The Application of Détente Instantanée Contrôlée (DIC) Technology to Minimize the Degradation Rate of Glucose

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Abstract. The most influential method for the production of glucose from biomass materials to-date was via the enzymatic processing system. However, the dilute acid processing system has recently gained popularity. In our present work, the DIC technology was employed to study the rate of glucose degradation into potential glucose degradation components such as 5-hydroxymethyl furfural, levulinic acid, acetic acid and formic acid. A model material of sago pith waste was used in this study during two types of thermal treatments to produce glucose. An extended hydrolysis process was done and monitored for the presence of the said glucose degradation products. The existence of levulinic acid, acetic acid and furfural was monitored as total indicator of glucose degradation chemicals. Result obtained from this study shows that the DIC heat exchange rate constant was 80 times higher than the conventional dilute acid hydrolysis process. In addition, the substrate cooling down to below 100 ℃ was achieved in less than a second. Maintaining the temperature of glucose at below 100 ℃ during the presence of dilute acid was found to contribute to a lesser amount of selected degradation indicators. Maximum glucose yield during single thermal treatment was 85% of the total polysaccharides available during treatment at 0.7 MPa for 5 minutes. Total degradation indicator for the treatment was found to be less than 0.8% of available polysaccharides as compared to about 10% with conventional thermal treatment.

Keywords: DIC technology, dilute acid hydrolysis, biomass, degradation, kinetics

1. Introduction

In principle, biomass containing cellulose, hemicelluloses and starch can be used to produce glucose with some modification of a certain initial process to ensure high quality of glucose obtained from process. Currently, the technologies that utilize cellulose as polysaccharides sources are progressing to be commercially significant including with enzymatic and chemical hydrolysis using thermal processing [1], [2].

Previously, it was shown that degradation of glucose was prevalent in the range beyond 160 ℃ [3]. Present work was concentrated to the dilute acid hydrolysis (DAH) technology and was designed to study the interim thermal processing gap with materials containing polysaccharides (cellulose, traces of hemicelluloses, and starch) to convert them into glucose. Based on this, the work will focus on the area of a specific feedstock (sago pith waste, SPW), with thermal pre-treatment at various operating conditions to study the characteristic of material and its degradation products.

The integration of Instant Controlled Pressure Drop (French: Détente Instantanée Contrôlée (DIC)) technology as pre-treatment process was done to capitalize unique DIC process with fast heating (due to saturated steam) and exceptionally fast cooling (due to a pressure drop towards vacuum). Combinations of both steps were used for hydrolysis of starch to glucose and for fast stopping the degradation of glucose from occurs.

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The objective of this work was to obtain important information of glucose degradation during dilute acid hydrolysis on DIC treated materials. This was an important step to understand the factors that affected glucose degradation and to develop suitable mechanism to avoid glucose degradation.

2. Experimental

2.1. Pre-Treatment with DIC System

DIC system was covered in details in several articles [4], [5]. Basically, DIC treatment involved with treatment of sample in an enclosed reactor with steam, followed by subjecting the reactor to vacuum condition which will immediately decrease the reactor body temperature towards below than 100 ℃. Fig. 1(i) shows the DIC schematic diagram and Fig. 1(ii) shows the treatment stages during processing. For the DIC pre-treatment, material was adjusted with water and acid prior to treatment according to condition in Table 1 and placed in a wire mesh container.

DIC treatment was done in reactor chamber by injecting saturated steam, maintaining for certain treatment time, followed by releasing the steam through instant relieve valve. Treated materials were collected and content of glucose and its degradation products was measured by injecting into a chromatography system.
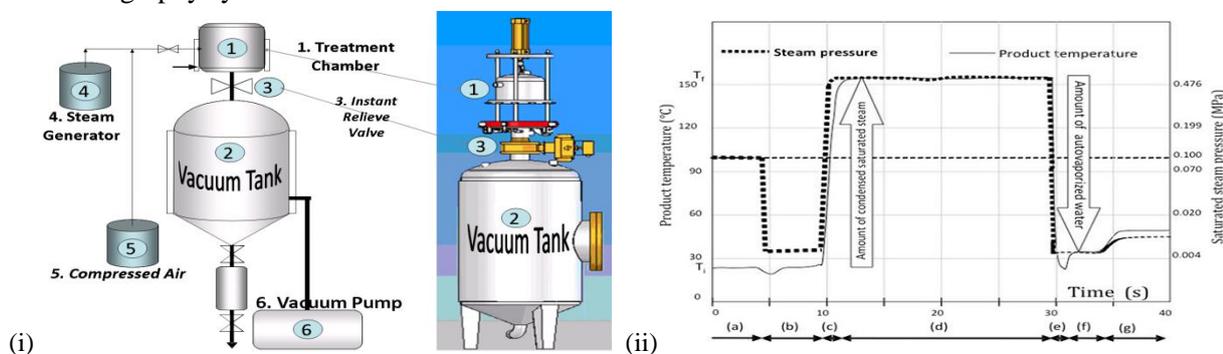

Fig. 1: (i) Schematic diagram of DIC equipment. (ii) Stages of DIC treatment including (a) DIC at atmospheric condition (b) setting-up an initial vacuum (c) injection of high pressure steam, (d) maintain steam pressure (e) an instant pressure drop towards vacuum, and (g) for putting back DIC system to atmospheric pressure condition. The present figure shows VSV combination of DIC process [5].

Table 1: DIC pretreatment conditions

Material loading	10 g
Moisture content	50% (on dry basis)
Steam pressure	0.7 MPa
Acid conc.	0.01 M
Vacuum	100 mbar
Holding time	5.0 min

2.2. Material and Method

Material that was used in this work was obtained as a waste material (sago pith waste, SPW) from a sago processing plant in Johor, Malaysia. Material was dried and sieved to obtain particles of 100 to 300 micron size. Prior analysis of SPW materials shows that starch was the dominant component (85%), total polysaccharides (consist of cellulose, hemicellulose and starch) was 95%, and the remaining 5% as a lignin.

Kinetic study was done for both DIC treated and non-DIC treated material to compare the effect of DIC pre-treatment against the non-treated material. Dilute acid hydrolysis was done using batch stainless steel reactor with volume of 20 ml. Material was subjected to hydrolysis in the reactor with specific processing parameters as in Table 2 for the respective DIC pre-treatment and dilute acid hydrolysis (DAH).

Investigation of the effect of vacuum towards polysaccharide conversion into glucose and its degradation products were studied using stage combination of DIC treatment cycles. There are four DIC treatment

combinations were possible including; (i) Vacuum-Steam-Vacuum (V-S-V) (ii) No Vacuum-Steam-Vacuum (NV-S-V) (iii) Vacuum-Steam-No Vacuum (V-S-NV), and (iv) No Vacuum-Steam-No Vacuum (NV-S-NV).

Handheld data logger [Omega HH147U] was used to obtain temperature profile of system to calculate the heating rate constant (h) of each system.

Table 2: Dilute Acid Hydrolysis (DAH) conditions

Material	DIC-SPW & SPW
Reactor loading	0.5 g/ 10 mL
Temperature	130 & 150°C
Acid concentration	0.01, 0.04 & 0.08 M
Hydrolysis	5, 15, 30, 90, 120 & 240 min

Determination of glucose and its degradation products as an output of the hydrolysis process was done using chromatography system (Agilent 1100 HPLC) with refractive index detector for glucose and UV-Vis detector for other component. Separation was done using ICE-COREGEL 87H3 (Transgenomic) column at 35°C that separate glucose and certain organic acid in solution. Mobile phase was a dilute sulphuric acid (5 mM) in deionised water at a flow rate of 0.5 ml/min. 10 μl sample and standards of different concentration are injected into system.

Kinetic model based on consecutive first order kinetic was used to study the starch hydrolysis and glucose degradation. Details of model were discussed elsewhere [6], [7]. Presently, biomass hydrolysis research has progressed to the point where the hydrolysis process and optimization only require generalized kinetic correlation, mechanism of glucose generation and glucose degradation only [3], [8]. Kinetic equation, $[A]_t = [A]_0 e^{-kt}$ was used to describe the kinetic operation. Data obtained from experiment was used to solve the equation to obtain the process rate constant, k_1 for SPW hydrolysis and k_2 for glucose degradation. Rate constant for process was obtained through fitting of data with calculated data and k with the lowest sum of $([A]_{act} - [A]_{cal})^2$ is obtained (using solver in Excel).

3. Result and Discussion

3.1. Effect of Vacuum on Glucose Degradation

The autohydrolysis of starch to glucose in DIC reactor or in DAH will start with a partial degradation of the starch polymeric chain from a longer chain into much shorter chain, and this process can never be reversed [9]. Extended exposure of glucose to acid and heat however will result to its degradation into 5-hydroxymethyl furfural, levulinic acid, acetic acid and formic acid [6].

Results for direct conversion of polysaccharides into glucose were presented in Fig. 2 and Fig. 3. DIC pre-treatment (V-S-V combination) on material with moisture content of 200% was found to give highest amount of glucose (300 mg glucose/ g SPW). In general, Fig. 3 shows that glucose yield from SPW material with moisture content less than 100% was less than 100 mg/g. It was observed that there was some drastic changes in glucose yield once the initial moisture content ≥150% for all four treatment combinations.

Statistical test indicates that moisture content gave very significant effects on the autohydrolysis of polysaccharides into glucose during DIC pre-treatment. This phenomenon suggest that as soon as dry steam enters the DIC chamber, the available moisture on the surface of materials will be heated and immediately, the proton [H+] on the surface will become reactive for hydrolysis reaction. High moisture content materials were found to enhance the conversion of polysaccharides (starch) to glucose, due to the ability for water movement due to fluidity on the surface as well as in the internal porous structure of SPW.

Low moisture level, however, does not allow the proton [H+] movement to other polysaccharide's reaction site to initiate other hydrolysis actions. The withholding of [H+] at the same point increase the potential degradation of glucose that present at that location. In comparison, movement of [H+] due to fluidity at high moisture level that enables new site for [H+] reaction to start and contribute to a higher glucose yield.
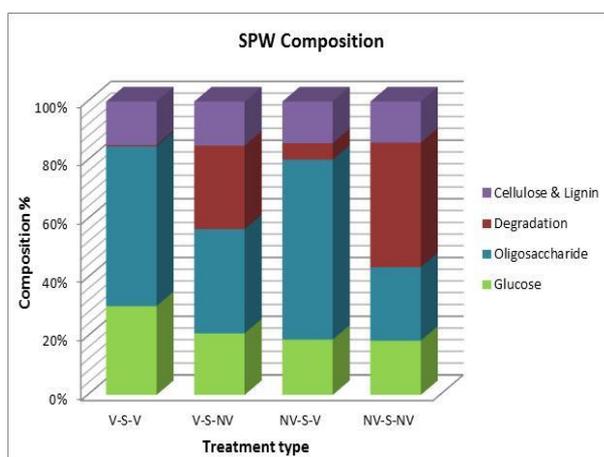
Fig. 2: Compositional analysis of SPW that was treated with different DIC combinations at 200% moisture level.

When the moisture content was increased from 100% to 150%, it was enhance the movement of a shorter chain starch thus further increase the rate of the partial degradation of starch and other polysaccharide's low molecular weight oligomers such as glucose and xylose.

In a similar manner, the rate for the degradation of glucose due to an extended exposure to high temperature was unavoidable for treatment without second vacuum cycle. This has decreased the yield of overall glucose for two treatments without vacuum as observed in Fig. 2. For the V-S-V treatment, the total amount of glucose and oligosaccharides was 850 mg/ g SPW, total degradation products was <5 mg/ g and lignin and cellulose were 148 mg/ g SPW. Combination of glucose, oligosaccharides and total degradation product was almost similar to the amount of starch in original SPW material. This shows that almost all starch components in SPW has been converted into lower chain starch polymer including glucose and oligosaccharides with DIC treatment.
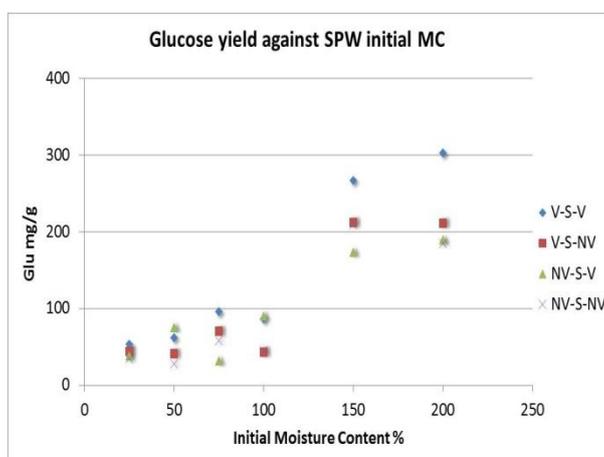

Fig. 3: Plot for glucose concentration (mg/g) against moisture content for all four stages combination. Treatment time and acid concentration were 4 minutes and 0.08 molar.

Fixed saturated steam pressure, 0.6 MPa (159 ℃) was used in this study. Treatment time of four minutes was decided based on minimum time for emptying and filling of the present vacuum tank to 100 mbar vacuum pressure.

The existence of oligosaccharides in DIC treated materials was due to incomplete hydrolysis of starch and non-starch polysaccharide into glucose. This observation suggests another potential utilization of DIC system, i.e. for a rapid liquefaction of starch or other non-starch polysaccharides components at high solid loading into short-chain oligosaccharides. The partially hydrolyzed starch can be used further for enzymatic saccharification to glucose syrup of varying level of dextrose equivalent [9].

Further determination for specific glucose degradation products show that traces of levulinic acid and acetic acid was detected for V-S-V and NV-S-V combinations. On the other hand, for combination without

vacuum at the second stage of DIC, (i.e V-S-NV and NV-S-NV), content of levulinic acid was 20 mg/ g SPW and acetic acid was 15 mg/ g SPW for both combinations. This would offer good explanation for lowering of temperature in an instant to below 100 ℃ is effective for controlling the degradation of glucose further during autohydrolysis process.

3.2. Kinetic Study

For the DAH kinetic study of the DIC treated materials, the following results in Fig. 4. (i) and Fig. 4 (ii) are presented and further summarized in Table 3 and Table 4. The two stages DIC pre-treatment on SPW followed by dilute acid hydrolysis shows the maximum glucose obtained from the DIC and raw SPW was 820 mg/g SPW and 508 mg/g SPW respectively.

Table 3: Data for kinetic using DIC as pretreatment

Rate constant, k_1	0.4569
Rate constant, k_2	0.0100
Glucose Max (Glu$_{max}$)	820 mg/g at 7 min
Total degradation at (Glu$_{max}$)	85 mg/g

Table 4: Data for kinetic without pretreatment

Rate constant, k_1	0.0426
Rate constant, k_2	0.0138
Glucose Max (Glu$_{max}$)	508 mg/g at 30 min
Total degradation at (Glu$_{max}$)	140 mg/g

Degradation was very high for raw SPW sample without pre-treatment. The glucose maximum point was shifted towards a longer hydrolysis time, resulted to a high degradation of glucose.

DIC treatment was found to contribute to the maximum amount of glucose and a short treatment time during dilute acid hydrolysis stage. The conversion of starch into oligosaccharides during DIC treatment has shorten the treatment time to about 7 minutes to obtain maximum glucose compared to 30 minutes for untreated materials with only 61% conversion of total glucose together with nearly 28% of glucose that was obtained during process degraded into levulinic acid, acetic acid and formic acid. Prolong dilute acid hydrolysis process is not possible; due to it will degrade further glucose for both process.

Heat exchange constant for both process (h_{DIC}) and dilute acid hydrolysis (h_{DAH}) was calculated and summarized in Table 5. Value of rate constant for heating was useful to describe the non-isothermal regime during start-up of the dilute acid hydrolysis kinetic. About 5 minutes was required to raise the product temperature towards oil bath temperature, while only about 5 seconds was required in DIC treatment. Calculated relative rate constant for heating for DIC and dilute acid hydrolysis as in Table 5 was about 45 to 80 times higher in DIC system depending on final temperature of the system.
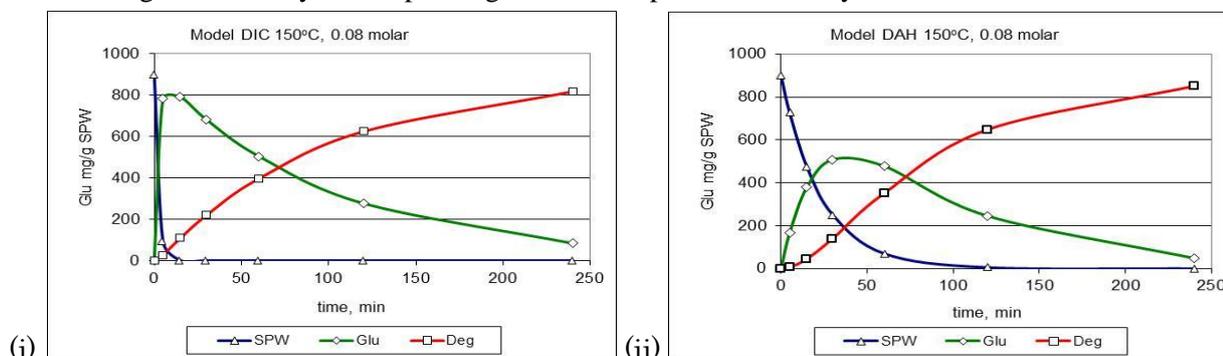

(i)   (ii)

Fig. 4: Graph (i) and (ii) above compare the effect of utilization of DIC as pretreatment against only non-treated SPW during dilute acid hydrolysis to obtain glucose.

This information offers an insight into the difference in heat transfer of both systems, and it can be associated with the requirement of rate constant k_1 and k_2 (in which $k_1 >> k_2$ was required for an optimum hydrolysis of polysaccharides into glucose). Fast hydrolysis kinetic operation during conversion of polysaccharides into glucose with minimum glucose degradation was required in this study.

Table 5: Value of h, relative rate constant for heating at 150 ℃ for both systems

DAH system, h, min^{-1}	0.565
DIC system, h, min^{-1}	45.030
Relative rate of heating: h_{DIC}/h_{DAH}	79.7

4. Conclusion

This work has successfully associated the degradation of glucose and effect of vacuum during dilute acid hydrolysis process. DIC treatment was successfully converting almost 100% of starch into oligosaccharides and glucose. High rate for conversion of polysaccharides into glucose in combination with fast cooling of the system to below 100 ℃ were required to minimize the degradation of glucose into its potential degradation products such as levulinic acid, formic acid, acetic acid and furfural.

5. Acknowledgment

6. References

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