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Branched Diol Monomers from the Sequential Hydrogenation of Renewable Carboxylic Acids

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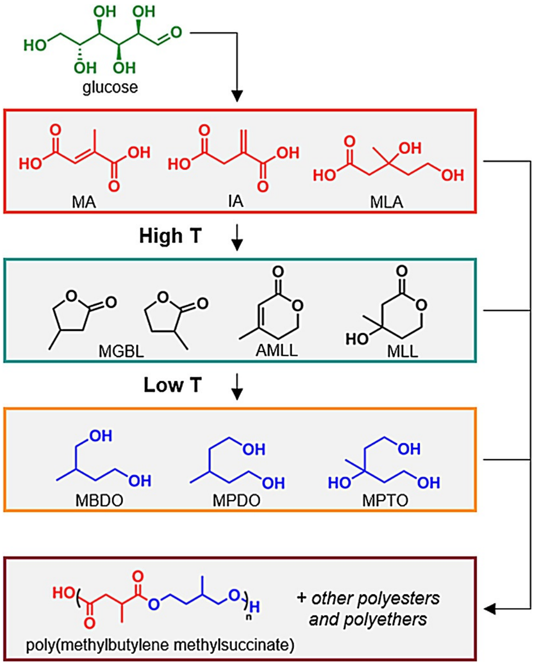
A prominent challenge in replacing petrochemical polymers with bioderived alternatives is the efficient transformation of biomass into useful monomers. In this work, we demonstrate a practical process for the synthesis of multifunctional alcohols from five- and six-carbon acids using heterogeneous catalysts in aqueous media. Design of this process was guided by thermodynamic calculations, which indicate the need for two sequential high-pressure hydrogenations: one, reduction of the acid to a lactone at high temperature; two, further reduction of the lactone to the corresponding diol or triol at low temperature. For example, the conversion of mesaconic acid into (α or β)-methyl-γ-butyrolactone was achieved with 95% selectivity at a turnover frequency of 1.2 min^{-1} over Pd/C at 240 °C. Subsequent conversion of (α or β)-methyl-γ-butyrolactone into 2-methyl-1,4-butanediol was achieved with a yield of 80% with Ru/C at 100 °C. This process is an efficient method for the production of lactones, diols, and triols, all valuable monomers for the synthesis of bioderived branched polyesters.

The current petrochemical industry is based on the inexpensive and efficient transformation of a few platform chemicals into a wide array of products, including solvents, fine chemicals, and monomers for modern plastics. Concerns over sustainability have motivated a return to natural feedstocks; this trend is particularly evident in the polymer industry, for which consumer awareness of the adverse environmental impacts of nondegradable plastics has driven the commercialization of biodegradable polymers (e.g., the polyesters polylactide and polyhydroxyalkanoates). However, there exist only a few efficient and environmentally benign processes for monomer synthesis from biomass.

Organic acids obtained by fermentation of glucose are attractive feedstocks for the synthesis of branched multifunctional alcohols from biomass. Itaconic acid (IA) was identified as one of the top-12 building-block chemicals owing to its potential value as a precursor for C5 chemicals [e.g., 2-methly-1,4-butanediol and (α or β)-methyl-γ-butyrolactone].[1] Globally, 80000 tons of IA are produced per year by using *Aspergillus terreus* in a high-yielding fermentation process (0.72 g g^{-1} from glucose, with titers of up to 86 g L^{-1}).[2,3] Mesaconic acid (MA), an isomer of IA, has similar potential as a precursor and was recently produced by using *E. coli*.[4] The low cost of these acids (≈ $2 kg^{-1}) enables their use in synthetic resins, plastics, rubbers, surfactants, and oil additives.[5,6] Mevalonic acid (MLA) is a third organic acid that can also be produced efficiently from the fermentation of carbohydrates.[7] MLA is a potentially valuable precursor for the synthesis of C6 alcohols, ethers, and lactones. However, there are a few reports that outline efficient, aqueous processes for the production of diols from five- and six-carbon organic acids, including MA, IA, and MLA.

As depicted in Scheme 1, we propose an efficient two-step catalytic method for the aqueous reduction of organic acids that proceeds through a lactone intermediate. In a specific example, MA is first reduced to (α or β)-methyl-γ-butyrolactone (MGBL), which is then used to produce 2-methyl-1,4-butanediol (MBDO); the same method can be used to reduce both IA and MLA to the corresponding diol and triol, respectively. Such



Scheme 1. Hybrid process for the production of bioderived lactones, diols, and branched polymers from glucose.

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a method would enable the efficient synthesis of branched C5 and C6 diols, which are useful for the synthesis of polymers such as polyesters, among numerous other applications.

Hydrogenation of multifunctional carboxylic acids was evaluated for a related four-carbon molecule, succinic acid (SA), which proceeds through 4-hydroxybutyric acid and γ-butyrolactone as intermediates to 1,4-butanediol (BDO). SA is used in combination with diols to prepare polyesters or as an intermediate for the synthesis of tetrahydrofuran (THF). BDO may be used as a chain extender in polyurethane synthesis, for example, whereas THF is useful both as a solvent and as a monomer for polyether synthesis. Specific to the reduction of SA, heterogeneous catalysts, including Re/C,[8] Pd-Re/C,[9] Pd-Re/TiO_2,[10,11] rhenium–copper–carbon composites,[12] Pd/TiO_2,[13] and Ru/C[14] have been utilized for aqueous BDO production at temperatures ranging from 160 to 240 °C and H_2 pressures ranging from 80 to 150 bar (10 bar = 1 MPa). Examples of high selectivity (over 50 %) for BDO were reported only at low temperatures (below 170 °C) and high H_2 pressures (over 140 bar). Presumably, these conditions are necessary to overcome the entropically unfavorable ring opening of γ-butyrolactone with hydrogen to form BDO.

Comparatively fewer examples of IA or MA hydrogenation to MBDO exist in the literature. Whereas MBDO has been produced in high yield (>90 %) from either IA or MGBL by using homogenous Ru–triphos catalysts[15,16] [triphos = bis(diphenylphosphinoethyl)phenylphosphine] and Ru complexes with tetradentate bipyridine ligands,[17] heterogeneous catalysts have enjoyed less success. The synthesis of MBDO from IA at moderate temperature and pressure produced a low yield (45 % at 150 °C and 100 bar H_2).[18] Several catalysts, including Ru/Starbon,[19] Ru/C,[20] Ru/TiO_2,[21] and Pd/C,[22] were previously proven ineffective for the reduction of IA to MBDO in a one-pot approach. Recently, Pd-Re/C was reported to be an effective catalyst under conditions of relatively high temperature and low H_2 pressure (>80 % yield of MBDO at 180 °C and 40 bar),[23] in conflict with the thermodynamics of the ring opening of the lactone to the diol, which should prevent higher yields of MBDO under these conditions (see Figure S5 in the Supporting Information).

Figure 1 a shows the detailed pathway for the hydrogenation of IA and MA to MBDO. The enthalpy and Gibbs energy of each reaction intermediate were calculated by DFT (M062X/6-311++G[3df,3pd] theory level, implicit solvent, additional details in the Supporting Information) to determine the conditions necessary to produce MBDO with high selectivity (Figure 1 b). As expected, isomers IA and MA exhibit similar thermodynamic properties with a difference in Gibbs energy (ΔG) of only 0.2 kcal mol^{-1}; hydrogenation to form methylsuccinic acid (MSA) is highly favorable under all conditions ($50 < P < 200$ bar, $80 < T < 220$ °C). Subsequent reduction of the carbonyl group to make (2 or 3)-methyl-4-hydroxybutyric acid (MHBA) followed by intramolecular esterification to form MGBL is also downhill in free energy, which suggests that MGBL is the thermodynamically preferred product for all high-temperature, low-H_2-pressure conditions (Figures S1–S3).

In contrast, the conversion of MGBL into MBDO is unfavorable at high temperature and low pressure ($\Delta G_{rxn} = 3.5$ kcal

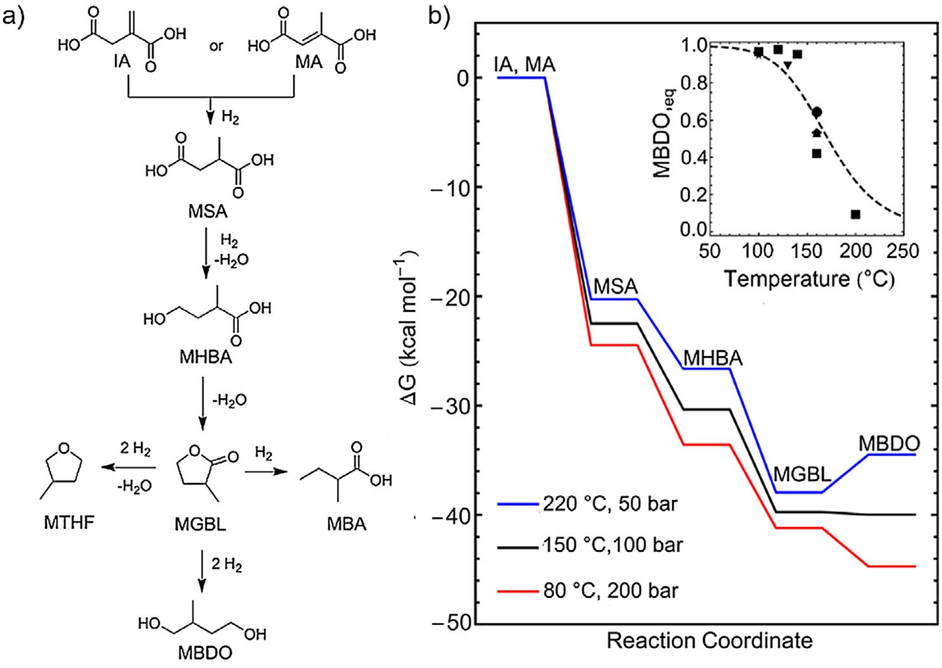

Figure 1. a) Reaction pathway for the hydrogenation of itaconic acid (IA) and mesaconic acid (MA) to methylsuccinic acid (MSA), (2 or 3)-methyl-4-hydroxybutyric acid (MHBA), (α or β)-methyl-γ-butyrolactone (MGBL), and 2-methyl-1,4-butanediol (MBDO). Side products include 3-methyl-tetrahydrofuran (MTHF) and (2 or 3)-methylbutyric acid (MBA). Note that the regioisomers of MHBA, MGBL, and MBA with alternate methyl positions are omitted from the drawing for clarity. b) Calculated reaction energy diagram for the hydrogenation of IA or MA to MBDO for three different sets of temperatures and pressures, demonstrating that high pressures and low temperatures promote MBDO formation. Inset shows theoretical temperature dependence (dashed line) and experimental overlay (markers) for the equilibrium ratio [MBDO]/([MBDO]+[MGBL]) at H_2 pressure of 140 bar. Conditions for experimental data are in Table S10.

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mol^{-1} at 220 °C and 50 bar) but is favorable at lower temperatures and higher pressures ($\Delta G_{rxn} = -3.5\ kcal\,mol^{-1}$ at 80 °C and 200 bar) (Tables S1–S9). The theoretical temperature dependence of the ratio [MBDO]/([MBDO] + [MGBL]) at 140 bar of H_2 is displayed in the inset of Figure 1 b (dashed line) (see the Supporting Information for complete details). Experimental results obtained from 10 hydrogenation trials at long reaction times close to thermodynamic equilibrium between MGBL and MBDO generally agree with these theoretical predictions (markers, see the Supporting Information for complete experimental information). Both theory and experiment show that low temperatures ($T < 140$ °C) are required to produce MBDO in high yield at 140 bar H_2 pressure.

Experimental results for the aqueous hydrogenation of IA or MA to MGBL using heterogeneous catalysts are shown in Figure 2. For the tested conditions, hydrogenation of IA or MA to form MSA was faster than the reduction and cyclization of MSA to MGBL. As indicated by the turnover frequency (TOF) reported in Figure 2, the rate of MGBL formation was dependent on catalyst and temperature. Pd catalysts exhibited higher TOFs than Pt, Ru, $Cu_2Cr_2O_5$, and Rh. At 160 °C and 70 bar H_2, Pd/TiO_2 and Pd/C demonstrated similar activities.

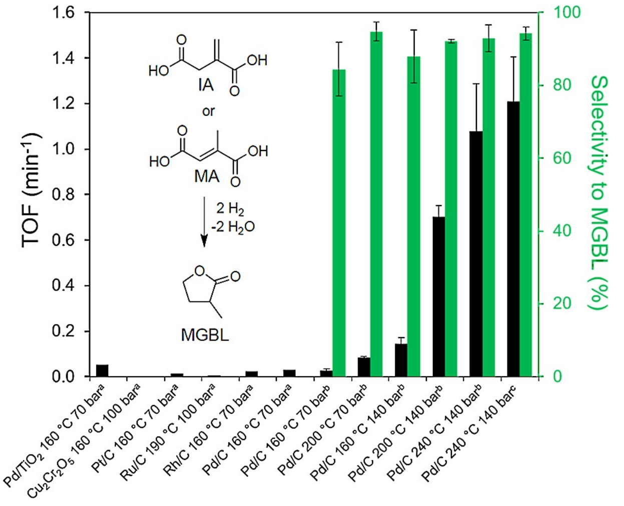

Figure 2. Temperature and pressure dependence of MA or IA hydrogenation to MGBL. Reaction conditions indicated by superscript a) 2 wt % MA in H_2O, b) 10 wt % IA in H_2O, and c) 10 wt % MA in H_2O. Total volume: 60 mL aqueous solution. Complete reaction details provided in the Supporting Information. Selectivity is only reported for reaction conditions b and c. MGBL is a mixture of α-methyl-γ-butyrolactone and β-methyl-γ-butyrolactone [(38 ± 2) and (62 ± 2) %, respectively]. Error bars represent a 95 % confidence interval.

Further optimization was performed with the commercial catalyst Pd/C. With this catalyst, increasing the reaction temperature and pressure from 160 °C and 70 bar to 240 °C and 140 bar resulted in a 40-fold increase in the TOF. The intermediate hydroxyacid, MHBA, was observed in small quantities (< 5 %) in reactions achieving high conversion into MGBL. Selectivity to MGBL was greater than 80 % in all reactions with the use of Pd/C. The maximum yield of MGBL at complete conversion of IA was 82 % at 200 °C and 140 bar H_2. Thermodynamic calculations indicate that the formation of the predominant byproduct, (2 or 3)-methylbutyric acid (MBA), from MGBL is a highly favorable reaction ($\Delta G = -17.6\ kcal\,mol^{-1}$ at 240 °C and 140 bar). However, this product was observed with selectivities less than 10 %. The targeted diol, MBDO, was not observed in these experiments owing to both thermodynamic limitations and the low selectivity of the selected catalyst, Pd/C.

Subsequent conversion of MGBL into MBDO was tested with Ru/C, Pd/C, and Pt/C at temperatures ranging from 80 to 200 °C (Figure 3). Pd and Pt produced low yields of MBDO, in contrast with Ru/C at all considered temperatures. Because the conversion of MBDO into isobutyl alcohol, *n*-butanol, and ultimately propane can occur in series with the formation of MBDO from MGBL, the data in Figure 3 are presented at the time of maximum MBDO yield. With Ru/C at long reaction times, hydrogenolysis of the MBDO C–O bonds occurs, which results in the formation of methane and propane. The observed mass-balance errors can presumably be attributed to the formation of these gaseous products, as only products in the aqueous phase were quantified. To maximize MBDO production, it was necessary to conduct the MGBL reduction reactions at low temperatures, for which both the rate of MBDO hydrogenolysis was lower and the production of MBDO from MGBL was thermodynamically favorable. For example, the experimentally observed values for the ratio of [MBDO]/([MBDO] + [MGBL]) were 0.98 and 0.10 at 100 and 200 °C, respectively, with Ru/C.

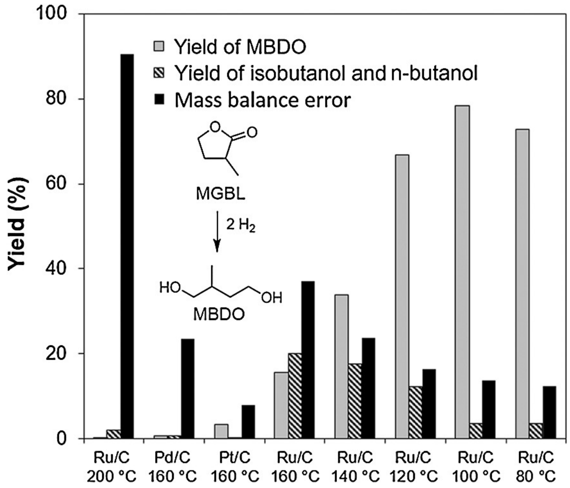

Figure 3. Temperature dependence of the hydrogenation of α-methyl-γ-butyrolactone to 2-methyl-1,4-butanediol. Reaction conditions: 2 wt % MGBL in 60 mL H_2O, 1.0 g 5 wt % Ru/C, 140 bar. Data reported at time of maximum MBDO selectivity: 80 °C (71 h—did not reach maximum), 100 °C (6.3 h), 120 °C (3.5 h), 140 °C (1.8 h), 160 °C (0.3 h), and 200 °C (0.3 h). Pd/C (1.5 h), Pt/C (1.5 h). TOF data is not presented for this reaction owing to the equilibrium that exists between MGBL and MBDO and the hydrogenolysis of MBDO that occurs readily at temperatures greater than 100 °C.

Encouraged by these results, we investigated the reduction of three C6 compounds: mevalonolactone (MLL) (more precisely a mixture of MLA and MLL, as the two are in equilibrium in

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water), anhydromevalonolactone (AMLL), and β-methyl-δ-valerolactone (BMVL). Under conditions similar to those used for the reduction of MGBL (100 °C, 140 bar H_2), we found that the reduction of MLL resulted in 3-methyl-1,3,5-pentanetriol (MPTO) with high selectivity (91 %). Additionally, the reduction of BMVL and AMLL both gave 3-methyl-1,5-pentanediol (MPDO) with similarly high selectivities (86 to 91 %). A more detailed description of this work is available in the Supporting Information.

Pd/C was previously demonstrated to be active for the conversion of IA into MGBL by Li et al., who examined the effects of active carbon pretreatment on selectivity for MGBL formation.[22] Here, we show the effect of temperature and pressure on the TOF for MGBL formation, demonstrating TOFs of $1.2\ \mathrm{min}^{-1}$ at 240 °C and 140 bar. The ability of palladium to incorporate hydrogen into its crystal lattice is possibly the reason why its performance is superior to that of other tested catalysts. Pd was highly active for both hydrogenation of the double bond in IA or MA and the reduction of the free carboxylic acid present in MSA, yet Pd/C did not catalyze the facile conversion of MGBL into MBDO. Studies of succinic acid hydrogenation by using Pd-based catalysts led to similar results, for which a low concentration of the diol was formed by using Pd-only catalysts.[13]

In the final step, thermodynamic calculations (Figure S5) indicated that at 140 bar, the conversion of MGBL into MBDO is only favorable at temperatures below approximately 140 °C (at higher H_2 pressures, the threshold temperature is higher); thus, a low-temperature-active catalyst was required for the final process step. Bimetallic catalysts composed of Pd-Re have been proposed for the conversion of closely related γ-butyrolactone into BDO.[9–11] Here, we found that monometallic Ru/C effectively promoted the conversion of MGBL into MBDO in approximately 80 % yield, as shown in Figure 3. The rate of Ru leaching from Ru/C was sufficiently low, demonstrating process viability (i.e., the rate of leaching was three to four orders of magnitude lower than a viable rate[24]) and that the reaction was catalyzed heterogeneously (complete details in the Supporting Information).

Previous work addressing the conversion of γ-valerolactone into 1,5-pentanediol with homogeneous Ru-based catalysts suggests that the intermediates for lactone hydrogenation to diols are the lactol and open-chain hydroxy aldehyde; the remaining carbonyl group is then hydrogenated to yield the diol.[15] It is apparent from the experiments performed here that Ru/C promotes the C–O bond breaking that is necessary for lactone ring opening. Re could also promote the ring-opening mechanism given the results obtained with Re for succinic acid and itaconic acid hydrogenation.[8,23] The undesired hydrogenolysis of MBDO to isobutyl alcohol and *n*-butanol over Ru/C catalysts is known; generically, $RCH_2OH + 2H_2 \rightarrow RH + CH_4 + H_2O$.[14] For MBDO, the end products of hydrogenolysis are $C_3H_8 + 2CH_4 + 2H_2O$.

Splitting the overall process into two sequential steps with monometallic catalysts enabled efficient production of MBDO from IA or MA in high yield. The initial hydrogenation of IA or MA at high temperatures (240 °C) produces high TOFs on Pd/C that stop at MGBL formation. If this first reaction was conducted with bimetallic catalysts that contained Re or Ru, then only a small amount of ring opening of MGBL would occur, as the thermodynamic equilibrium ratio of [MBDO]/([MBDO] + [MGBL]) approaches zero at this temperature. The high temperature exacerbates the entropic penalty of combining MGBL and two hydrogen molecules to produce MBDO (Figure S4). Moreover, the high reaction temperature would lead to undesirable hydrogenolysis reactions of the little amount of MBDO that was produced. Alternatively, a single low temperature for the entire process (MA to MGBL to MBDO) would lead to negligibly slow overall rates that are limited by the conversion of MA into MGBL.

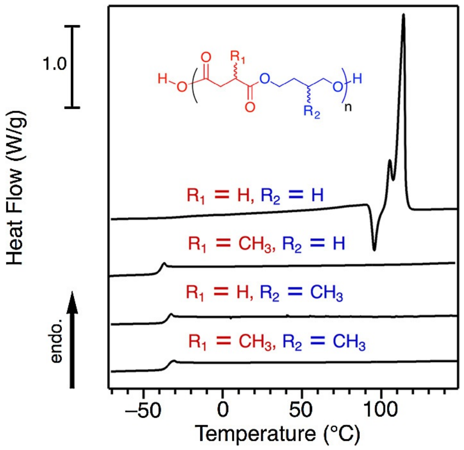

Figure 4. Differential scanning calorimetry traces comparing the effect of methyl substitution on glass-transition temperature of methyl-substituted poly(butylene succinate) with non-methyl-substituted poly(butylene succinate); the molar masses of these four samples are similar (each is ≈10 to 15 $\mathrm{kg\,mol^{-1}}$). Neither methylsuccinic acid nor 2-methyl-1,4-butanediol is symmetric, and the two monomers may be oriented head-to-tail, head-to-head, tail-to-tail, or tail-to-head within the polymer backbone.

To demonstrate the potential of these branched alcohols as monomers, we prepared a variety of aliphatic polyesters by using condensation polymerization with tin(II) 2-ethylhexanoate as a catalyst. As described in detail in the Supporting Information, BDO, MBDO, and MPD were each treated with either SA or MSA to prepare each of the six possible polyesters. As summarized in Figure 4, the addition of a methyl substituent to either the diacid or diol had a significant impact on the thermal properties of the resulting polyester.[25,26] Whereas polybutylene succinate, the polymer resulting from the polymerization of succinic acid and 1,4-butanediol, is semicrystalline with a melting point of $T_m = 114$ °C, the methyl-substituted polyesters were all fully amorphous with low glass-transition temperature values (T_g below −35 °C for each sample). These soft, rubbery polyesters may be appropriate for numerous applications, including use in coatings, adhesives, sealants, elastomers, and foams.[27,28]

As illustrated here as well as in previous examples, biomass-derived feedstocks can be utilized in hybrid fermentation/thermocatalytic processes to produce drop-in replacements or en-

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tirely new chemicals that extend into new applications.[29] For example, our method efficiently produces MBDO, a branched C5 diol that imparts new physical properties to ordinarily straight-chain polyesters. Anhydromevalonolactone can be converted into MPDO, a drop-in replacement monomer in the synthesis of specialty resins. Similarly, we also demonstrated the reduction of mevalonolactone to produce MPTO, a C6 triol qualitatively similar to glycerol. Although both MBDO and MPTO were previously too expensive for most commercial applications, the development of an efficient reduction method that utilizes inexpensive and abundant precursors (i.e., IA, MA, and MLA) will enable their low-cost production and use.

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Keywords: biomass · diols · heterogeneous catalysis · polymers · sustainable chemistry

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