



US008367851B2

(12) **United States Patent**
Lilga et al.(10) **Patent No.:** **US 8,367,851 B2**
(45) **Date of Patent:** ***Feb. 5, 2013**(54) **HYDROXYMETHYLFURFURAL
REDUCTION METHODS AND METHODS OF
PRODUCING FURANDIMETHANOL**(75) Inventors: **Michael A. Lilga**, Richland, WA (US);
Richard T. Hallen, Richland, WA (US);
James F. White, Richland, WA (US);
Michel J. Gray, Mesa, WA (US)(73) Assignee: **Battelle Memorial Institute**, Richland,
WA (US)(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.This patent is subject to a terminal dis-
claimer.(21) Appl. No.: **13/173,942**(22) Filed: **Jun. 30, 2011**(65) **Prior Publication Data**

US 2011/0306780 A1 Dec. 15, 2011

Related U.S. Application Data(63) Continuation of application No. 11/760,634, filed on
Jun. 8, 2007, now Pat. No. 7,994,347.(60) Provisional application No. 60/804,409, filed on Jun.
9, 2006.(51) **Int. Cl.****C07D 307/02** (2006.01)(52) **U.S. Cl.** **549/503**; 549/502(58) **Field of Classification Search** 549/502,
549/503

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

1,903,850 A 4/1933 Peters, Jr.
1,906,873 A 5/1933 Peters, Jr.
2,077,409 A 4/1937 Graves
2,077,422 A 4/1937 Lazier
2,082,025 A 6/1937 Peters, Jr.
2,094,975 A 10/1937 Adkins et al.
2,487,054 A 11/1949 Howk
2,763,666 A 9/1956 Mastagli
3,040,062 A 6/1962 Hales
3,083,236 A 3/1963 Utne et al.
3,847,952 A 11/1974 Smimov et al.
4,182,721 A 1/1980 De Thomas et al.
4,185,022 A 1/1980 Kozinski
4,251,396 A 2/1981 Frainier et al.
4,261,905 A 4/1981 Preobrazhenskaya et al.
4,302,397 A 11/1981 Frainier et al.
4,335,049 A 6/1982 Hamada et al.
4,400,468 A 8/1983 Faber4,728,671 A 3/1988 Hinnekens
4,764,627 A 8/1988 Diebold et al.
4,780,552 A 10/1988 Wambach et al.
5,591,873 A 1/1997 Bankmann et al.
6,479,677 B1 11/2002 Ahmed
7,994,347 B2* 8/2011 Lilga et al. 549/503

FOREIGN PATENT DOCUMENTS

EP 0096913 A1 12/1983
FR 2556344 A1 12/1983
JP 59190984 10/1984

OTHER PUBLICATIONS

Morikawa, "Reduction of 5-Hydroxymethylfurfural", Noguchi
Kenkyusho Jiho (1980), (23), 39-44.Balandin et al., "Selective Hydrogenation of Furan Compounds",
Doklady Akademii Nauk SSSR (1955), 100, 917-20.Schiavo et al., "Hydrogenation Catalytique du
5-hydroxymethylfurfural en milieu aqueux", Bull. Soc. Chim. Fr.
(1991) 704-711.Vaidya et al., "Kinetics of Liquid-Phase Hydrogenation of
Furfuraldehyde to Furfuryl Alcohol over a PUC Catalyst", American
Chemical Society, Jun. 11, 2003, 5 pages.Liaw et al., "Catalysis of CuB/SiO₂ Catalysts for Hydrogenation of
Furfural, Crotonaldehyde, and Citral", J. China Inst. Chem. Engrs.,
vol. 34, No. 6, 667-674, Oct. 29, 2003.

PCT/US2007/070802, Oct. 12, 2008, IPRP.

PCT/US2007/070802, Nov. 26, 2007, Search Report.

PCT/US2007/070802, Nov. 11, 2007, Written Opinion.

Lewkowski, "Synthesis, Chemistry and Applications of
5-Hydroxymethyl-furfural and Its Derivatives", General Papers
Arkivoc 2001 (i) 17-54. ISSN 1424-6376.Moye et al., "Reaction of Ketoheoses with Acids", J. appl. Chem.,
1966, vol. 16, July, pp. 206-208.Huber et al., "Production of Liquid Alkanes by Aqueous-Phase Pro-
cessing of Biomass-Derived Carbohydrates" Science, vol. 308, 2005,
pp. 1446-1450, XP002458811.

* cited by examiner

Primary Examiner — Nizal Chandrakumar(74) *Attorney, Agent, or Firm* — Wells St. John P.S.(57) **ABSTRACT**A method of reducing hydroxymethylfurfural (HMF) where a
starting material containing HMF in a solvent comprising
water is provided. H₂ is provided into the reactor and the
starting material is contacted with a catalyst containing at
least one metal selected from Ni, Co, Cu, Pd, Pt, Ru, Ir, Re and
Rh, at a temperature of less than or equal to 250° C. A method
of hydrogenating HMF includes providing an aqueous solu-
tion containing HMF and fructose. H₂ and a hydrogenation
catalyst are provided. The HMF is selectively hydrogenated
relative to the fructose at a temperature at or above 30° C. A
method of producing tetrahydrofuran dimethanol (THFDM)
includes providing a continuous flow reactor having first and
second catalysts and providing a feed comprising HMF into
the reactor. The feed is contacted with the first catalyst to
produce furan dimethanol (FDM) which is contacted with the
second catalyst to produce THFDM.**14 Claims, 80 Drawing Sheets**