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Reaction of D-glucose in water at high temperatures (410 °C) and pressures (180 MPa) for the production of dyes and nano-particles

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ABSTRACT

An autoclave (120-mL) and an optical micro-reactor (50-nL) were used to study the hydrothermal decomposition of D-glucose at high temperatures and high pressures. During slow heating (0.18 °C/s) to 350 °C in the autoclave, water-soluble glucose (0.9 M) began to decompose at 220 °C and reacted completely at 280 °C. The initial decomposition products were 5-(hydroxymethyl)furfural and levoglucosan, and these subsequently converted into oil and solid residue, and finally to solid particles at a 65 wt% yield at 350 °C. When the same heating rate and temperature were used on glucose solutions in the micro-reactor, yellow and orange materials decomposed from glucose were produced. Numerous particles precipitated at 251 °C, and at 350 °C, all the glucose changed to an orange film and solid particles, which were nanoparticles as confirmed by SEM. However, when the glucose solution was rapidly heated to 410 °C (9.5–17 °C/s), yellow, brown and orange sugar-like materials were produced. A homogeneous phase with yellow color still remained at temperatures as high as 380 °C, and few particles formed until 410 °C. It can be concluded that micron-sized particles and colored solutions can be produced by slow heating, while rapid heating resulted in the formation of dye-like substances with glucose-like structures. The formation of colored solutions and particles may have technological implications in food or materials formation processes that use high temperature water with biomass feedstocks.

1. Introduction

There are many possible applications for using hydrothermal or high temperature water (HTW) as a solvent in thermal and chemical conversion processes [1,2]. HTW behaves as a weakly polar solvent with both acidic and basic characters [3,4] and since its physicochemical properties can be widely varied with relatively small changes in temperature, HTW can replace many organic solvents. The properties of HTW and water in its supercritical state have been exploited for destruction of toxic organic wastes [5–7], synthesis of nanoparticles [8], production of organic chemicals [9,10], solubilization of biomass [11,12], hydrolysis of biomass-related compounds [12–14], gasification of wood and biomass [15–19] and biomass liquefaction [17,18].

Glucose, which is a monosaccharide unit in many biopolymers, has been studied extensively in HTW for biofuels and chemicals [16,17,19–38]. Glucose can be converted to biofuels and a 100% gasification rate has been demonstrated with activated carbon or KOH catalyst [23,24] or without catalyst at high temperatures (700 °C) [32], but its liquefaction rate is generally low (ca. 21%) with formic acid and cobalt catalyst at 300 °C [33]. Conversion rates of glucose to glycolaldehyde and erythrose are almost 50 wt% by non-catalytic hydrothermal methods at 400 °C and 30 MPa [31,34].

Glucose can be reacted in water to obtain yields of 5-(hydroxymethyl)furfural (5-HMF) as high as 27% at 180 °C in 3 min reaction time [39], and when glucose is reacted in ionic liquid solvents with $CrCl_2$, 5-HMF yields of 70% can be obtained at 100 °C in 3 h [40]. Kabyemela et al. [35,36] give detailed reaction pathways, mechanisms and kinetics of glucose reactions in HTW and supercritical water. The decomposition pathways are proposed as [18,35–38,41,42]: glucose isomerizes to fructose, or decomposes to erythrose, glycolaldehyde, dihydroxyacetone, glyceraldehyde, levoglucosan and pyruvaldehyde. The fructose formed decomposes to glyceraldehyde, dihydroxyacetone and erythrose. Then, the glyceraldehyde and dihydroxyacetone dehydrate to pyruvaldehyde, and pyruvaldehyde, erythrose and levoglucosan decompose to acids, aldehydes and alcohols of 1–3 carbons. Part of glucose degrades to

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furfurals and 5-HMF, that condense to phenols and dehydrate to acids (e.g., levulinic and formic acids). As reaction time increases, all of these compounds are highly reactive and readily polymerize to form water insoluble humic acids that are commonly called humins. Hydrothermal conversion of glucose to biofuels, chemicals and materials has been well studied.

Glucose has been used to study the formation of other chemical products that have technological interest. Non-catalytic reaction of glucose in water has been studied to produce colored compounds at 130 °C for 18 h reaction time [43], and nanoparticles at 170–180 °C and 0.7–0.8 MPa for 2 h reaction time [44]. However, few studies have examined the possible types of solids formed under hydrothermal conditions. For example, it is not known for what conditions solids are formed and what type of properties they could have. Information on the conditions for homogeneous reaction and solid formation could provide a method for controlling glucose reaction products or possibly making new types of materials. In this work, non-catalytic decomposition of glucose was studied at temperatures up to 410 °C with the objective to produce fine particles and dye-like materials. Two types of reactors were used: (i) an autoclave (120 mL) for the study of decomposition at long reaction times and slow heating rates, and (ii) a 50-nL optical micro-reactor, hydrothermal diamond anvil cell for visual observation of the phase and color changes during the decomposition process.

2. Materials and methods

2.1. Materials

Glucose particles (>99.0% purity) used was from Fluka (BioChemika). HPLC standard distilled water (Aldrich) had a maximum conductivity of 5.5 S m^{-1}. Aqueous solutions of 0.9-M glucose were made for the experiments.

2.2. Autoclave experiments

Aqueous glucose solutions (0.9-M, 30 mL) were reacted in a 120-mL autoclave (18-mL dead space). An initial 3-MPa N_2 pressure was applied to the headspace to minimize water vaporization. After being sealed, the autoclave was heated to 200–350 °C (4.3–16.5 MPa) at a heating rate of 0.18 °C/s and stirred by a magnetic stirrer. After reaching the desired maximum temperature and holding time (0, 30 min, 1 h), the autoclave was cooled by turning off the electrical power. The gas volume was measured using a gas meter (Shinagawa corporation, W-NK-0.5B), and its composition was analyzed by gas chromatography (GC; Shimadzu, GC-12A with a TCD detector or GC-9A with an FID detector). The reaction mixture was separated into three phases: (i) aqueous phase, (ii) oil phase (acetone-soluble), and (iii) water-insoluble fraction (residue). The aqueous phase was analyzed for total organic carbon (TOC) with a Yanaco TOC-8L analyzer and for glucose with a Shimadzu UV-160A absorption spectrometer. After freeze-drying, sugars in the aqueous phase as trimethylsilyl derivatives were analyzed with a GC (Hewlett-Packard, 5890A; CBP-10 column). Organic elements (C, H) of the oil and residue were analyzed by an elemental analyzer (AMCO NA-1500). Details of the experimental procedures have been described in a previous work [45].

2.3. Diamond anvil cell experiments

An optical micro-reactor, Bassett-type [46] hydrothermal diamond anvil cell (DAC) was used for visual observations of aqueous glucose solution during heating process. The reaction chamber, which consisted of a hole drilled in an Inconel gasket (50 nL; 500-μm i.d. and 250-μm thickness) loaded with glucose solution was sealed by compression with two opposing diamond anvils, and heated by two electric micro-heaters and observed under 110× magnification with a stereomicroscope (Olympus SZ11). The images were recorded with a Panasonic 3-CCD camera (AW-E300). Inconel gaskets were used in the experiments because of their relatively inert properties and long term stability to corrosion under supercritical water conditions [7]. Negligible leachability of metals would be expected to occur under the solution conditions for the given reaction time periods in this work. Temperature of the system was measured and recorded by a data acquisition unit (Strawberry Tree, Model DS-12-8-TC, Sunnyvale, CA). Water density (ρ = water mass/chamber volume, kg/m^3) was adjusted by changing the size of argon gas bubbles introduced into the chamber [7,47]. The technique involves gently opening and releasing hand pressure on the DAC while it is in an argon atmosphere at ambient conditions. The density was calculated from the homogenization temperature (T_h) at which gas bubbles disappeared when heated. After reaching the desired maximum temperature (262–410 °C), the chamber was rapidly cooled to room temperature. The residues deposited on the lower and upper diamond anvils were analyzed by FT-IR microscopy (UMA 500, Bio-Rad, Cambridge, MA) and their micrographs were determined by scanning electron microscopy (SEM; JEOL 840A, Tokyo). Details on the DAC techniques, applications and future prospects for studying supercritical water systems can be seen in a previously published review [47].

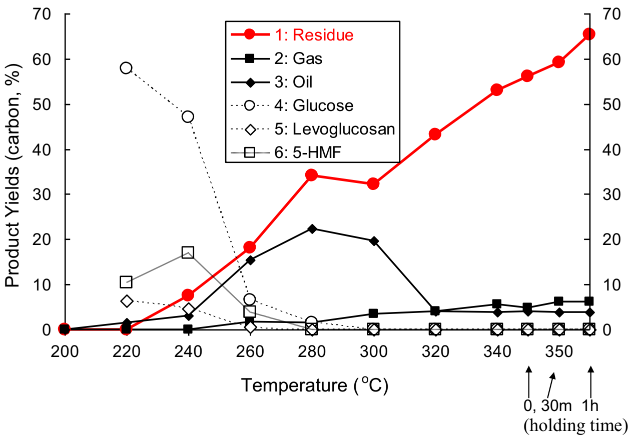


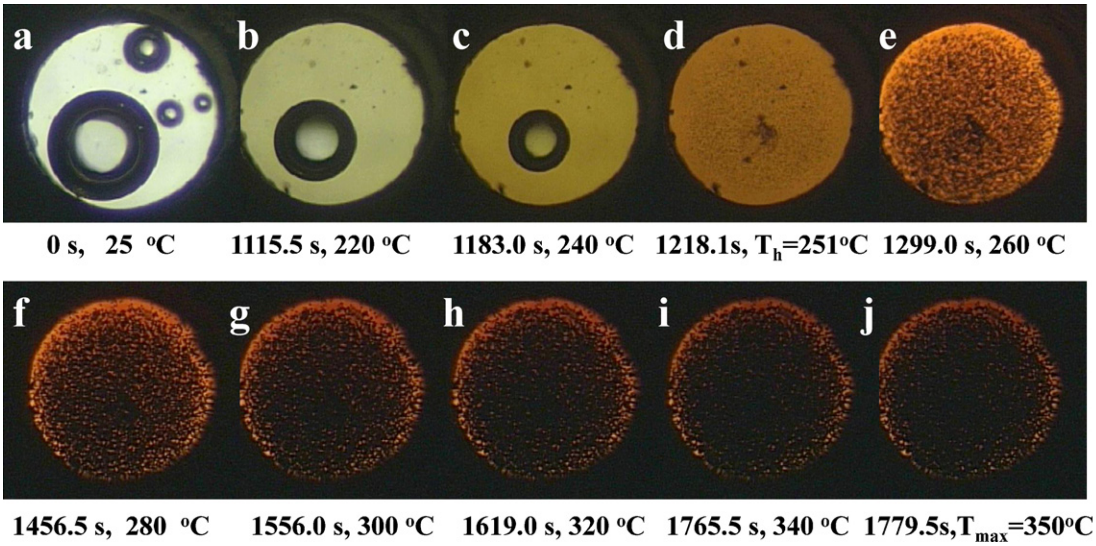
Fig. 1. Product yields (carbon %) *vs.* temperature for decomposition of glucose in water at saturation conditions. Initial glucose concentration was 0.9 M.

2.4. Arrangement of batch and DAC experiments

One group of experiments was performed in the autoclave at temperature, pressure conditions ranging from (200 °C, 4.3 MPa) to (350 °C, 16.5 MPa). Two types of phase behavior experiments in the DAC were conducted at: (i) slow heating rates (ca. 0.18 °C/s) at temperatures up to 350 °C, and (ii) rapid heating rates (ca. 9.5–17.0 °C/s) at temperatures up to 410 °C. Slow heating (0.18 °C/s) in both autoclave and DAC, many rapid heating (4.6–17.0 °C/s) DAC experiments were conducted, and the results are summarized below.

3. Results and discussion

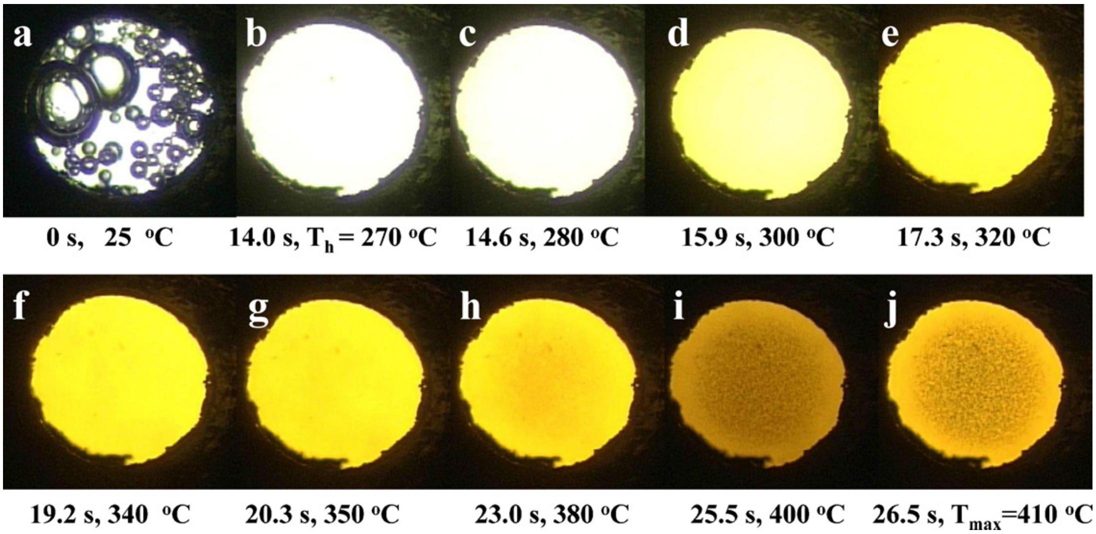
Autoclave experimental results are given in Fig. 1, and DAC results are presented in Figs. 2–6. Fig. 1 gives product yields (%) based on carbon for the three phase products (gas, oil and residue) and aqueous product (glucose, 5-HMF and levoglucosan) from the glucose decomposition. Visual observations of the reactive phase behavior of glucose are given in Fig. 2 (for slow heating) and Fig. 3 (rapid heating). SEM image of a residue is given in Fig. 4. FT-IR spectra of the residues are given in Figs. 5 and 6.



0 s, 25 °C 1115.5 s, 220 °C 1183.0 s, 240 °C 1218.1s, T_h=251°C 1299.0 s, 260 °C

1456.5 s, 280 °C 1556.0 s, 300 °C 1619.0 s, 320 °C 1765.5 s, 340 °C 1779.5s,T_{max}=350°C

Fig. 2. Visual observation of {glucose + water} mixtures during slow heating up to 350 °C and 136 MPa (heating rate = 0.18 °C/s; water density = 796 kg/m^3).



0 s, 25 °C 14.0 s, T_h = 270 °C 14.6 s, 280 °C 15.9 s, 300 °C 17.3 s, 320 °C

19.2 s, 340 °C 20.3 s, 350 °C 23.0 s, 380 °C 25.5 s, 400 °C 26.5 s, T_{max}=410 °C

Fig. 3. Visual observation of {glucose + water} mixtures during rapid heating up to 410 °C and 181 MPa (heating rate = 14.3 °C/s; water density = 768 kg/m^3).

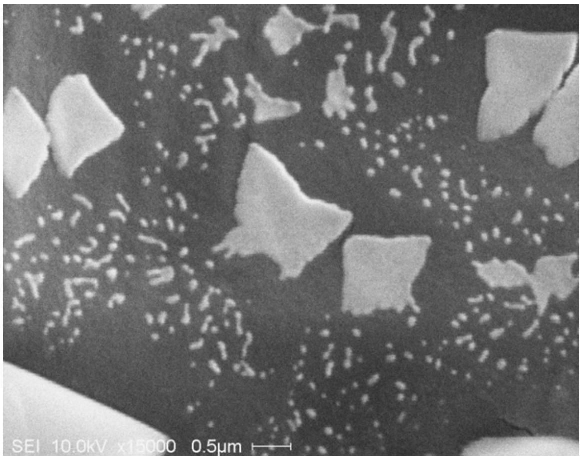


Fig. 4. SEM image for the residue cooled from slow heating (0.18 °C/s) glucose solution to 350 °C.

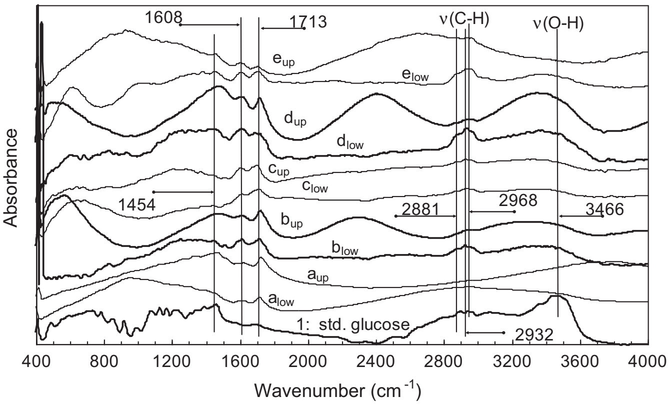


Fig. 5. IR spectra for residues a–e cooled from slow heating (0.18 °C/s) glucose solution up to 350 °C and 30 min holding time (curves denote, a–e: measurements after cooling from 262, 300, 313, 350 °C and {350 °C + 30 min}) (subscripts; low: lower anvil; up: upper anvil).

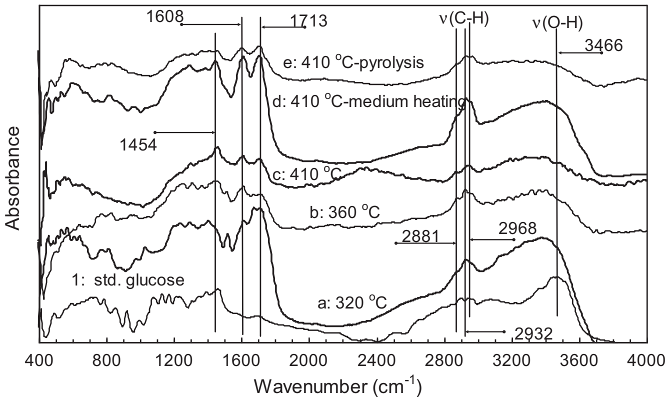


Fig. 6. IR spectra for residues a–e on lower anvils cooled from rapid heating (9.5–17.0 °C/s) glucose solution up to 410 °C (curves denote, a–c: measurements after cooling from 320, 360 and 410 °C; d: medium heating at 4.6 °C/s to 410 °C; e: pyrolysis by rapid heating to 410 °C).

Fig. 7 gives UV/vis absorbance spectra of initial glucose and decomposed glucose solutions. Fig. 8 shows reaction paths for the production of particles, gas and oil. The details of the experiments are discussed in the sections below.

3.1. *Autoclave experiments*

Non-catalytic decomposition of glucose was studied with the autoclave by slow heating (heating rate of 0.18 °C/s) from room temperature to the maximum temperature (200–350 °C, up to 30-min heating time). Glucose started decomposing sharply at 220 °C and completely disappeared at 280 °C (Fig. 1, curve 4). The initial decomposition products were 5-HMF and levoglucosan that subsequently disappeared at 280 °C (Fig. 1, curves 5–6). A solid residue (Fig. 1, curve 1) appeared at 240 °C, and its yield gradually climbed to a value of 65% at 350 °C and 1 h reaction time. Oil yield (Fig. 1, curve 3) exhibited a maximum and increased smoothly up to 22% at 280 °C and then it decreased to 4% at 320 °C and remained at this value over the temperatures studied. Gas started to appear at 260 °C and gradually reached 6% at 350 °C and 1 h. From these results, a simplified reaction pathway to residue particles or char must occur as:

$$\text{glucose} \rightarrow \text{water solubles (5-HMF, levoglucosan)} \rightarrow \text{oil} + \text{residue} \qquad (1)$$

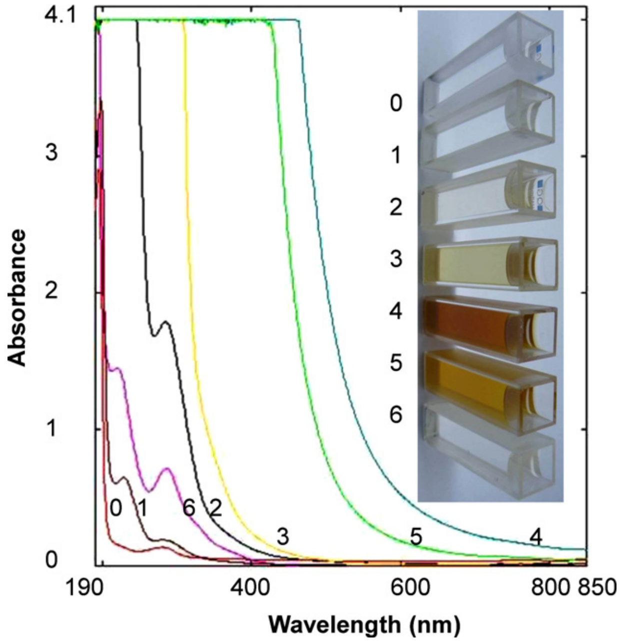


Fig. 7. UV/vis absorbance spectra when glucose solution was heated to 350 °C at 0.2 °C/s (lines denote, 1–5: measurements after cooling from 250, 320, 350 °C, {350 °C + 5 min} and {350 °C + 10 min}; 0: standard initial glucose solution; 6: aqueous solution of caramelized glucose by heating solid glucose to 160 °C for 15 min).

$$\text{oil} \rightarrow \text{residue} \rightarrow \text{char} \qquad (2)$$

where reactions (1) and (2) occur in parallel.

3.2. *Diamond anvil cell experiments*

In the DAC experiments, aqueous glucose solutions were reacted at much higher pressures (ca. 180 MPa) than for the autoclave experiments. High pressures can promote [41,42] or suppress reactions so some discussion of the effects is appropriate. Aida et al. [41] studied hydrothermal reaction of glucose at high temperature and found that increasing pressure from 40 to 80 MPa enhanced the dehydration reactions to 5-HMF, and also enhanced hydrolysis of 5-HMF leading to the production of 1,2,4-benzenetriol. On the other hand, for the cases where gases are formed, it is possible that high pressures can suppress gasification rates due to Le Chatelier's principle. Due to the tiny product amounts in the DAC,

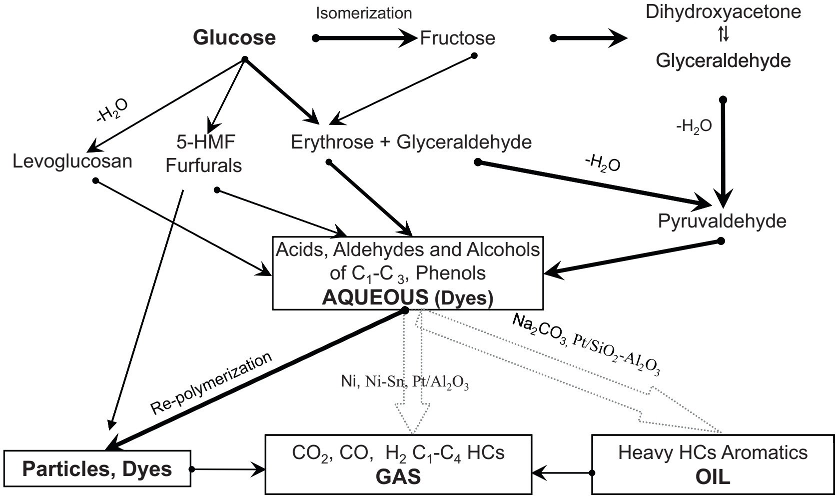


Fig. 8. Reaction paths for the production of particles, gas and oil from decomposition of glucose under hydrothermal conditions.

only micro-spectroscopic (e.g., IR or Raman microscopy) analyses of product residues can be conducted and these are limited to qualitative measurements, since the O–H and C–H vibrations can be assigned to many types of compounds (e.g., alcohols, sugars and hydrocarbons). Analyses of the gases formed are not possible with our setup although specialized techniques do exist in the literature [48]. The IR spectra presented give qualitative changes of the decomposed glucose products as compared with the standard glucose spectrum.

3.2.1. Slow heating experiments

The same heating rate as that used for the autoclave (0.18 °C/s) was used in the DAC experiments observed with transmitted optical light. In Fig. 2, aqueous glucose with gas bubbles was slowly heated to 350 °C and 136 MPa. At 220 °C, the solution color changed to light yellow (Fig. 2b), indicating glucose conversion to 5-HMF and levoglucosan (Fig. 1, curves 4–6) that were immediately polymerized to colored solutions via caramelization. Gas bubbles disappeared and the solution changed to an orange color along with the precipitation of numerous particles at 251 °C (Fig. 2d). The orange color became more brilliant as further particles precipitated (Fig. 2e). At 280 °C (Fig. 2f), the entire chamber was practically filled with black particles that seemed to become slightly denser as temperature increased further to 350 °C (Fig. 2f–j). After reaction, an orange film was formed on the upper diamond anvil, and particle residue remained on the lower anvil (supplementary material Fig. S1). IR analyses of the upper (Fig. 5d_{up}) and lower (Fig. 5d_{low}) anvils were made. The lower anvil (Fig. 5d_{low}) results showed that the particle residue decomposed but still had a glucose-like character as can be seen that it remained three broad characteristic peaks at around 2932 cm^{-1} and had an additional peak at 1608 cm^{-1}, as compared with the standard glucose spectrum. The oil-film (Fig. 5d_{up}) had little glucose-like character since no peaks were present at around 2932 cm^{-1}. The solid residue was analyzed by SEM which showed that sub-micron size particles were formed (Fig. 4, 100 nm). Images of the residues obtained from 262 to 350 °C showed that yellow or orange oil-like films were formed in 1320–1800 s reaction time on the upper anvil, while solid particles precipitated on the lower anvil at temperatures above 262 °C. IR spectra revealed that all the precipitated particles were glucose-like with a similar chemical structure as that of the residue d_{low} (Fig. 5).

3.2.2. Rapid heating experiments

Aqueous glucose solutions were subjected to rapid heating was studied (ca. 9.5–17.0 °C/s) to 410 °C and observed with microscopy. In Fig. 3, aqueous glucose was heated to 410 °C and 181 MPa (heating rate, 14.3 °C/s; water density, 768 kg/m^3). Little changes in the solution appearance occurred at temperatures up to 280 °C (Fig. 3c) besides the disappearance of the gas bubbles due to the expansion of the liquid water phase. The solution color changed from clear to light yellow at 300 °C and then to dark yellow which deepened in color at 320 °C (Fig. 3d–e). There was little change in the deep yellow color until 400 °C, at which numerous particles precipitated along with the appearance of an orange color (Fig. 3e–i). After the chamber was cooled from its maximum temperature of 410 °C (Fig. 3j), yellow sugar-like residues were found on the lower diamond anvil (supplementary material Fig. S2). IR results showed that the residues had more glucose-like character than the particle residues that were formed during slow heating experiments even at the lower temperatures (350 °C) as shown by the remaining peak at 1454 cm^{-1} (Fig. 6c *vs.* Fig. 5d_{low} and 1). Colorful sugar-like residues and black particles were obtained on the lower anvil that were formed by rapid heating (9.5–17 °C/s) to 320–410 °C in 17–44 s and medium heating (4.6 °C/s) to 410 °C in 820 s reaction time. As temperature increased to 410 °C, the residue color changed from red at 320 °C, to brown at 360 °C and then to yellow at 410 °C, whereas the medium heating rate to 410 °C gave black particles and a black film by pyrolysis (supplementary material Fig. S2). All the residues had similar chemical structures as glucose (Fig. 6). It is possible that the colorful sugar-like residues that formed below 410 °C could be used as food colorants due to their appearance and stability relative to the other residues.

When aqueous glucose solutions are heated at slow heating rates, solid particles form at very low temperatures which then undergo heterogeneous decomposition to aromatic char [18]. However, when the solutions remained as a homogenous phase for the case of rapid heating rates up to 380 °C as studied in this work, little char was formed. This phenomenon was observed by Modell and co-workers in the 1970s, who found that at supercritical water conditions, little char and tar were found and the glucose solutions became gasified [49–51]. In the work of Chuntanapum and Matsumura for the decomposition of 5-HMF (0.15 M for 3000 s), no char particles were detectable under supercritical conditions, but particles could be observed under subcritical conditions [52].

The color change of glucose solution during heating to high temperature is similar to the well-known caramelization that is one of the more important types of browning processes in food science. However, the initial caramelization of glucose starts at much lower temperatures of 160 °C, after condensation, isomerization, dehydration and fragmentation reactions (flavor production) occur, and colors are produced by polymerization to various high molecular weight components (e.g., caramelans: $C_{24}H_{36}O_{18}$; caramelens: $C_{36}H_{50}O_{25}$; caramelins: $C_{125}H_{188}O_{80}$) [53,54]. We measured UV/vis absorbance spectra (Shimadzu, UV-1800) of the decomposed glucose solutions after they were cooled from different temperatures (up to 350 °C and holding for 10 min) (Fig. 7). It was found that the wavelength shifted to higher values when reaction temperature increased to 350 °C and was held for 5 min at those conditions (Fig. 7, lines 0–4), but shifted to lower wavelengths and the solution color became lighter at 350 °C as the holding time increased to 10 min (Fig. 7, line 5 *vs.* 4). The possible reason for this phenomenon is that colored solutions further polymerized and then precipitated as char particles such that concentrations would be reduced for long reaction times or higher temperatures. Chuntanapum and Matsumura [52,55] found that glucose produces char particles 2 orders of magnitude faster than 5-HMF feedstock. The interaction of 5-HMF with the other glucose decomposition products seems to play an important role in the production of char. They proposed simplified formation pathways of char particles: char was formed from the decomposed products of furfural, 5-HMF and other water soluble products [55].

Based on the above discussions and our previous work [18], reaction paths are proposed for the production of dyes, particles, gas and oil (Fig. 8): colorful dye-like substances are produced via caramelization upon both slow and rapid-heating; char particles are produced by non-catalytic decomposition of glucose to aqueous products (including furfurals, 5-HMF, levoglucosan and colored materials), and subsequent re-polymerization during slow heating up to 350 °C or rapid heating to higher temperatures. The particles are submicron or nano-sized biochar with aromatic structures [18], and these are difficult to convert further to gas and oil at low temperatures (<400 °C). A high heating rate can be used to produce dyes and to avoid further polymerization of products to char particles. For the case of heating the aqueous glucose solution with catalysts to high temperatures, gas (with Ni, Ni–Sn, Pt/Al_2O_3) [18,56,57], oil (with Na_2CO_3) [18], liquid alkanes (with $Pt/SiO_2–Al_2O_3$) [58] and chemicals (with $Pt/\gamma\text{-}Al_2O_3$) [59] can be produced under homogeneous conditions.

From the above experimental results, it can be seen that dyes or particles can be produced by non-catalytic hydrothermal decomposition of glucose. The glucose required for dyes can be produced from renewable resources by simultaneous hydrolysis of cellulose or wood under hydrothermal conditions [14,37,60]. The microparticles can possibly find applications as fertilizers, support for catalysts, activated carbon, explosives and composite materials. Recently, Peterson et al. [61] demonstrated that adding glycine increased or decreased brown colors and characteristic odors associated with the Maillard reaction, which can be used for the production of dyes and particles. The results presented here show the nature of the homogeneous reaction conditions and its importance for converting glucose into products of dyes, particles, oil and gases.

4. Conclusions

When aqueous glucose solutions are slowly heated to 350 °C, the solutions change color from clear to light yellow, and then to yellow and finally to orange. Aqueous glucose solutions begin decomposing at 220 °C, and particles precipitate at 251 °C. At 280 °C with slow heating, particles readily form. At 350 °C with slow heating, aqueous glucose solutions react to form 65% solid residue that consist of nanoparticles can be obtained as identified by SEM.

When aqueous solutions of glucose are heated rapidly, they remain homogenous until about 380 °C, and colorful materials are produced with little particle precipitation up to 410 °C. From these findings, the heating process can be used to produce dyes and catalytically gasify and liquefy glucose or synthesize chemicals under a homogeneous reaction environment. The appearance of the reacting phase of glucose in water can be used to control product distribution and even the nature of the chemical products.

Slow heating of aqueous glucose solutions produce particles at the sub-micron or possibly nanometer order that have aromatic structures, which is most likely due to condensation reactions involving 5-HMF. The aromatic structures have the potential use as activated carbon, support for catalysts, and in energetic materials and composites. Rapid heating rates lead to sugar-like products that are yellow and then become orange depending on the conditions. These orange like compounds can be possibly used as dyes or further decomposed into oil and gas with catalysts.

In the reaction of aqueous glucose solutions, it is possible to monitor the progress of the reaction through color changes if optical access is available. In the reaction of glucose in high temperature water, color or UV/Vis spectra can be possibly used to monitor or control the products formed or the product distribution. The glucose decomposition products may have use as colorants in the food industry or as additives in the printing and coating industries.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.supflu.2010.11.009.

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