METHOD FOR CONVERSION OF CARBOHYDRATE POLYMERS TO VALUE-ADDED CHEMICAL PRODUCTS

This invention was made with Government support under Contract DE-AC05-76RLO1830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

FIELD OF THE INVENTION

The invention generally relates to conversion of carbohydrates, and more particularly, to conversion of carbohydrate polymers in ionic liquids using mixed metal halide catalysts to obtain value-added chemical products.

BACKGROUND OF THE INVENTION

Cellulose is a complex polymer chain present in biomass. To convert cellulose to other fuels, hydrolysis is necessary to obtain the monomer building blocks from which desired chemicals may be derived. The hydrolysis reaction is strongly affected by structural and compositional features such as crystallinity and polymer chain length, all of which affect the desired product yields. At present, depolymerization is a recognized bottleneck in the conversion of cellulose feeds. While considerable research effort has been aimed at improving cellulose depolymerization processes in aqueous systems, progress has been limited, in part, due to the lack of solubility of cellulose in water. Enzymatic hydrolysis of cellulose is effective but is characteristically slow at ambient temperatures, and is also sensitive to contaminants originating from the various biomass components. Mineral acids have been extensively investigated to catalyze hydrolysis at a variety of acid concentrations and temperatures, but degradation of resulting products continues to be an issue. One such product, 5-hydroxymethylfurfural (HMF), also known as 5-Hydroxymethyl-2-furaldehyde, is a versatile platform chemical for the production of a broad range of chemicals and fuels currently produced from petroleum. It is therefore desirable to be able to use cellulose feeds directly as a source of glucose for production of HMF. Inability to hydrolyze cellulose to glucose at low temperature presents a substantial barrier to direct utilization of cellulose. Accordingly, new methods are needed for converting carbohydrate polymers at low temperatures to value-added chemicals. Advantages and novel features of the present invention will be set forth hereafter, and will be readily apparent from the descriptions and demonstrations herein. These descriptions should be seen as illustrative of the invention and not as limiting in any way.

SUMMARY OF THE INVENTION

The present invention is a process for selective conversion of carbohydrate polymers to value-added intermediate and end-use chemicals. The process includes: heating a carbohydrate polymer at a preselected temperature in an ionic liquid that includes a catalyst comprising a preselected ratio of at least two metal halides or metal salts for a time sufficient to convert the carbohydrate polymer to desired carbohydrate derivatives and products. Carbohydrate polymers include, but are not limited to, e.g., cellulose, hemicellulose, cellobiose, maltodextrin, starch, or other selected carbohydrates. Reaction processes described herein employ ionic liquids as a reaction medium and various mixed metal halides as reaction catalysts. In the reaction medium, these mixed metal halides catalyze the necessary decrystallization and hydrolysis reactions for conversion of the carbohydrate polymers or parent polysaccharides to desired and/or value-added reaction products. In various embodiments, the mixed metal halide catalyst includes $CuCl_2$ and at least one other metal halide, e.g., $CrCl_2$, $CrCl_3$, $PdCl_2$, $FeCl_3$, $LaCl_3$, $NiCl_2$, $CoCl_2$, but is not limited thereto. The mixed metal halide catalyst includes at least two metal halides, or metal salts, with a first metal halide or metal salt comprising from 50 percent to 99 percent of the total moles of catalyst and a second metal halide or metal salt comprising from 50 percent to 1 percent of the total moles of catalyst. In another embodiment, the carbohydrate polymer is cellulose, the catalyst is a paired metal halide, e.g., [$CuCl_2$:$CrCl_2$], and the carbohydrate product includes HMF. In another embodiment, the carbohydrate product includes a carbohydrate monomer, e.g., glucose. In another embodiment, the carbohydrate product includes HMF. Temperatures and reaction times are selected to maximize the selected carbohydrate products and to minimize product degradation. Temperatures for conversion are preferably in the range from about 100° C. to about 180° C. More preferably, temperatures for conversion are below about 120° C. Time to achieve conversion of carbohydrate polymers is preferably a time in the range from about 0.01 hours to about 8 hours, but is not limited. A more complete appreciation of the invention will be readily obtained by reference to the following description of the accompanying drawings in which like numerals in different figures represent the same structures or elements.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a flow chart showing generalized process steps for conversion of carbohydrate polymers in ionic liquids to value-added chemical products.

FIG. **2** presents product yields obtained from conversion of cellulose using a paired [$CuCl_2$:$CrCl_2$] metal halide catalyst comprising various quantities of constituent metal halides.

FIG. **3** presents product yields obtained from conversion of cellulose using a paired [$CuCl_2$:$PdCl_2$] metal halide catalyst comprising various quantities of constituent metal halides.

FIG. **4** presents product yields obtained from conversion of cellulose using a paired [$CuCl_2$:$CrCl_2$] metal halide catalyst at selected catalyst loading values.

FIG. **5** presents product yields obtained from conversion of cellobiose and maltose using a paired [$CuCl_2$:$CrCl_2$] metal halide catalyst at selected catalyst loading values.

DETAILED DESCRIPTION OF THE INVENTION

Described here is a process and catalyst composition for conversion of cellulose and other carbohydrate polymers in an ionic liquid. The following terms are defined for ease of understanding. "Ionic Liquids" are salts that have a melting point, or that are liquid at, temperatures below about 100° C. Ionic liquids used in conjunction with the present invention comprise a 1-R_1-3-R_2-imidazolium halide, where R_1 and R_2 are alkyl groups of formula (C_xH_{2x+1}) where X=1 to 18. Exemplary ionic liquids include, but are not limited to, e.g., 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl); 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-ethyl-3-methylimidazolium bromide ([EMIM]Br), and combinations thereof. Nomenclature used herein to denote ionic liquids identifies the cationic portion of the ionic liquid, e.g., 1-ethyl-3-methyl-imidazolium, by bracket, e.g., [EMIM] or $[EMIM]^+$. The anionic portion of the ionic liquid, e.g., halides (e.g., Cl or Br; or Cl^- or Br^-) is identified by placement outside the bracket (e.g., [EMIM]Cl or $[EMIM]^+Cl^-$). Unless otherwise noted, nomenclature for ionic liquids with or with-