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RESEARCH ARTICLE

Activated Carbon-Mediated Decolourisation in Glucose Isomerisation to Obtain High-Purity Fructose - A Preliminary Study

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Abstract

The caramelisation process, involving sugar breakdown at elevated temperatures, produces brown-coloured compounds known as caramel compounds, contributing to both colour and flavour. This study addresses discolouration in carbohydrate conversion utilizing activated carbon (AC) during the glucose isomerisation into fructose, catalysed by the tertiary amine; N-[3-(dimethylamino)propyl]methacrylamide (DMAPMA). Powder-like (G-135-ID1000) and particle-like (G-306-4070) AC were introduced to the reaction medium to remove brown colour while preserving carbohydrate quantity. The AC-treated samples underwent analysis using high-performance liquid chromatography (HPLC) and UV-visible spectrophotometry. Successful adsorption of coloured byproducts onto the AC was indicated by the resulting colourless solution. HPLC analysis revealed nearly unchanged concentrations of glucose, fructose and mannose, indicating selective removal of undesired coloured compounds by AC. The UV-visible spectrum of the reacted glucose sample shifted leftward after purification, confirming the effective removal of absorbance peaks within the 260-380 nm range. This study presents a promising approach to enhance the visual and compositional qualities of glucose isomerisation reactions catalysed by DMAPMA. AC as a purification agent effectively addresses undesirable colouration, offering a pathway for developing high-quality products with improved characteristics for diverse applications in the food and industrial sectors.

Keywords: Activated carbon, DMAPMA, Glucose isomerisation, Remove brown colour, Tertiary amine

Introduction

Biomass stands out as the most appealing substitute material, as it represents the sole abundantly accessible carbon source besides oil and coal. Biomass is composed of various elements such as carbohydrates, fatty acids, lignin, lipids, proteins, and additional components. Notably, carbohydrates hold significant potential due to their status as the predominant organic carbon reservoir (van Putten et al., 2013; Lu et al., 2022; Dharmapriya et al., 2023a). Among the constituents of plant biomass, glucose stands as the most prevalent foundational component (Velvizhi et al., 2022). Isomerisation is a well known carbon-efficient method for forming rare monosaccharides from abundant ones (Delidovich and Palkovits, 2016). The isomerisation of glucose into fructose constitutes a crucial stage in the production of biofuels through the subsequent dehydration of fructose which is a ketose that is not as abundant in nature as glucose but is used for a wide range of products. Fructose has the highest relative sweetness of any naturally occurring sugar while also having the lowest glycemic index (Bantle, 2006). It is highly soluble in water and has a higher tendency to absorb and retain moisture than other sugars (Yang et al., 2013; Delidovich, 2021; Guo et al., 2023). Furthermore, fructose is gaining popularity as a starting material in the synthesis of bio-based chemicals like 5-hydroxymethylfurfural (5-HMF), levulinic acid, and others (Dharmapriya et al., 2023b,c). In today's industrial processes within the food and pharmaceutical sectors, the conversion of aldose (glucose) into ketose (fructose) through isomerisation holds significant importance (Li et al., 2017; Guo et al., 2023). Though fructose exists in nature as a monomer of inulin or levan, biotechnological fructose production via glucose isomerisation appears to be more economical (Delidovich and Palkovits, 2016; Ventura et al., 2022). As a result, glucose isomerisation to fructose is a vital reaction/industrial process with current and future applications (Marianou et al., 2016; Gao et al., 2024).

The emergence of brown colour in carbohydrate conversion reactions is frequently linked to the generation of Maillard reaction byproducts and the occurrence of caramelisation reactions (Agcam, 2022). The Maillard reaction denotes a complex chemical process that transpires when amino acids interact with reducing sugars such as glucose and fructose upon exposure to heat. On the other hand, caramelisation represents an additional mechanism capable of imparting a brown colour to the medium (Yang et al., 2023). This process entails the decomposition of sugars at elevated temperatures resulting in the creation of an array of brown-coloured compounds recognized as caramel compounds. These substances are responsible for both the brown colouration and the characteristic flavour associated with caramelisation (Lee et al., 2022). One of the crucial steps in carbohydrate conversion involves discolouration, aiming to eliminate the brown colour while preserving the quantity of primary products (Yang et al., 2016; Chen et al., 2020). For this purpose, in this study, a typical glucose isomerisation reaction conducted with an N-3-(dimethylamino)propyl methacrylamide (DMAPMA) homogeneous catalyst was mixed with powder-like (G-135-ID1000) and particle-like (G-306-4070) activated carbon (AC) to remove the brown colour of the medium while maintaining the amount of carbohydrate in the medium at a nearly constant.

Materials and Methods

Materials

D-glucose ($C_6H_{12}O_6$, 99.5%), and D-fructose ($C_6H_{12}O_6$, 99.5%), choline chloride ($C_5H_{14}NO \cdot Cl$, 99%) were purchased from Sigma-Aldrich (Germany).

N-3-(dimethylamino)propyl methacrylamide (DMAPMA) ($C_9H_{18}N_2O$, 99%) was purchased from Sigma Aldrich (Japan). Powder-like (G-135-ID1000) and particle-like (G-306-4070) AC were obtained from China Carbon Industry Co., Ltd.: Activated Carbon. All chemicals used were of analytical grade. The quality of the experimental procedure was maintained using analytical grade chemicals while all chemicals used for analysis were in certified analytical grade. All initial preparation and the ultimate rinsing process were carried out using freshly generated deionized (DI) water.

Glucose isomerisation into fructose and analysis

For the standard reaction procedure, 10% of the Bronsted base DMAPMA homogeneous catalysts (concerning mass of glucose), along with 0.2 g of glucose, 1.0 g of choline chloride (ChCl), and 4.0 g of DI, were prepared within a 20 mL high-pressure glass bottle and placed in a temperature-controlled oil bath. The experiment was conducted at a temperature of 120 °C for 2 h. Afterward, the sample was quenched in an ice bath to rapidly cool them down and halt the ongoing reaction. The resulting solution was then diluted and analysed using high-performance liquid chromatography (HPLC). Quantitative analysis of glucose, fructose, and mannose was performed using a Waters Alliance e2695 HPLC system with a Waters RI 2414 refractive index detector. Samples were analysed utilizing an ion-exchange chromatography column (Benson Polymeric-800 Ca, column size $300 \times 7.8\ mm$) purchased from Benson Polymeric Inc., under specific conditions including a sample size of 20 μL (30 mg mL^{-1}), temperature of 85 °C, flow rate of 0.6 mL min^{-1}, and DI water as the eluent. Calibration curves for the HPLCs were generated using a series of standard solutions, which allowed for the quantification of glucose and fructose (Kourieh et al., 2013; Choudhary et al., 2013; Kumar et al., 2020; Dharmapriya et al., 2023b).

Purification the medium containing fructose

After isomerisation of glucose into fructose, the colour of the reacted sample was changed to brown due to the formation of caramel. This reduces the value of the main product as well. To remove the caramel colour, AC was used while keeping the monosaccharide concentration constant. In a typical experiment, the concentration of the various sugars present in the reacted sample was first determined using HPLC. Following that, 10 mL of the reacted sample was placed in a 20 mL sample bottle, and 0.05 g of powder-activated carbon or particle-activated carbon was added. The sample bottles were then shaken for 12 h at a speed of 110 rpm. The solutions were then placed in 50 mL centrifuge tubes and centrifuged at 10,000 rpm for 10 min. The supernatant was collected and analysed using HPLC to determine the concentrations of different sugars present in the sample, which were then compared with the initial concentrations of sugars present in the sample before removing the colour of caramel (glucose, fructose and mannose). Prior to AC treatment, samples reacted were analysed using UV-visible spectrophotometer (Hitachi U-2900) at room temperature, within a wavelength range of 200 - 800 nm. The samples for analysis were diluted 200 times, and DI water served as the control sample. The AC-treated samples were then analysed with a UV-vis spectrophotometer to compare the spectrum before and after AC treatment.

Results and Discussion

Figure 1 shows the resulting colour of experiments involving 20 times diluted reaction samples obtained using homogeneous catalyst DMAPMA. These samples were collected at various time points, specifically at 0, 2, 5, 15, 20, 30, 45, 60, and 120 min.

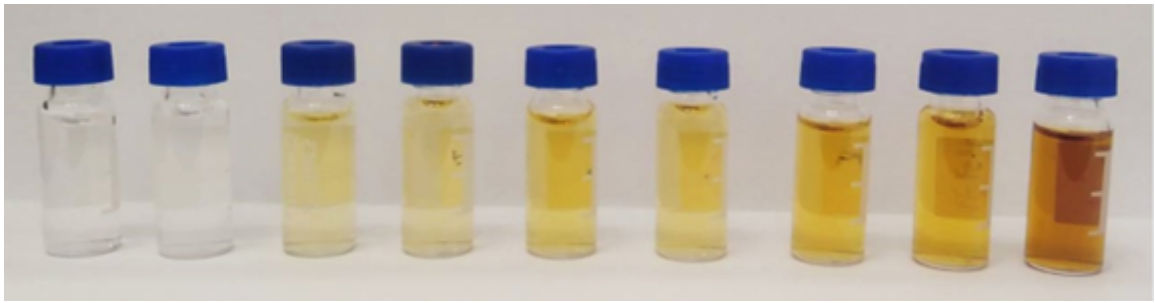

Figure 1. Photograph of reacted glucose samples with DMAPAM catalyst with reaction time after 20× dilution (0, 2, 5, 15, 20, 30, 45, 60, and 120 min).

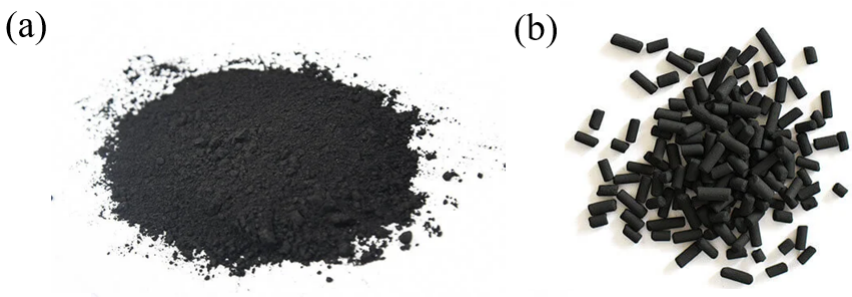

Figure 2. Physical appearance of (a) powder-like (G-135-ID1000) and (b) particle-like (G-306-4070) AC, obtained from China Carbon Industry Co., Ltd.

Figure 2 shows the physical appearance of powder-like (G-135-ID1000) and particle-like (G-306-4070) AC samples.

Purification of reacted samples

The Maillard reaction is an intricate chemical process that takes place when amino acids, or primary/secondary amines, come into contact with reducing sugars, such as glucose or fructose, under the influence of heat. This reaction is accountable for the browning and flavour development in a variety of food when they are cooked, baked, roasted, or subjected to other heat-related procedures. Nevertheless, it is worth noting that tertiary amines, such as triethylamine, do not seem to participate in the Millard reaction. It is suggested that the majority of the observed coloured byproducts result from the thermal breakdown of carbohydrates, a process known as caramelisation (Liu et al., 2014).

DMAPMA is a tertiary amine and a coloured byproduct of the glucose-reacted medium mainly resulting from caramelisation. The purification of the reaction mixture is difficult given the fact that the complexity of removal of undesired coloured byproducts through a straightforward purification method using AC. The resulting solution becomes colorless after filtration through PTFE filters (0.45 μm) to remove AC, indicating that the coloured byproducts have been adsorbed onto the AC as shown in Figure 3. Subsequent HPLC analysis of the purified solution demonstrates that the concentrations of glucose, fructose, and mannose remain nearly unchanged. This suggests that the activated carbon selectively remove the undesired coloured compounds.

Table 1 displays the HPLC data before and after the purification process using two types of activated carbon. Another observation reveals that the monosaccharide content after

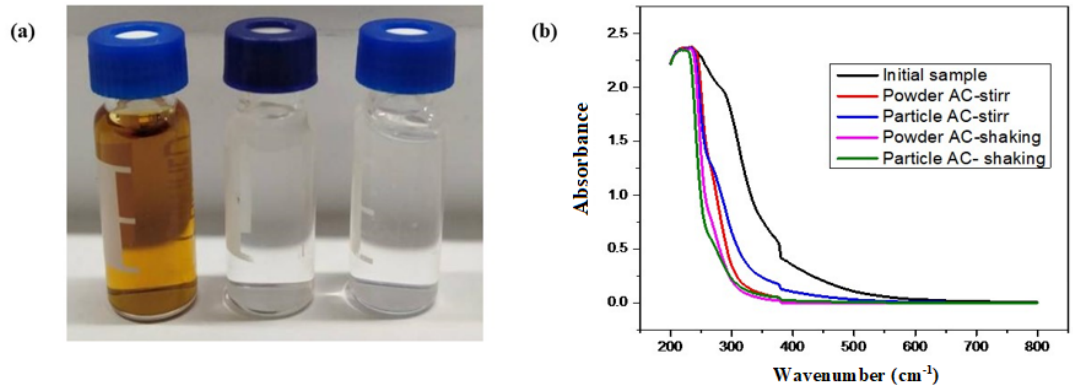

Figure 3. Purification of the reacted glucose samples using AC. (a) Photograph of reacted samples before and after purification: Left to right: before purification by AC, after purification by powder-activated carbon, after purification by particle-activated carbon, (b) UV-vis spectrum of application of different purification methods using activated carbon.

activated carbon purification was significantly higher in the particle-activated carbon-treated sample than in the powder-activated carbon-treated samples. This difference arises because the powder-activated carbon possesses a larger surface area compared to the particle-activated carbon, even though they were present in equal amounts in the treated sample. The enhanced adsorption of monosaccharide into the pores of AC occurred more efficiently in the powder-like activated carbon than in the particle-like activated carbon.

Liu et al. (2014) noted that the UV-vis spectra of the solution, both before and after purification, provided evidence that the peaks at 286 and 340 nm, attributing to the 1,2-enediol intermediate and the coloured byproducts respectively, removed by filtration. Previous studies have demonstrated that AC has been utilized for the removal of caramel colour from various dietary and consumer products (Nasehi et al., 2012; Ahdno and Jafarizadeh-Malmiri, 2015).

The effectiveness of particle and powder-activated carbon applications for colour removal in reacted glucose samples was assessed through two experimental methods: stirring using a magnetic stirrer and shaking on a digital orbital shaker. In the stirring method, 10% (with respect to glucose amount) of either particle or powder-activated carbon was submerged in the typical reacted glucose sample containing the homogeneous DMAPMA catalyst (0.2 g glucose, 1.0 g ChCl, 4.0 g H_2O, 10% DMAPMA, 30 min).

The mixture was then stirred for 2 h using a magnetic stirrer at a speed of 200 rpm. In the other method, 10% of either powder- or particle-activated carbon was combined with the samples and agitated using an orbital shaker at a speed of 120 rpm for 2 h. Subsequently, the filtered samples were subjected to analysis with a UV-vis spectrometer to determine the most efficient method for removing the brown color. As depicted in Figure 3(b), the initial UV-vis spectrum of the reacted glucose sample prior to purification exhibited absorption between 260 nm and 380 nm. After purification, the spectrum shifted to the left, indicating the removal of the absorbance peak within the 260-380 nm range. When comparing the effectiveness of the removal methods, it was observed that particle-shaped AC applied with the orbital shaker demonstrated the most effective colour removal, as illustrated in the UV-vis spectra.

Table 1. Comparison of carbohydrate concentrations before and after AC treatment.

Experiment	Glucose (mol L^{-1})	Fructose (mol L^{-1})	Mannose (mol L^{-1})
1. Before activated carbon treatment	0.111	0.034	0.009
2. After particle-activated carbon treatment	0.106	0.032	0.007
3. After powder-activated carbon treatment	0.102	0.031	0.007

Conclusion

In conclusion, the study focused on addressing challenges posed by coloured byproducts, particularly those resulting from caramelisation during the glucose isomerisation reaction catalysed by the tertiary amine N-3-(dimethylamino)propyl methacrylamide (DMAPMA). The Maillard reaction, a complex chemical process involving amino acids and reducing sugars, is well known for its role in browning and flavour development during various heat-related cooking processes. Findings align with previous observations that tertiary amines, exemplified by DMAPMA, do not actively participate in the Maillard reaction. To mitigate undesirable colouration arising from caramelisation in glucose isomerisation by DMAPMA, AC in both powder-like (G-135-ID1000) and particle-like (G-306-4070) forms were employed to the reacted media. The resulting solution underwent a remarkable transformation from a coloured medium to colorless, signifying the successful adsorption of the coloured byproducts onto AC. This purification process was further validated through HPLC analysis, revealing nearly unchanged concentrations of glucose, fructose, and mannose. The retention of these crucial carbohydrate components underscores the effectiveness of AC in selectively removing undesired coloured compounds. The spectral analysis of the initial UV-visible spectrum of the reacted glucose sample provided additional insights. The absorbance peak observed between 260 nm and 380 nm, indicative of coloured compounds, shifted to the left after purification. This spectral change supports the conclusion that AC successfully removed the absorbance peak within the 260-380 nm range, further affirming the efficient removal of coloured compounds from solution. The research introduces a promising method for improving the visual and compositional attributes of glucose isomerisation reactions under the influence of DMAPMA as a catalyst. Employing AC as a purification agent proves successful in overcoming the issue of undesired colouration, paving the way for the creation of high-quality products. This advancement holds significant potential for diverse applications in the food and industrial sectors, offering enhanced characteristics for end products.

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