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(54) **PROCESS FOR THE SYNTHESIS OF
5-HYDROXYMETHYLFURFURAL FROM
SACCHARIDES**

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(56) **References Cited**

FOREIGN PATENT DOCUMENTS

CN 101811066 A 8/2010
CN 101906088 A 12/2010
JP 2007 196174 A 8/2007

OTHER PUBLICATIONS

Chareonlimkun, et al., Reactions of C5 and C6-sugars, cellulose, and lignocellulose under hot compressed water (HCW) in the presence of heterogeneous acid catalysts, *Fuel* 89: 2873-2880 (2010).*

International Search Report mailed by the International Searching Authority on Jun. 17, 2014 in International Application PCT/EP2014/059538 (4 pages).

Harishandra Jadhav et al. "Conversion of D-glucose into 5-hydroxymethylfurfural (HMF) using zeolite in [Bmim]Cl or tetrabutylammonium chloride (TBAC)/CrCl₃"; *Tetrahedron Letters* 53: 983-985 (2012).

Zhongshun Yuan et al. "Catalytic conversion of glucose to 5-hydroxymethyl furfural using inexpensive co-catalysts and solvents"; *Carbohydrate Research* 346: 2019-2023 (2011).

Fabio Carniato et al. "Ti-POSS covalently immobilized onto mesoporous silica: A model for active sites in heterogeneous catalytic epoxidation"; *Inorganica Chimica Acta* 380: 244-251 (2012).

Wei Zeng et al. "Catalytic Conversion of Glucose on Al—Zr Mixed Oxides in Hot Compressed Water"; *Catal Lett* 133: 221-226 (2009).

A. Chareonlimkun et al. "Reactions of C₅ and C₆-sugars, cellulose, and lignocellulose under hot compressed water (HCW) in the presence of heterogeneous acid catalysts"; *Fuel* 89: 2873-2880 (2010).

Per-Erik Tegehall "Synthesis of Crystalline Titanium (IV) Phosphates by Direct Precipitation from Ti(III) Solutions and Ion Exchange Properties of Some of the Prepared Phases"; *Acta Chemica Scandinavica A* 40: 507-514 (1986).

Fabio Carniato et al. "Titanosilsesquioxane Anchored on Mesoporous Silicas: a Novel Approach for the Preparation of Heterogeneous Catalysts for Selective Oxidations"; *Chem. Eur. J.* 14: 8098-8101 (2008).

Giulio Alberti et al. "Layered and Pillared Metal (IV) Phosphates and Phosphonates***"; *Adv. Mater.* 8, No. 4: 291-319 (1996).

Stephen Brunauer et al. "Adsorption of Gases in Multimolecular Layers"; the Bureau of Chemistry and Soils and George Washington University 60: 309-319 (1938).

* cited by examiner

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(57) **ABSTRACT**

This invention relates to a process for the synthesis of 5-hydroxymethylfurfural (HMF) from saccharides. In particular this invention relates to a process for the dehydration of monosaccharides having 6 carbon atoms (hexoses), disaccharides, oligosaccharides, and polysaccharides to yield highly pure 5-hydroxymethylfurfural (HMF) in high yield.

20 Claims, 2 Drawing Sheets