DOI: 10.1002/cssc.201000396

Reactive Extraction of Levulinate Esters and Conversion to γ-Valerolactone for Production of Liquid Fuels

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Biomass has been identified as a source of renewable carbon for the production of energy, fuels, and chemicals, facilitating a decreased dependence upon petroleum and a global reduction in greenhouse gas emissions. A promising approach for the utilization of lignocellulosic biomass is the controlled reduction of the biomass feedstock's oxygen content, to produce platform chemicals that retain sufficient functionality for upgrading to a variety of end products. In this respect, levulinic acid (LA) has been identified as an attractive platform molecule from which fine chemicals (e.g., δ-aminolevulinic acid, diphenolic acid) and fuel additives (e.g., levulinate esters, methyltetrahydrofuran) can be produced.[1] A particularly promising derivative of LA is γ-valerolactone (GVL),[2] from which gasoline, jet fuel, and diesel fuel components can be produced.[3–6] The production of equimolar quantities of levulinic acid and formic acids can be achieved, in good yield, from lignocellulosic biomass[7,8] and cellulose[5] through hydrolysis with dilute sulfuric acid. The hydrolysis of cellulose has been demonstrated through several strategies. For example, treatments that use dilute sulfuric acid,[5] concentrated hydrochloric acid,[9] solid acids,[10] or ionic liquids[11] all yield levulinic and formic acids as degradation products. To date, the preparation of levulinic acid through hydrolysis with dilute sulfuric acid appears to offer the most promising balance of cost, yield, and scalability, although further developments are needed in product recovery and sulfuric acid management. GVL can be obtained through the reduction of levulinic acid over a metal catalyst, preferably by consuming hydrogen generated in situ via the decomposition of formic acid.[12–14] However, the production of GVL by catalytic reduction of LA is complicated by the need to separate LA from sulfuric acid, as residual sulfur leads to low catalytic activity and deactivation with time-on-stream.[5,15] Although promising strategies have been demonstrated for the production of GVL from levulinic and formic acids,[16,17] these strategies are carried out without sulfuric acid and its carryover must be addressed. Therefore, the motivation of the present work is to demonstrate improved sulfuric acid management in levulinic acid-centered biorefining. In the present state of the art, H_2SO_4 is recovered from LA in an energy-intensive process that involves solvent extraction combined with distillation. Herein, we report an improved, synergistic biorefining strategy that does not require the use of external solvents or energy-intensive distillation steps to separate the levulinic and formic acids from H_2SO_4, and instead employs reactive extraction, using butene, to produce hydrophobic esters of levulinic and formic acids. Moreover, we show that these esters spontaneously separate from H_2SO_4 and can be converted to GVL over a dual-catalyst-bed system. As we have shown previously, GVL can be converted to butene and CO_2 by catalytic decarboxylation over an acid catalyst,[3] thereby providing the source of butene required for the reactive extraction step.

The process proposed herein relies on the extraction of levulinic and formic acids using alkenes (i.e., butene), in lieu of using alcohols, for the production of levulinate and formate esters, as first proposed by Manzer et al.[18] In particular, even though Ayoub[19] has demonstrated the reactive extraction of LA using alcohols, such as 1-pentanol, to form hydrophobic levulinate esters, this extraction requires an external source of alcohol and necessitates a distillation step for solvent recovery from the ester product. In contrast, the use of butene as an extracting solvent is particularly advantageous, because butene can be produced from GVL[3] and separates spontaneously from the ester product upon decreasing the system pressure, eliminating both the use of externally produced extracting solvents and the need for distillative solvent recovery. The ester products can be used directly as fuel additives[18,20] or to provide a platform for the production of specialty chemicals.[21] Importantly, we show in the present manuscript that levulinate esters can be converted to GVL in good yield using a dual-catalyst-bed in a single reactor system, while utilizing formate esters and unconverted formic acid (FA) as in situ sources of hydrogen. This dual-catalyst-bed system achieves almost quantitative yields of H_2 from FA and formate esters (over a Pd/C catalyst) as well as high rates of GVL production from LA and levulinate esters (over a Ru/C catalyst), whereas the simultaneous utilization of FA and formates to reduce LA and levulinates cannot be achieved using either of these catalysts alone.

The strategy presented in this paper, summarized in Figure 1, begins with the production of an aqueous solution containing equimolar concentrations (2 M) of LA and FA by hydrolysis of cellulose at 423 K using sulfuric acid (0.5 M).[5] Some of the water and the FA co-product are then removed by an evaporation step to obtain a more concentrated solution of LA and sulfuric acid, containing residual amounts of water and FA, analogous to the initial stages of the Biofine Process.[7,8] The FA product in water is retained for downstream hydrogen production (in the dual-catalyst-bed system mentioned above), and the concentrated LA product is contacted with butene, generating sec-butyl levulinate (BL) and sec-butyl formate (BF) esters as major and minor products, respectively, using H_2SO_4 as a catalyst. We have demonstrated that high yields, 85%, of the levulinate ester can be attained at moderate temperatures

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Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201000396.

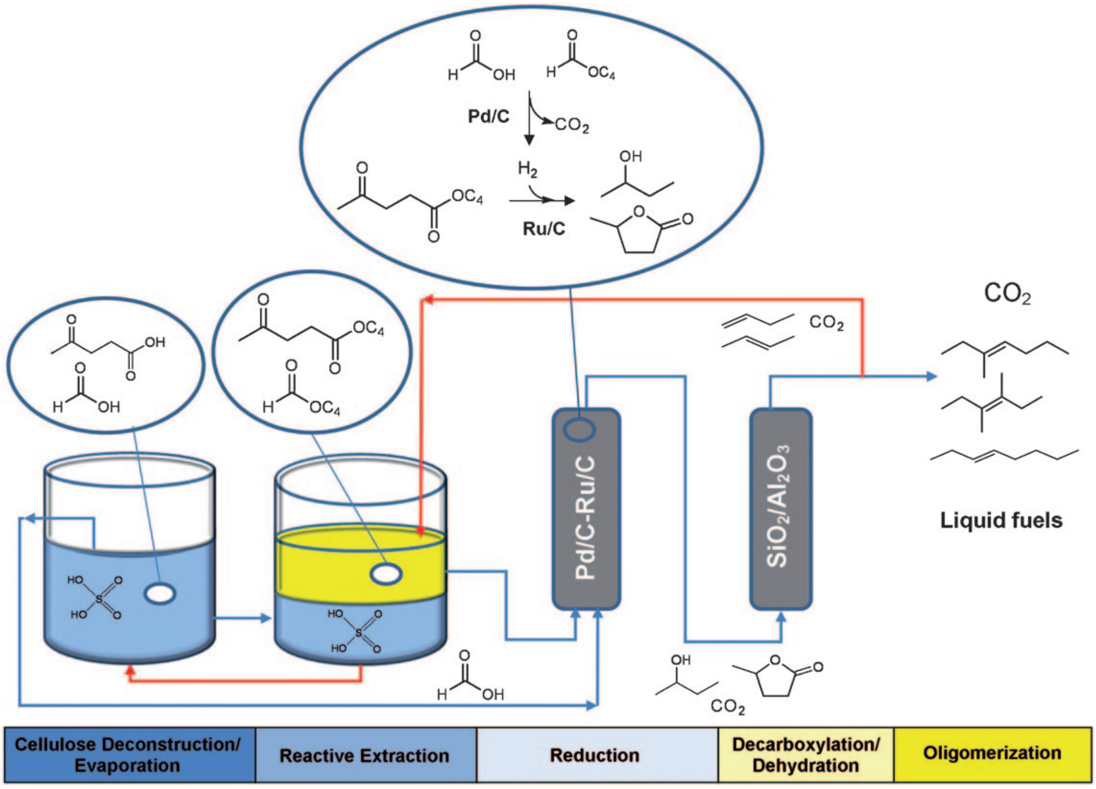

Figure 1. Overall processing strategy, using first a single vessel for cellulose deconstruction and extraction of levulinic and formic acids, followed by a cascade of flow reactors for production of GVL and butene. The red arrows represent streams that are recycled. Butene can be converted into liquid fuels by oligomerization reactions.

(<373 K) and short contact times (<120 min). Excess butene can be recovered by vaporization, and the concentrated ester product is then contacted with water, during which the hydrophobic ester separates spontaneously from the aqueous phase, the latter of which retains 99 % of the sulfuric acid to be recycled for use in biomass deconstruction. The BL and BF esters are subsequently processed in combination with the aqueous FA product stream (obtained from the evaporation step) using a dual-catalyst-bed in a single reactor to produce GVL in nearly quantitative yields with 2-butanol and CO_2 as co-products. The liquid effluent from this reactor, consisting of an aqueous solution of GVL and 2-butanol, can undergo decarboxylation and dehydration (of GVL and butanol, respectively) over a SiO_2/Al_2O_3 catalyst to obtain butene and CO_2.[3] Our experiments for the simultaneous conversion of GVL and a secondary alcohol over SiO_2/Al_2O_3 resulted in almost quantitative yields to the corresponding alkenes from both lactone and alcohol. A portion of the butene can be recycled for the reactive extraction step, and the remainder of the butene (with inert CO_2) can be upgraded by oligomerization to obtain high-molecular weight alkenes suitable for jet-fuel applications.[3] The details for the butene oligomerization step have been published previously,[3] where an 87 % yield was reported for C_{8+} alkenes from an equimolar mixture of butene and CO_2. Table 1 shows results for reactive extraction of levulinic and formic acids at various conditions. As shown in entry 1, esterification of the aqueous solution obtained directly from the cellulose

Table 1. Levulinic and formic acid conversions with sec-butyl levulinate and sec-butyl formate yields obtained for butene extraction experiments with different aqueous phase concentrations, temperatures, and reaction times. Butene:LA molar ratio is equal to 5:1.

Entry	T [K]	t [h]	Feed [M] LA	FA	H_2SO_4	H_2O	Conversion LA [%]	Yield [%] BL	LA org[a] [%]	LA aq[a] [%]	H_2O [g g^{-1} LA]	H_2SO_4 aq [M]
1	403	16	2	0	0.5	40	0	0	0	100	-	-
2	353	2	8	0	2	4.5	91	85	2	7	5	0.4
3	333	4	8	0	2	4.5	86	78	2	12	5	0.4
4	403	2	8	0	2	4.5	85	73	3	12	5	0.4
5	373	2	8	0	2	4.5	91	82	2	7	5	0.4
6	353	2	4	0	1	30	0	0	0	100	-	-
7	353	2	6.4	0	1.6	16.5	55	48	5	40	6	0.4
8	353	2	6.3	2.3	1.6	11.3	84 (48)[c]	78 (43)[c]	5 (28)[c]	11 (24)[c]	1	1.5
9[b]	353	12	6.3	2.3	1.6	11.3	60 (49)[c]	59 (47)[c]	20 (27)[c]	20 (24)[c]	1	1.6

[a] The percentages are calculated based on LA in the initial feed. Partition coefficient ($M_{org}/M_{aq} = 1$). [b] Butene:LA molar ratio is equal to 2:1. [c] Refer to FA/BF.

deconstruction step, described by Serrano-Ruiz et al. (2 M LA and FA in 0.5 M H_2SO_4),[5] does not take place at our reaction conditions, which are similar to conditions suggested by Manzer et al.[18] Importantly, however, we have found that the formation of butyl esters can be achieved with high yields by employing a concentration step (see Supporting Information) to remove at least a portion of the water. Increasing the concentration of LA and H_2SO_4 results in high yields of levulinates (>85%) at short contact times (2 h; entry 2) and allows for quantitative recovery of the sulfuric acid upon contact with water. It is important to note that the concentration step can be accomplished with a single evaporation, and it is the only energy-demanding separation in this process. Through the formation of hydrophobic butyl esters, the need for solvent extraction and distillation are eliminated, reducing the energy demand of levulinic acid recovery. Increasing the temperature leads to a decrease in the yields (entries 2–5), an increase in the production of degradation products, and a reduction in the amount of H_2SO_4 recovered. The amount of FA present in the LA solution is determined by the extent of evaporative concentration step (see Supporting Information). The presence of FA decreases the concentration of water and increases the yield of BL from 48% (entry 7) to 78% (entry 8), with 43% yield of BF from FA. Upon contact with water after the esterification step, the aqueous phase contains the H_2SO_4 and a portion of the unconverted LA and FA, and this aqueous solution can be recycled to the cellulose deconstruction reactor, in which the LA and FA species are essentially inert.[5] The organic phase after the esterification step and contacting with water contains the BF and BL esters and the rest of unconverted LA and FA (see Table 1 and Supporting Information for detailed analysis). The final amounts of LA and FA in the organic phase depend on the amount of water added to phase separate the esters (see Supporting Information). For example, as shown in entry 7, at 55% conversion of LA, when 6 g of water per gram of LA is added, only 11% of the unconverted acid is retained in the organic phase, whereas 89% remains in the aqueous phase. At a similar LA conversion (60%), in entry 9, when only 1 g of water per gram of LA is added, 50% of the unconverted LA is partitioned into the organic phase and the remainder (50%) remains in the aqueous phase. At these conditions the organic stream contains 80% of the LA initially present in the aqueous feed solution with sulfuric acid, 60% being in the form of the ester product and 20% being the unconverted LA, while 99% of the SA is recovered (1.6 M) in the aqueous phase with the remainder of the unconverted LA (20%).

Table 2. Butyl levulinate and butyl formate conversions with GVL and CO_2 yields and production rates for various feed compositions over 10 wt% Pd/C, 5 wt% Ru/C or the dual-catalyst-bed system. $P=35$ bar, $T=423$ K for entries 3 and 4 and $T=443$ K for the other entries.

Entry	Feed	Catalyst	WHSV [h^{-1}]	Conversion [%] BL/BF	Yield [%] GVL/CO_2	Gas phase conversion [%][f]
1[a]	2 M BL	Ru/C	5.5[b]	21/-	19/-	0.5
2[a]	2 M BL & 6 M H2O	Ru/C	5.5[b]	78/-	76/-	0.9
3[a]	1 M BL & 6 M H2O	Ru/C	0.9[b]	91/-	89/-	1.5
4[a]	1 M BL & 1 M BF & 6 M H2O	Ru/C	1.3[b]	24/45	22/22	0.7
5[a]	2 M BF	Pd/C	0.5[b]	-/10	-/5	-
6[a]	2 M BF & 6 M H2O	Pd/C	0.5[b]	-/43	-/41	-
7	Simulated feed[c]	Pd/C	1.5[e]	51/98 (including FA)	4/95	0
8	Extraction product[d] (Table 1, entry 9)	Pd/C +Ru/C	0.9[e]	96/98 (including LA & FA)	95/92	12

[a] 1-butanol is the solvent. [b] WHSV is calculated using the weight of only the esters in the feed. [c] Organic stream: 4.43 M BL and 1.55 M BF (no additional solvent), aqueous stream: 1.96 M FA. [d] Organic stream: 3.40 M BL, 1.23 M LA and 0.96 M BF, 0.67 M FA (no additional solvent), aqueous stream: 1.83 M FA. [e] WHSV is calculated using total weight of feed and catalyst. (aq. stream volume/org. stream volume = 1.5) For entry 8, the weight ratio of Pd/C to Ru/C = 1.3. [f] Light alkanes produced from the total butanol (solvent + obtained from conversion of butyl esters) and butene present.

Table 2 shows that it is possible to convert BL to GVL and butanol over a Ru/C catalyst (entry 1). While this conversion has been proposed in a patent by the Shell Oil Company,[22] we demonstrate here that the rate of GVL production can be increased significantly by co-feeding water along with the ester (entry 2). We suggest that the presence of water leads to hydrolysis of the ester and thereby enables the reduction to proceed through an LA intermediate, leading to a higher overall rate for GVL production. However, an important deficiency of the Ru/C catalyst is that it does not achieve effective conversion of LA and BL in the presence of FA and BF. For example, it can be seen from entries 3 and 4 in Table 2 that BF inhibits the production of GVL from BL over Ru/C. Moreover, the Ru/C catalyst leads to the undesirable dehydration of FA to produce CO and H_2O, as well as the desirable dehydrogenation pathway to yield CO_2 and H_2,[23] thereby decreasing the hydrogen production rate from BF. In addition, the Ru/C catalyst leads to methanation of CO[24] (formed by dehydration of formic acid), which consumes additional H_2 (required for LA reduction).

The limitations of the Ru/C catalyst for the combined conversion of levulinic and formic esters can be alleviated by using an upstream bed of Pd/C, which favors the desirable dehydrogenation of FA to H_2 and CO_2 compared to dehydration reactions leading to H_2O and CO. In particular, it has been reported that nearly quantitative yields of CO_2 and H_2 can be obtained from FA over Pd/C at temperatures from 360 to 470 K.[25] As seen in entries 5 and 6, we have observed that water is necessary to achieve high rates of BF conversion over Pd/C, suggesting that this conversion takes place through the intermediate formation of FA. In the presence of water, CO_2 is obtained with almost 100% selectivity, confirming a negligible rate of dehydration compared to the dehydrogenation of FA. The positive effect of water on the conversion of levulinic and formic esters is particularly advantageous, since it allows co-feeding over the dual-catalyst-bed system of the aqueous solution of FA, obtained from the evaporation step prior to reactive extraction, along with the organic ester stream. Entry 7 of Table 2 shows that a Pd/C catalyst alone is not effective to convert a feed mixture that contains BL and BF in the organic stream and FA in the aqueous stream. Specifically, while 50% of BL is converted to LA over Pd/C, further reduction to GVL takes place at a very slow rate (0.002 mmol min^{-1} g^{-1}). In contrast, it has been demonstrated that nearly quantitative yields of GVL can be obtained from the reduction of LA over Ru/C[6,18,26,27] at higher activities compared to Pd/C, Pt/C, Rh/C, Re/C, and Ni/C.[26] Thus, given the comparable reaction conditions for decomposition of formate esters over Pd/C and for hydrogenation of levulinate esters over Ru/C, along with the lack of CO_2 methanation over Ru/C,[24] synergy is achieved by combining the catalytic properties of Pd/C and Ru/C in a dual-catalyst-bed reactor to achieve in situ hydrogen generation alongside GVL production. To study this hypothesis, a dual-catalyst-bed of Pd/C followed by Ru/C was used to convert the organic solution of levulinate and formate products obtained by reactive extraction with butene (see Table 1, entry 9), along with the aqueous solution of FA obtained in the evaporation step prior to reactive extraction. Entry 8 in Table 2 shows that BF and FA are converted to CO_2 and H_2 over Pd/C (92% yield), and the conversion of BL and LA to GVL over Ru/C is excellent (95% yield). In the effluent from this dual-catalyst-bed reactor, a small amount of sulfuric acid was detected (0.01 M); however, the catalytic process is stable versus time-on-stream with this feed stream, as demonstrated in Figure 2, where the GVL production rate remains constant at 0.05 mmol min^{-1} g^{-1} after 400 h on stream, corresponding to 94% conversion of LA and BL. Finally, for proper evaluation of the proposed process, we consider a detailed material balance (see Supporting Information) for the results described in Table 2, Entry 8. If unconverted LA and FA are recycled to cellulose deconstruction, approximately 98% GVL and 88% butene yields can be obtained. These estimates consider all the losses in the process, including the generation of unidentified side products and butane (deep hydrogenation product). On a mass basis, 18.3 kg of butene can be obtained from 100 kg of cellulose, and this number corresponds to 88% of the theoretical maximum butene yield, with 60% yield of levulinic and formic acids from cellulose considered as the basis. For the current experimental conditions, the ratio of the butene recycle stream to the butene product stream is equal to 1.5 and could be decreased by increasing the amount of formic acid evaporated and optimizing extraction conditions to minimize the formation of 2-butanol.

In summary, we have described an integrated biorefining strategy for the production of butyl esters and GVL starting from cellulose and utilizing reactive extraction of levulinic and formic acids with butene. This strategy simplifies the recovery and recycle of sulfuric acid for cellulose deconstruction and enables downstream catalytic processing in the absence of sulfur. The mixture of levulinic and formic esters, along with residual levulinic and formic acids, can be converted to an aqueous solution of GVL and 2-butanol in a single step over a dual-catalyst-bed consisting of Pd/C followed by Ru/C, in which H_2 generated from FA and its ester over Pd/C is used for the reduction of LA and its ester to GVL over Ru/C. This dual-catalyst-bed system operates over a wide range of organic acid and ester concentrations, making it adaptable to various extraction conditions. In addition, the biorefining strategy described here eliminates the need for extraction/distillation to recover sulfuric acid and purify levulinic acid, thus potentially advancing the cost effective production of alkenes from renewable lignocellulosic resources. Finally, with minor alterations to this strategy, levulinic acid, levulinates or GVL can be obtained as alternative end-products. In the case of GVL production, increased processing cost due to product isolation may be justified in value added applications, such as the production of α-methylene-γ-valerolactone,[26] caprolactone,[28] or adipic acid.[28]

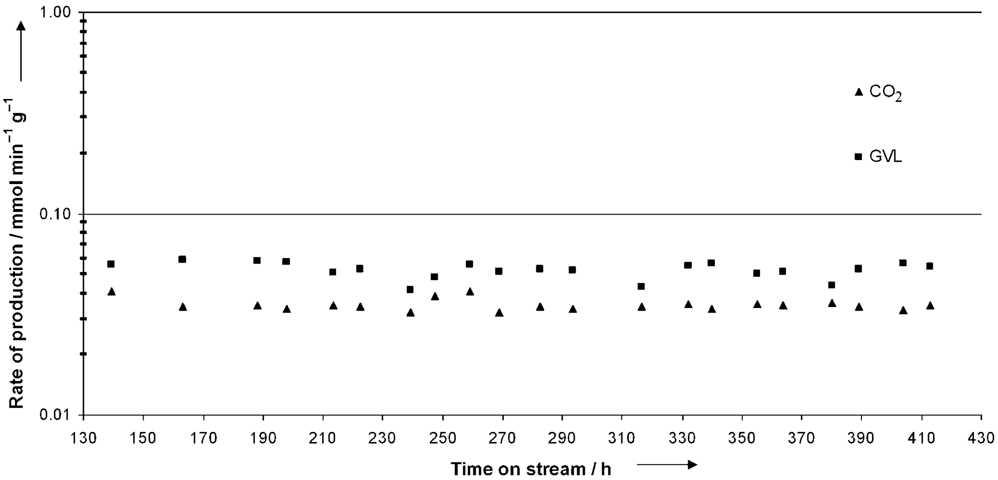

Figure 2. Rates of production of GVL (squares) and CO_2 (triangles) versus time-on-stream over the dual-catalyst-bed reactor system (2 g 10 wt% Pd/C followed by 1.5 g 5 wt% Ru/C) co-feeding the organic stream prepared from the butene extraction step and the aqueous stream obtained from the evaporation step prior to extraction. $T=443$ K, $P=35$ bar.

Experimental Section

Details for feed compositions prior to the reactive extraction step, and for compositions of aqueous and organic solutions formed after reactive extraction with butene in a batch system are given in the Supporting Information. Carbon-supported catalysts containing either 5 wt% Ru or 10wt% Pd were purchased from Sigma–Aldrich. Both catalysts were reduced in situ under H_2 flow at 673 K (ramp rate of 0.5 K min^{-1}) for 2 h. The catalytic reaction kinetics studies were carried out in a fixed bed, down-flow reactor consisting of a half-inch stainless steel tube followed by a gas–liquid separator at room temperature to collect the liquid effluent phase for off-line analysis. Gas chromatography was used to analyze the organic liquid samples, whereas liquid chromatography was used to analyze aqueous phase samples. Gaseous products were analyzed on-line by gas chromatography. Details of the experimental set-up and procedures are given in the Supporting Information.

Acknowledgements

This work was supported in part by the U.S. Department of Energy Office of Basic Energy Sciences, and by the DOE Great Lakes Bioenergy Research Center (httü://www.greatlakesbioenergy.org), which is supported by the U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research, through Cooperative Agreement DE-FC02–07ER64494 between The Board of Regents of the University of Wisconsin System and the U.S. Department of Energy. In addition, this work was supported in part by the Defense Advanced Research Projects Agency (DARPA) and Army Research Lab (ARL) through the Defense Science Office Cooperative Agreement W911NF-09–2–0010/09–005334 B 01 (Surf-Cat: Catalysts for production of JP-8 range molecules from lignocellulosic biomass). The views, opinions, and/or findings contained in this article are those of the authors and should not be interpreted as representing the official views or policies, either expressed or implied, of the Defense Advanced Research Projects Agency or the Department of Defense.

Keywords: biofuels · heterogeneous catalysis · reactive extraction · sustainable chemistry · valerolactone

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Received: November 16, 2010