CHEMICAL ENGINEERING TRANSACTIONS

VOL. 57, 2017

A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš, Laura Piazza, Serafim Bakalis
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ISBN 978-88-95608- 48-8; **ISSN** 2283-9216

DOI: 10.3303/CET1757025

A Green Chemical Production: Obtaining Levulinic Acid from Pretreated Sugarcane Bagasse

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The Bio Based Press wrote “The production of levulinic acid is gaining momentum”. Today, researches are focusing efforts to convert biomass on new chemicals platforms, including levulinic acid (LA), which has gained increased attention for being an attractive platform for products with high added value. LA can be obtained through the acid hydrolysis of some types of saccharides such as glucose and xylose, the constituent unit of cellulose and hemicelluloses.

In this work, three substantial steps to convert biomass, in this case sugarcane bagasse, in LA were investigated. Sugarcane bagasse was pretreated with acid (121 °C, 1.0 % w/v H_2SO_4, and 80 min) and alkali delignificated (80 °C, 0.5 % w/v NaOH, and 90 min reaction time) both with 20 % w/v of solids loading. Experiments were carried in a discontinuous reactor at different variations of temperature (160, 170 and 180 °C), acid concentration (3, 7 and 5 % w/v H_2SO_4), hydrolysis reaction time (55, 75 and 95 min) and substrate loadings (6, 8 and 12 % w/v).

This research has demonstrated that LA production at 170 °C, 5% w/v H_2SO_4, 75 min and 6 % w/v of solids loading conditions achieved a LA yield of 55.00 ± 0.36 % and selectivity about 45.65 ± 0.26 %.

1. Introduction

Nowadays, biomass as a replacement for petroleum has attracted increasing interest to use a renewable source for fuels and to obtain high added value materials with different properties. Among other biomass types, sugarcane bagasse, in several countries, is generated in large volume as by-products of agro-industrial production. It has been one of the most important industrial crops in Brazil, as part of the ethanol, sugar and electricity co-generation business. According to the Brazilian Sugarcane Association (UNICA, 2016), the 2015/2016 harvest estimate for South-Central Brazil resulted in the production of 618 million tons of sugarcane biomass. Although this work is focused on this feedstock, great part of the knowledge may be used for other biomass, which are region dependent, but potentially available as by-product of agro-food industries.

Levulinic acid (LA) can potentially be obtained with high productivity from agro-industrial residues with a relatively lower market price when compared to the current price (US$ 5-8 per kilo) (Moens 2002; Grand View Research, 2015).

LA stands out among the 12 most promising sugar-based building blocks selected by the U.S. Department of Energy (DOE) as “Top Value Added Chemicals from Biomass” (Werpy and Petersen, 2004). It is a versatile chemical platform with numerous potential applications such as textile dye, antifreezing agent, animal feed, coating material, solvent, food flavouring agent, pharmaceutical compounds, fuel additives, polymer and resin precursors. LA has been employed as a precursor for the production of a variety of chemicals, such as α-angelica lactone, benzodiazepines, butyl levulinate, ethyl levulinate, γ-valerolactone, 1,4pentanediol, 2-methyl-tetrahydrofuran (MTHF), aminolevulinic acid, acetylacrylic acid, diphenolic acid, among others.

Due to the strong bond between cellulose, hemicelluloses and lignin, it is necessary to perform pretreatments because the lignocellulosic biomass requires the selective separation of those bonds. To obtain LA from biomass, degradation reactions occur. After obtaining the glucose, this is dehydrated to 5-

Please cite this article as: Lopes E.S., Dominices K., Lopes M., Tovar L., Maciel Filho R., 2017, A green chemical production: obtaining levulinic acid from pretreated sugarcane bagasse, Chemical Engineering Transactions, 57, 145-150 DOI: 10.3303/CET1757025

hydroxymethylfurfural, which undergoes to further decomposition to LA and formic acid (FA). This process is carried out in an aqueous phase using acid catalysts (mineral acids, inorganic salts, solid Lewis/Brønsted acid catalysts) to release the sugars and to separate the lignin (Kang et al., 2013; Rong et al., 2012). Reaction temperature, acid concentration, substrate loadings and reaction time are considered the most important variables that affect LA production (Fang and Hanna, 2002). Under acidic conditions at elevated temperatures (>150 °C), carbohydrate decomposition can result in a variety of soluble and humins products, with LA and FA (Figure 1) (Chang et al., 2007).

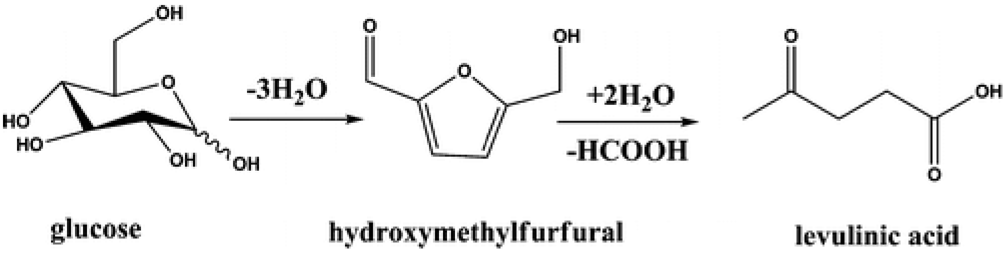

Figure 1: Simplified scheme of LA formation from glucose (Assary et al., 2010).

In 1942, it was reported the first LA production by Moyer patent entitled “preparation of LA”. In sequence, Redmon (1956) mentioned in his patent the use of an acidic cation exchange resin for LA production with minimal formation of insoluble by-products. A recent process for furfural and LA production from lignocellulose-comprising biomass was patented for Vries et al. (2016). The biomass is slurred using water and optionally an acid, subjected to hydrolysis, and then subjected to a solid/liquid separation to yield at least an aqueous fraction comprising C5 and C6 sugars and a solid fraction comprising cellulose and lignin. Furfural is obtained by adding an organic solvent to the aqueous fraction, heating to 120-220 °C for a sufficient time to form furfural, then cooling, and separating an organic phase comprising at least part of the furfural from an aqueous phase. LA is obtained by suspending the solid fraction in water and optionally in an acid, heating the suspension to 140-220 °C, and separating the aqueous fraction comprising the LA from a solid fraction.

The first commercial-scale plant for the synthesis of LA was built in Caserta, Italy, through a process developed by Biofine Renewables (GFBiochemicals). This plant produces LA from cellulose gleaned from local tobacco bagasse and paper mill sludge. The Biofine process involves two stages of acid-catalyzed hydrolysis for the optimal product yield and minimum product degradation and tar formation (Hayes et al., 2008, Ramli and Amin, 2016).

Despite the advantages of LA, there has been limited work reported on its production from biomass and carbohydrates fractionating each biomass compound. Accordingly, this work was aims at identifying the process variables of the acid hydrolysis of cellulose pulp after two previous pretreatment (acid and alkaline pretreatments), and specifically, at defining the operational conditions of temperature, acid concentration, and hydrolysis time in order to obtain high yields and selectivities for LA.

2. Material and methods

Sugarcane bagasse (SCB) was donated by a Brazilian sugar-alcohol-co-generation mill (Usina São João, Araras, São Paulo - Brazil) and its composition is presented in Table 1.

For LA production, the following sequence of procedures were carried out: the acid pretreatment (AP conditions: 121 °C, 1.0 % w/v H_2SO_4, 80 min and 20% solids loading) (Tovar et al., 2014), the alkali delignification (DLG conditions: 80 °C, 0.5 % w/v NaOH, 90 min and 20 % solids loading) and the acid hydrolysis. The last step was carried out in three different conditions: AcH1 with 160 °C, 3 %w/v H_2SO_4, 95 min and 8 % w/v of solids loading, AcH2 with 170 °C, 5 %w/v H_2SO_4, 75 min and 6 % w/v of solids loading and AcH3 with 180 °C, 7 % w/v H_2SO_4, 55 min and 12 % solids loading. The batch tests were conducted in triplicate.

The insoluble solid fraction (ISF), insoluble solid fraction-delignification (ISF-D) and liquid streams were analyzed based on standard procedures (Canilha et al., 2011, Gouveia et al., 2009, Sluiter et al., 2008).

The LA mass yield (%) and selectivity (%) equations are presented below in Eq(1) and Eq(2), respectively. Whereas 0.9 = $C_6H_{10}O_5$ molecular weight / $C_6H_{12}O_6$ molecular weight, 1.397 = $C_6H_{10}O_5$ molecular weight / $C_5H_8O_3$ molecular weight, 1.286 = $C_6H_{10}O_5$ molecular weight / $C_6H_6O_3$ molecular weight and 3.523 = $C_6H_{10}O_5$ molecular weight / CH_2O_2.

$$Yield_{LA} = \frac{LA\ amount\ x\ 1.397}{cellulose\ amount\ inlet} x\ 100 \quad (1)$$

$$S_{LA} = \frac{LA\ amount\ x\ 1.397}{glucose\ amount\ x\ 0.9 + (5\text{-}HMF\ amount\ x\ 1.286) + (LA\ amount\ x\ 1.397) + (FA\ amount\ x\ 3.523)} x100 \quad (2)$$

3. Results and discussions

Acid pretreatment produced an insoluble solid fraction (ISF), or so-called cellulignin. Regarding the chemical composition of the ISF (Table 1), based on a mass in a 20-g batch of raw sugarcane bagasse; the recovered solid material after pretreatment was 11.758 g, which indicates that approximately half of the raw sugarcane bagasse was solubilized.

Table 1: Chemical composition of the raw sugarcane bagasse, cellulignin and cellulosic pulp.

Component	Content (w/w)			Mass in a 20 g batch of raw bagasse, g		
	In raw bagasse	In cellulignin-ISF	In cellulosic pulp	In raw bagasse	In cellulignin- ISF	In cellulosic pulp
Cellulose	40.45	62.47	61.97	8.09	7.35	6.85
Hemicelluloses	30.61	12.48	12.57	6.12	1.47	1.39
Lignin	19.09	23.24	5.85	3.82	2.73	0.65
Others	11.44	1.70	18.78	2.29	0.19	2.08
Total	101.58	99.89	99.17	20.0	11.76	9.41

The hemicellulose was the main solubilized fraction in the sugar-rich liquid stream; it was about 30.61 wt % and it was dissolved to 12.48 wt % after pretreatment. Simultaneously, since a lower percent of soluble hemicellulose remains in the ISF samples, the xylose degradation in sugar-rich liquid occurs, forming degraded products such as furfural and acetic acid.

Analyzing the sugar-rich liquid, results showed that xylose (released sugar) was the main product reporting about 22.00 g/100 g_{SCB}. Moreover, the glucose yield was about 5.42 ± 0.11 % and arabinose about 1.81 ± 0.09 %. For furfural and 5-HMF, the values found were about 0.20 ± 0.01 % and 0.05 ± 0.01 %, respectively.

Alkali (NaOH) delignification plays an important role in order to obtain a cellulose-rich pulp (ISF-D) from cellulignin material from acid pretreatment. At the studied point, it was found a lignin removal around 75.41 ± 0.73 % and 80.00 ± 0.63 % of process yield.

The mass of cellulosic pulp obtained after delignification was 9.41 g, which is equivalent to 80 % of the cellulignin entering delignification.

Analyzing the ISF-D, it is possible to notice a high recovery of cellulose (61.97 w/w) and the percentage of hemicelluloses stays low (12.57 w/w) due to pretreatment. This values allied with the efficient lignin removal prove that the delignification process, in the conditions cited earlier, is a potential procedure to be used in the bioprocess development.

Rocha et al. (2012), when pretreating the sugarcane bagasse and performing subsequent alkaline delignification with 1 % NaOH at 100 ± 2 °C and for 60 min, reached values of 86 % for cellulose, 4 % of hemicelluloses and 6 % of lignin.

In sequence, with the acid hydrolyses, it was achieved of 15.00 ± 0.52 % for AcH1, 55.00 ± 0.36 % for AcH2 and 51.75 ± 0.46 % for AcH3 for LA yield. For the selectivity, it was achieved 38.99 ± 0.15 % for AcH1, 45.65 ± 0.26 % for AcH2 and 46.86 ± 0.14 % for AcH3.

The LA yields in relation to the raw sugarcane bagasse were around 1.79 % for AcH1, 5.08 % for AcH2 and 9.45 % for AcH3.

In Figure 2 is presented the mass balance with the values obtained for glucose, 5-HMF and levulinic acid, in the three conditions applied. The lignin values were not considered since the severity of hydrolyses makes the content of such chemical not significant.

Analyzing the variations in temperature, it is possible to observe an increase in LA yields with such operational variable (in this case from 160 for 180 °C). The value at 160 °C was the smallest (15.00 ± 0.52 %), whereas at 170 °C and 180 °C the values seem to be promising with yields around 55.00 ± 0.36 % and 51.75 ± 0.46 %, respectively.

It is still possible to note that the glucose and 5-HMF contents are present only in AcH1 (160 °C), in small amounts, indicating that the glucose was totally degraded by the process and the 5-HMF was totally converted to LA.

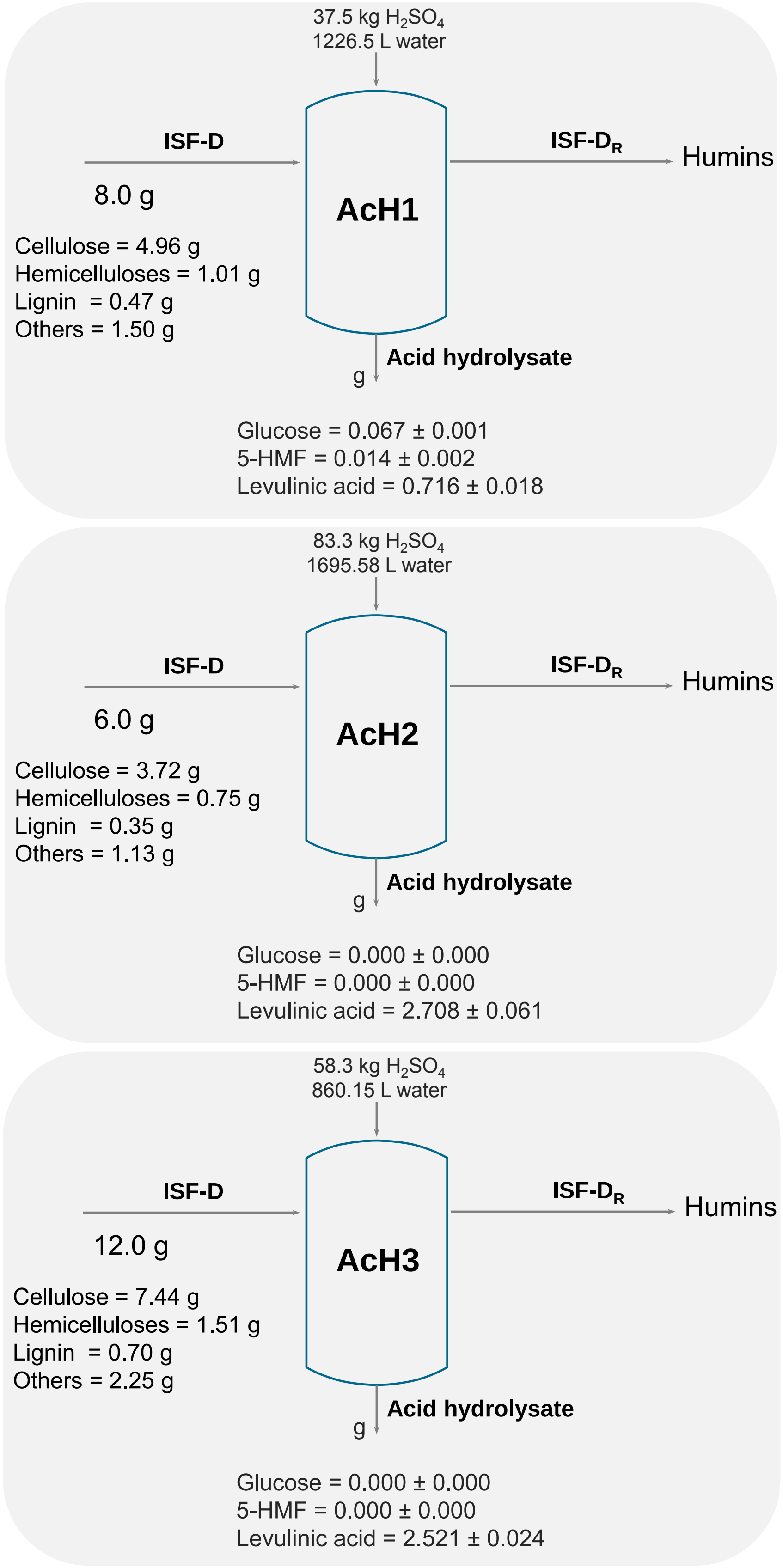

Figure 2: Mass balance for AcH1, AcH2 and AcH3.

It is worthwhile mentioning that, the acid concentrations may play a significant role in LA formation. When this is associated with high temperatures, it was observed that the acid concentrations make LA yields increase, varying from 3 % w/w H_2SO_4 at 160 °C to 7 % w/w H_2SO_4 at 180 °C.

In relation to the operation time, it is noted that a short time is enough when the highest temperature was used. In other words, for LA production, a process at 170 °C and 75 min leads to higher conversion and yields than a process at 160 °C and 95 min.

Puccini et al. (2016) carried out a hydrothermal carbonization (HTC) in orange peel waste for several hours to obtain LA. The experimental results showed that the yield of levulinic acid depends strongly of the reaction conditions. The temperature (from 150 to 180 °C) had a small effect on the LA yield. Instead, the acid concentration had a significant effect, higher concentrations led to higher yields. In strong acidic medium (1 M), the formation of LA was favoured reaching an LA yield of about 21.3 % at 160 °C. This work, differently of the above mentioned one, revealed that the use of higher temperatures is fundamental to achieve higher yields.

Factorial design was employed by Bevilaqua et al. (2013) to optimize the operational conditions looking for the highest yield of LA. They found 59.4 % w/w of LA yield for Soxhlet aqueous extraction of pretreated rice husks using 4.5 % v/v HCl, 170 °C, 56 bar and 60 min. Although the differences in biomass and catalyst the yield value found by the authors is very close to that one achieved for AcH2 (55.00 ± 0.36 %) with the same temperature.

Zheng et al. (2017) used FeCl3 as catalyst in LA production with corn stalk as substrate. Through the experiment, a maximum LA concentration of 16.14 g/L and LA yield of 48.89 % were obtained under 180 °C with 0.5 mol/L $FeCl_3$, 40 min and a solid-to-liquid ratio of 1:9. Like the previous case, although the process differences, with the same temperature (180 °C), the yield value for AcH3 (51.75 ± 0.46 %) is not far from the value reported by the authors.

Regarding selectivity it is possible to note that if increases with temperature (38.99 ± 0.15 % for AcH1 at 160 °C to 46.86 ± 0.14 % for AcH3 at 180 °C).

Ramli and Amin (2016) investigated the glucose conversion using Fe/HY zeolite catalyst in a batch reactor with a temperature range between 120 and 200 °C. They achieved the best LA selectivity with 180 °C. At 180 °C and 60 min, the selectivity value was about approximately 39 %. They concluded that prolonged reaction time at higher reaction temperature has increased the LA production, which could be confirmed from the LA selectivity. The LA yield and selectivity increased due to the increase in reaction temperature and time. However, lower LA yield and selectivity were attained at 200 °C since the LA precursor decomposed to unwanted products, such as humins.

Taking into account the literature results and this work, it is notorious that the use of high temperatures (up to 170 °C) to obtain LA is fundamental to achieve satisfactory results, with the total glucose degraded and high process yield and selectivity.

4. Conclusions

The application of acid pretreatment and alkali delignification in biomass are important to remove the hemicelluloses and lignin content, respectively. These processes allied with an acid hydrolyses contemplate the biorefinery concept. The use of high temperatures in LA production process offers a promising scenario when analyzing the results of LA yields. With 170 °C, 5 % w/v H_2SO_4, 75 min and 6 % w/v of solids loading a LA yield of 55.00 ± 0.36 % and selectivity of 45.65 ± 0.26 % were achieved.

Acknowledgments

The authors gratefully acknowledge the financial support provided by São Paulo Research Foundation-FAPESP (Grant N° 2008/57873-8 and 2015/17592-3).

Reference

Assary R.S., Redfern P.C., Hammond J.R., Greeley J., Curtiss L.A., 2010, Computational Studies of the Thermochemistry for conversion of glucose to levulinic acid, The Journal of Physical Chemostry B, 114, 9002-9009.

Bevilaqua D.B., Rambo M.K.D., Rizzetti T.M., Cardoso A.L., Martins A.F., 2013, Cleaner production: levulinic acid from rice husks, Journal of Cleaner Production, 47, 96-101.

Canilha L., Santos V.O., Rocha G.M., Almeida E Silva J., Giulietti M., Silva S., Felipe M.A., Ferraz A., Milagres A.F., Carvalho W., 2011, A study on the pretreatment of a sugarcane bagasse sample with dilute sulfuric acid, Journal of Industrial Microbiology and Biotechnology, 38, 1467-1475.

Chang C., Cen P., Ma X., 2007, Levulinic acid production from wheat straw, Bioresource Technology, 98, 1448-1453.

Fang Q. and Hanna M. A., 2002, Experimental studies for levulinic acid production from whole kernel grain sorghum, Bioresource Technology, 81, 187-192.

Gouveia E.R., Nascimento R.T.D., Souto-Maior A.M., Rocha G.J.D.M., 2009, Validação de metodologia para a caracterização química de bagaço de cana-de-açúcar, Quimica Nova, 32, 1500-1503.

Gran View Research, 2015, Levulinic acid market to grow at 5.7% CAGR from 2014 to 2020 <http://www.grandviewresearch.com/press-release/global-levulinic-acid-market> accessed 08.03.2017

Hayes D.J., Fitzpatrick S., Hayes M.H.B., Ross J.R.H., 2008, The Biofine process – production of levulinic acid, furfural, and formic acid from lignocellulosic feedstocks, in: Biorefineries-Industrial Processes and Products, Wiley-VCH Verlag GmbH, 139–164.

Kang K.E., Park D.H., Jeong G.T., 2013, Effects of inorganic salts on pretreatment of Miscanthus straw, Bioresource Technology, 132, 160–165.

Moens L., 2002, Sugar cane as a renewable feedstock for the chemical industry: Challenges and opportunities, in Sugar Processing Research Conference.: New Orleans, USA, 26-41.

Puccini M., Licursi D., Stefanelli E., Vitolo S., Galletti A.M.R.G., Heeres H.J., 2016, Levulinic acid from Orange peel waste by hydrothermal carbonization (HTC), Chemical Engineering Transactions, 50, 223-228.

Ramli N.A.S. and Amin N.A.S, 2016, Kinetic study of glucose conversion to levulinic acid over Fe/HY zeolite catalyst, Chemical Engineering Journal, 283, 150-159.

Redmon B.C., 1956, Process for the production of levulinic acid, US Patent 2,738,367.

Rocha G.J.M., Gonçalves A.R., Oliveira B.R., Olivares E.G., Rossell C.E.V, 2012, Steam explosion pretreatment reproduction and alkaline delignification reactions performed on a pilot scale with sugarcane bagasse for bioethanol production, Industrial Crops and Products, 35, 274-279.

Rong C., Ding X., Zhu Y., Li Y., Wang L., Qu Y., Ma X., Wang Z., 2012, Production of furfural from xylose at atmospheric pressure by dilute sulfuric acid and inorganic salts, Carbohydrate Research, 350, 77–80.

Sluiter A., Hames B., Ruiz R., Scarlata C., Sluiter J., Templeton D., Crocker D., 2008, Determination of structural carbohydrates and lignin in biomass - NREL/TP-510-42618, Laboratory Analytical Procedure (LAP), Revised August 2012 ed.: National Renewable Energy Laboratory.

Tovar L.P., Maciel M.R.W., Filho R.M., 2014, Plug flow reactor model to analyse operating conditions on the dilute H2SO4-acid hydrolysis of sugarcane bagasse at high-solids loading, Chemical Engineering Transactions, 37, 325-300.

UNICA (Brazilian Sugarcane Industry Association), 2016, BI-WEEKLY BULLETIN − 2015/2016 SUGARCANE HARVEST IN SOUTH − CENTRAL BRAZIL <http://english.unica.com.br/files/documents/sid/40196004/> accessed 04.01.2017

Vries D.J.G., Kroon J.A., Parton R.F.M.J., Woestenborghs P.L., Rijke D.A., 2016, Process for the production of furfural and levulinic acid from lignocellulosic biomass, US Patent 9,346,730 B2.

Zheng X., Zhi Z., Gu X., Li X., Zhang R., Lu X., 2017, Kinetic study of levulinic acid production from corn stalk at mild temperature using $FeCl_3$ as catalyst, Fuel, 187, 261-267.

Werpy T., Petersen G., 2004, Top value added chemicals from biomass, Pacific Northwest National Laboratory, National Renewable Energy Laboratory.