretreatment selection, design and process optimization.

Authors' contributions

Oluwakemi Mafe carried out the modelling, and drafted the manuscript. John Hancock provided guidance on the calculations and direction of the research. Both John Hancock and Scott Davies proofread, edited and provided feedback on the manuscript. Chenyu Du is the academic responsible for funding and supervising the research in addition to proofreading the manuscript and providing feedback. All authors read and approved the final manuscript.

Acknowledgements

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.biombioe.2014.11.024.

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