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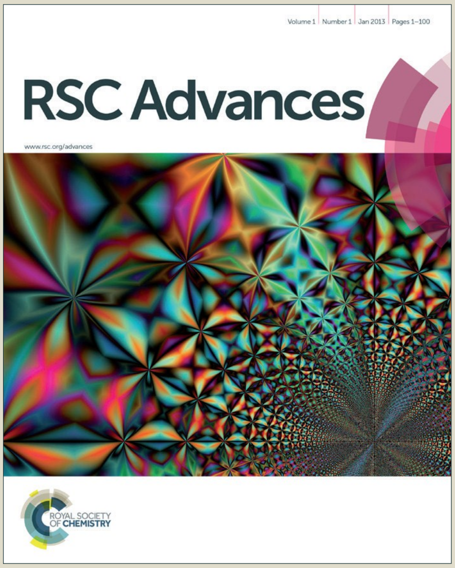

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ARTICLE TYPE

Synergistic catalytic effect of $ZnBr_2$-HCl system for levulinic acid production using microwave irradiation

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A catalytic process for the selective conversion of carbohydrates to levulinic acid is developed. A synergy in the catalytic action is observed when a combination of $ZnBr_2$ and HCl was used as catalyst which is attributed to the *insitu* generation of HBr. Carbohydrates, namely, glucose, molasses and sucrose, were employed as feedstock for levulinic acid production. Microwave irradiation of glucose either in the presence of HCl alone or both HCl and $ZnBr_2$ as catalysts yielded the formation of levulinic acid. But the conversion of glucose to levulinic acid was much faster (only 6 min) when both HCl and $ZnBr_2$ were employed together. The effect of the reaction parameters like, the time of irradiation, % power, and amount of substrate and catalyst on the yield of levulinic acid were studied. The reaction products in each case were analysed using ^1H and ^{13}C NMR. The yield of levulinic acid was estimated using HPLC. The maximum yield of levulinic acid obtained from glucose was 53 wt. %.

1. Introduction

Production of fine and bulk chemicals from renewable sources is one of the current trends in chemical research. Most of the industrial chemicals are currently being derived from petroleum-based resources.[1-3] The industrial chemicals in turn are involved in the production of a wide variety of products forming an essential and integral part of trade and economic activities. Alternate feedstock for the production of chemicals are inevitable owing to the uncertainty in the sustainability of fossil based resources and also because of the adverse effects on the environment.[4-5]

Lignocellulosic biomass is an abundant and renewable resource. The possibility of employing the same as a feedstock for chemicals production is being explored vigorously. Cellulose, a complex polymer of glucose, is the major constituent of the lignocellulosic biomass. Glucose is the obvious monomeric sugar that could be obtained upon the hydrolysis of cellulose in the plant materials. A wide variety of new chemicals are being produced on a lab scale using platform chemicals such as glucose[6], levulinic acid, LA[7], and hydroxyl methyl furfural, HMF[8]. LA is a platform chemical which can be obtained from a wide range of cellulosic biomass feedstock including wastes like paper sludge.[9, 10] Levulinic acid is particularly important owing to its chemical structure with ketonic and carboxylic functional groups. The feasibility of converting levulinic acid to a variety of fine chemicals is high.[11]

For instance, the reduction compound of levulinic acid, i.e., 4 hydroxyvaleric acid is a fuel precursor.[12] The oxidation product of levulinic acid, i.e., succinic acid has a huge market.[13] As a result, the demand for levulinic acid is huge. Faster and economically feasible process for levulinic acid production is being intensely researched.[14, 15]

Recently, Ronen et al. have examined the activity of ZrP and SnP for the conversion of glucose to levulinic acid and concluded that Bronsted sites are necessary for the selective production of levulinic acid.[16] Girisuta et al. have produced 63 mol % of levulinic acid from sugar cane bagasse under the optimal hydrothermal acid hydrolysis conditions (423 K, 0.55 M H_2SO_4).[17]

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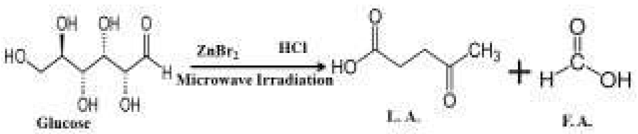
Table 1. Strategies for the production of levulinic acid

Feedstock	Catalytic process	Yield	Reference
Gelidium amansii	Hydrothermal; H_2SO_4 (3 wt. %), 40 h, 180 °C	45.84 wt.%	7
Carbohydrate (glucose, hemicellulose)	Microwave; H_2SO_4, 120 min., 160 °C	69 mol %	23
Sucrose (0.1 M)	Amberlyst-36, 150 °C, 100 min.	65 mM	24
glucose, cellulose, cedar	Pretreatment with [EMIM]P at 150 °C, 60 min; Hydrolysis with H_2SO_4 (5 wt.%) at 220 °C for 2 h	72. 9 mol %	25
Glucose (0.1 M)	H_2SO_4 (1 M), 140 °C, 12 h.	60 mol. %	26
Steam exploded rice straw	$S_2O^{2-}_8$ - ZrO_2-SiO_2-Sm_2O_3; 200 °C; 10 min., 13. 3 wt.% of solid acid catalyst	22.8 wt.%	27
Wheat straw	Hydrothermal process; 209 ºC; acid catalyst (3.5 wt. % of biomass), 37.6 min.	19.9 wt. %	28
Glucose	Hydrothermal process; MFI-type zeolite (SiO_2/ Al_2O_3 = 30 mol. %); 180 °C; 8 h.	35.5 wt. %	29
Cicer arietinum, cotton, *pinus radiata and* sugar cane bagasse	Hydrothermal process , 423 K, 2 h; HCl (1 M)	19 – 44 wt.%	30

Using water hyacinth as feedstock, Girisuta obtained 53 mol % levulinic acid based on the C6 sugar content in the biomass.[18] Najalina et al. have designed a hybrid catalyst (HY-$CrCl_3$) to covert glucose to levulinic acid (62 wt. %) in a reaction under oil bath at 433 K for 180 min.[19] Bevilaqua et al. have used the residual rice husks for the production of levulinic acid. A levulinic acid yield of 59.4 wt. % using 4.5 % (v/v) HCl at 443 K and 56 bar N_2 pressure for 60 min.[20] A lowering of pyrolysis temperature of cellulose from 623 to 473 K was achieved in the presence of $ZnCl_2$ as catalyst resulting in the formation of useful chemicals like levulinic acid, furfural and 5-hydroxy methyl furfural in low yields.[21] Hegner et al. obtained glucose and levulinic acid from cellobiose at 463 K for 24 h using solid acid catalysts (SAC 13 and $FeCl_3$/silica).[22] Some of the recent reports on the conversion of biomass to levulinic acid were summarized in Table 1.

The objective of the current research work is to develop a fast process for the conversion of carbohydrates to levulinic acid under mild reaction conditions. In this article we report faster production of levulinic acid from carbohydrates owing to the unique synergistic effect of HCl-$ZnBr_2$ catalytic system under microwave irradiation. The levulinic acid production process developed was represented in Scheme 1.



Scheme 1. Conversion of glucose to levulinic acid under microwave irradiation

Experimental:

Materials used:

Glucose, sucrose, levulinic acid, formic acid and $ZnBr_2$ were procured from Sigma Aldrich. HCl was purchased from Merck. Molasses (by-product of sugar manufacturing) was procured from a health food supermarket. All the chemicals were used as received. Typical process of converting carbohydrates to levulinic acid involve taking known amounts of carbohydrate (glucose/sucrose/cellulose/molasses) (0.2 g), catalyst (either $ZnBr_2$ (0.5 g) or HCl (1 M, 10 mL) or both together) in a 100 mL round bottom flask and subjecting the contents to microwave irradiation for 1-6 min. Microwave irradiation was conducted in a modified domestic microwave oven operated at 2.45 GHz with an output power of 1200 W at 100 % power.[31] The effect of reaction conditions, like carbohydrate type, microwave irradiation time, ratio of the amount of reactant and the catalyst (wt. /wt. % or wt./vol. %), were evaluated so as to improve the yield of levulinic acid. The reaction temperature attained as a result of microwave irradiation was evaluated using a pyrometer (Fluke, 65 Infrared thermometer) and was found to be 363 K. The reaction products obtained in each case were analysed by ^{1}H and ^{13}C NMR spectroscopic as well as HPLC analysis. NMR spectroscopic analysis was carried out on a Bruker Avance DPX 300 instrument. D_2O was used as a solvent. HPLC analysis was carried out on a Shimadzu system with a refractive index detector (RID-10A). Chromatographic separation was carried out using a strong cation-exchange column (Aminex HPX-87H, 300X 7.8 mm). Levulinic acid, formic acid and glucose in the analytes were qualitatively analyzed by NMR and quantified using HPLC. The yield of reaction products (levulinic acid or formic acid) was calculated based on the following equation:

$$Product\ yield\ (wt.\%) = \frac{Weight\ of\ product}{Initial\ weight\ of\ glucose} X100 \ (1)$$

3. Results and discussion:

3.1. Synergistic effect of HCl and $ZnBr_2$ on the conversion of glucose to levulinic acid

Microwave irradiation of aq. glucose solution (0.2 g in 10 mL) was carried out for 6 min. under three different reaction conditions, namely, (a) without catalyst (neither HCl nor $ZnBr_2$), (b) with HCl (1 M, 10 mL) alone as catalyst, (c) with $ZnBr_2$ (0.5 g) alone as catalyst and (d) with both HCl (1 M 10 mL) and $ZnBr_2$ (0.2 g) as catalyst. The products obtained in each of the four cases were analysed by ^{13}C NMR as shown in Fig. 1. No change in glucose structure was observed without catalyst (neither HCl nor $ZnBr_2$) (Fig. 1 (a)). Also use of $ZnBr_2$ alone has no effect on glucose structure indicating that $ZnBr_2$ as such is not a catalyst for glucose conversion to levulinic acid (Fig. 1 (c)). In the presence of HCl as catalyst, even though glucose was converted to levulinic acid, the conversion of glucose was not complete (Fig. 1 (b)). Intense peaks typical of glucose (60.3 (C6), 69.2 (C4), 72.4 (C2), 73.7 (C3), 75.3 (C5), 92 (C1α) and 95.3 (C1β)) were still present in the reaction product mixture containing levulinic (27.9 (C1), 29.1 (C2), 37.7 (C3) and 177.4 (C4) ppm) and formic (166.3 ppm) acids. Interestingly, when a combination of HCl (1 M, 10 mL) and $ZnBr_2$ (0.2 g) was used as a catalyst, complete conversion of glucose was observed. Peaks characteristic of only levulinic and formic acids were observed in the reaction product and no trace of glucose was noticed (Fig. 1 (d)). This indicate the synergistic effect of HCl and $ZnBr_2$ in the catalytic conversion of glucose to levulinic acid. No synergistic effect was observed, when similar studies were carried with HCl-$ZnCl_2$ catalytic system. This indicate that the *insitu* generation of HBr, according to the following equation, in the case of HCl-$ZnBr_2$ leads to the acceleration of glucose conversion to levulinic acid as HBr is a stronger acid than HCl.

$$HCl + ZnBr_2 \longrightarrow HBr + ZnCl_2$$

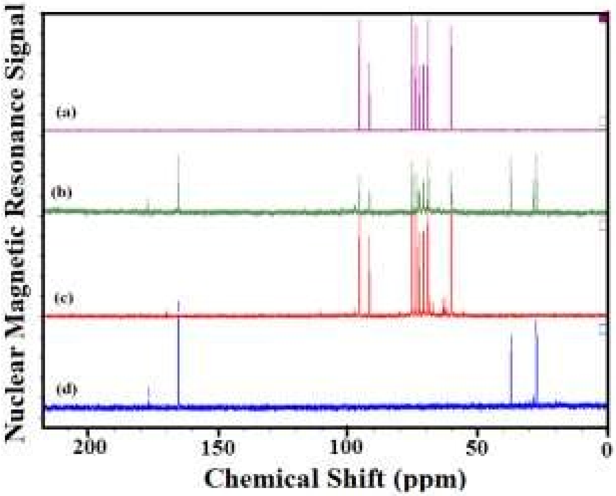


Fig. 1.^{13}C NMR spectra of the product obtained from microwave irradiation (6 min) of glucose in (a) the absence of catalyst (neither HCl nor $ZnBr_2$) (b) with HCl alone (c) with $ZnBr_2$ alone (d) with HCl and $ZnBr_2$.

Such a combination of HCl-$ZnBr_2$ catalyst has never been examined for the conversion of carbohydrates to levulinic acid indicating the significance of the study. Eventhough, no direct evidence for the *insitu* formation of HBr could be provided at this stage, the absence of the synergistic effect in HCl-$ZnCl_2$ system, indicate that *insitu* generation of HBr could be the reason for the observed acceleration of the process.

3.2. Effect of time of microwave irradiation on the conversion of glucose

So as to evaluate the minimum time of irradiation required for the complete conversion of glucose to levulinic acid, the glucose conversion was carried out at different irradiation times (2, 3, 5 and 6 min). Lower the irradiation time, lower is the energy input.

This is one of the requirements for a process to be economically viable. Having learnt that the presence of both HCl and $ZnBr_2$ as a combination are vital for the complete conversion of glucose to levulinic acid, the effect of time of irradiation was studied in the presence of both $ZnBr_2$ and HCl. The reaction mixture comprising of glucose (0.2 g), HCl (1M, 10 mL) and $ZnBr_2$ (0.5 g) was irradiated for 2, 3, 5 and 6 min. The ^{13}C NMR spectra of the reaction products obtained after irradiation for different reaction times were shown in Fig. 2.

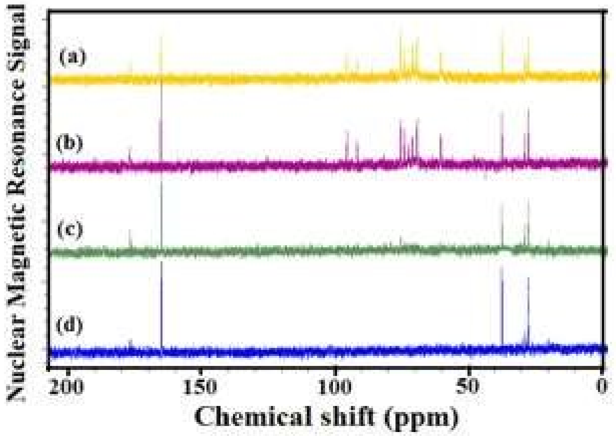


Fig. 2. ^{13}C NMR spectra of the products obtained from microwave irradiation of glucose with HCl and $ZnBr_2$ as catalysts at different irradiation times: (a) 2 min. (b) 3 min. (c) 5 min. (d) 6 min.

Microwave irradiation for 2 and 3 min. was found to be insufficient for the complete conversion of glucose to levulinic acid (Fig. 2a and 2b). The presence of unreacted glucose was observed in the reaction product after 2 and 3 min. of irradiation. Upon increasing the time of irradiation to 5 min. majority of glucose was converted to levulinic acid but still traces of glucose were seen. So as the convert the unreacted glucose, the irradiation time was further increased to 6 min. A complete conversion of glucose to levulinic acid was observed with an irradiation time of 6 min. (Fig. 2 (d)).

3.3. Optimization of amount $ZnBr_2$

After finding that a minimum of 6 min. of irradiation was the optimum for the complete conversion of glucose to levulinic acid and formic acid, the least amount of $ZnBr_2$ that was required to be added to HCl (1 M) for the completion conversion of glucose to levulinic acid was evaluated. The amount of $ZnBr_2$ was systematically varied from 0.1 to 0.5 g. The ^{13}C NMR spectra of the reaction products obtained were shown in Fig. 3.

With the addition of 0.1 g $ZnBr_2$, the conversion of glucose was incomplete and the reactant glucose was still present in the hydrolyzate (Fig. 3(a)). With an increase of $ZnBr_2$ amount from 0.1 to 0.2 g, a steady decrease in in the intensity of peaks typical of glucose and a corresponding increase in the intensity of peaks characteristic of levulinic acid was observed. When the amount of $ZnBr_2$ was increased to 0.5 g, complete conversion of glucose to levulinic and formic acids was noticed.

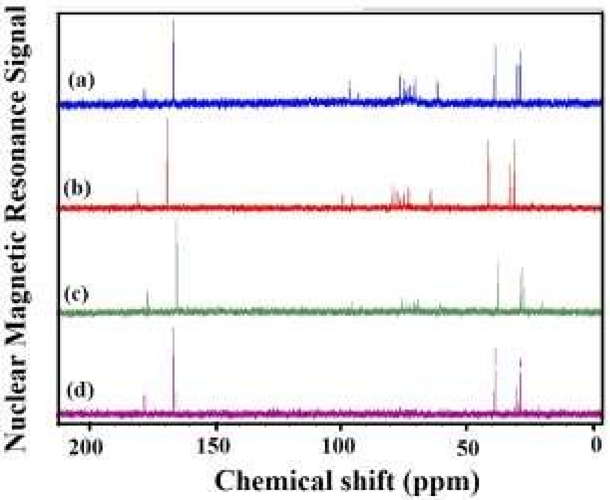


Fig. 3. ^{13}C NMR spectra of the products obtained from 6 min. microwave irradiation of glucose with HCl (1 M) and different amounts of $ZnBr_2$: (a) 0.1 (b) 0.15 (c) 0.2 (d) 0.5 g

3.4. Optimization of concentration of HCl:

After evaluating the optimum time of irradiation and the amount of $ZnBr_2$ required for the complete conversion of glucose, the effect of concentration of HCl on the reaction was studied. With either 0.25 or 0.5 M HCl, the glucose conversion was not complete and traces of glucose were still observed (Fig 4 (a) and (b)). As the concentration of HCl was increased to 1 M, the reaction product mixture contained only levulinic and formic acids (Fig. 4 (c)). Thus, 1 M HCl was the optimum concentration required for the completion of the reaction in 6 min.

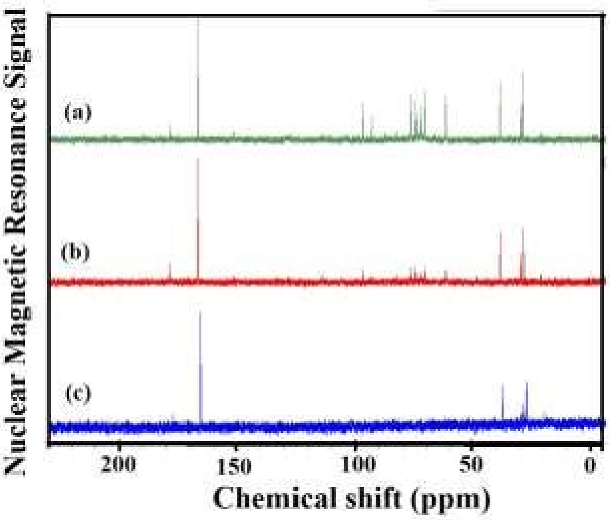


Fig. 4. ^{13}C NMR spectra of the products obtained from 6 min. microwave irradiation of glucose with $ZnBr_2$ (0.5 g) and different concentrations of HCl (10 mL): (a) 0.25 (b) 0.5 and (c) 1 M

3.5. Conversion of sucrose and molasses to levulinic acid

The developed methodology for the catalytic conversion of glucose to levulinic acid was further extended to other carbohydrate feedstock such as sucrose and molasses. The ^{13}C NMR spectra of the reaction products obtained from sucrose and molasses feedstock, upon subjecting them to microwave irradiation under the optimal conditions for glucose conversion were depicted in Fig. S2. In addition to the desired product, the reactant either molasses or sucrose was still present in the product mixture as evidenced from the peaks in the range of 60-100 ppm which were typical of carbohydrate resonance peaks. It could be noticed that, even though sucrose and molasses serve as appropriate feedstock for levulinic acid production, they are less preferred relative to glucose. This is due to the fact that glucose is more readily converted to levulinic acid compared to either sucrose or molasses (Fig. 2(d) Vs Fig. S2).

Thus the order of relative ease of conversion of various carbohydrates to levulinic acid under the reaction conditions was as follows: glucose > molasses ≈ sucrose. This is due to the fact that glucose is a simple C6 sugar whereas sucrose is a disaccharide of comprising of a glucose and fructose monomers. Similar to sucrose, molasses is a mixture of both glucose and fructose. Thus glucose is a potential starting material for the production of the key platform chemical levulinic acid.

3.6. Determination of the yield of levulinic acid from glucose using HPLC analysis:

The final quantification of levulinic acid and formic acid was carried out by HPLC analysis. In concurrence with the ^{13}C NMR analysis, the reaction product obtained from the microwave irradiation of glucose in the presence of HCL (1 M, 10 mL) and $ZnBr_2$ (0.5 g) for 6 min., HPLC analysis also indicated complete absence of glucose and the presence of levulinic and formic acids in the product.

A steady increase in the yield of levulinic acid from 34 to 53 wt. % as the irradiation time was increased from 3 to 6 min. was noticed as depicted in Fig. 5.

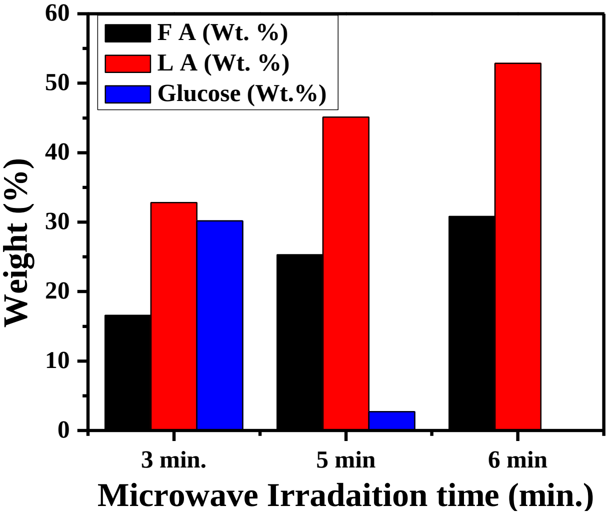


Fig. 5. Quantification of levulinic acid, formic acid and glucose by HPLC in hydrolyzate obtained after the reaction at different microwave irradiation time. (FA = formic acid and LA = levulinic acid).

After 6 min. of irradiation, the formic acid amount was found to be 30 wt. %. Theoretically, equimolar amounts of levulinic and formic acids were expected from the conversion of glucose through the intermediate hydroxy methyl furfural.[1] Thus a 2.5 wt. / wt. % ratio of levulinic acid to formic acid was expected. On the contrary in the present case, a lower value of 1.76 was observed indicating the existence of alternate reaction pathways other than the usual process involving the dehydration of glucose to HMF and its subsequent rehydration to levulinic and formic acids. Moreover, Zeng et al., reported a much lower value of 0.57 (wt. / wt. % ratio of levulinic/formic acids) in the conversion of glucose to levulinic acid using MFI-zeolite and the discrepancy from the usual value of 2.5 was attributed to the properties of the catalyst leading to parallel reaction pathways other than the usual process involving HMF intermediate.[29] Girisuta et al., made a detailed study of the kinetics of the conversion of glucose to levulinic acid. The mechanism of levulinic acid formation from glucose was found to involve the formation of a variety of reaction intermediates, including the formation of reversion products which were difficult to be determined accurately indicating the complexity of the acid catalysed conversion of glucose to levulinic acid.[26]

A comparison of the recent catalytic processes developed for levulinic acid production from carbohydrates indicates that either higher reaction temperature or longer reaction times were usually required, which lead to polymer degradation products like humins and carbon residues (Table 1). Unlike the report of Hassenzadeh et al.,[23] which deals with the synergistic effect of H_2SO_4 and microwave irradiation for the conversion of cellulose to levulinic acid (69 mol %) at a temperature of 433 K for 120 min., the process reported herewith exploits the unique synergistic effect between HCl and $ZnBr_2$ under microwave irradiation yielding 53 wt.% levulinic acid under modest reaction conditions. Such a catalytic system ($HCl-ZnBr_2$) leading to *insitu* HBr formation aiding the faster conversion of carbohydrates to levulinic acid has been reported for the first time.

Conclusion

The present method demonstrates the unique synergistic effect exhibited by the $ZnBr_2$-HCl system for the fast conversion of carbohydrates to levulinic acid. Glucose is the most feasible C6 carbohydrate for the production of levulinic acid. A catalytic process for the high yield (53 wt. %) synthesis of levulinic acid under microwave irradiation was thus demonstrated. The new method for the synthesis of the keto-acid (levulinic acid) was particularly important as it constitutes a key starting material for generating diesel range chemicals.

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TOC

Synergistic catalytic effect of $ZnBr_2$-HCl system for levulinic acid production using microwave irradiation

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Fast production of levulinic acid from carbohydrates owing to the unique synergistic effect of HCl-$ZnBr_2$ catalytic system under microwave irradiation.