Electronic Supplementary Material (ESI) for Energy Advances.

Supplemental Material

Literature Review

Numerous studies have detailed the acid-catalysed hydrolysis of carbohydrates in other alcohols in a one-pot system. These reports were recently addressed in a comprehensive review by Galletti and co-workers [1].

The reaction of ethanol, in the presence of a Brønsted and/or Lewis acid catalyst, with; glucose [2-23], fructose [2, 5-7, 10-12, 16, 18, 20, 21, 23-32], sucrose [2, 4, 5, 9, 12, 16, 18, 21, 27, 29, 33], mannose [16], maltose [16], inulin [2, 5, 9, 10, 16, 18, 20, 27], cellulose [7, 9, 34-41], starch [10] and a range of biomasses [8, 42-54] has been shown to form ethyl levulinate. These reports use a diverse range of catalysts including mineral (Brønsted) acids [2-5, 38, 40], metal salts (Lewis acids) [6, 37, 41, 55], ion exchange resins [10, 38, 55], sulfonated nanomaterials [4, 7, 10, 18, 30, 33, 55], polyoxometalates [9, 11, 18, 20, 23, 27, 36, 39], zeolites [3, 8, 14, 16, 17, 20, 56], ionic liquids [29, 34] and other miscellaneous nanomaterials [10, 12-15, 17, 19, 22, 24, 25, 28]. Generally, reaction temperature ranges from 120 – 200 °C, while reaction times from 0.5 – 24 hours. The ethyl levulinate yields (mol%) achieved by these catalysts on the ethanolysis of glucose are presented in the results and discussion section of this paper.

The majority of these investigations have focused on investigating the effect of the catalyst on the resulting yield of ethyl levulinate. Both homogeneous and heterogeneous Brønsted and Lewis acids (and combinations thereof) have been investigated intensively. The archetypal catalyst for this reaction is sulphuric acid (H_2SO_4). Sulphuric acid has several benefits, including low price and abundance on an industrial scale. Silva *et al.* have performed a rigorous techno-economic-analysis on the production of ethyl levulinate from lignocellulosic biomass [57]. They analysed 148 individual production process scenarios and identified fifty-three as the most commercially viable processes, all using sulphuric acid as a catalyst. This shows that complex catalysts appear unlikely to allow economic viability despite notable efforts in identifying new catalytic systems for these reactions.

To date, the highest yield of ethyl levulinate from glucose, 81 %, results from combining acid SnO_2 (Lewis acid) and zeolite H-USY (Brønsted acid) [22]. Similarly, the highest reported yield of ethyl levulinate from cellulose is 75 %, using a combination of the Lewis acid $Y(OTf)_3$ and the Brønsted acid, H_3PO_4 [35]. Lewis acids are proposed to catalyse the isomerisation of glucose to fructose and consequently produce higher yields of ethyl levulinate [22]. This can be used to rationalise the observation that the maximum yields of ethyl levulinate from glucose and cellulose via Lewis acid-catalysed isomerisation are approximately equivalent to those obtained from fructose. Thus, the synergistic combination of Lewis and Brønsted acids appears to be a viable strategy to improve the yield of ethyl levulinate from glucose and cellulose. Notably, however, despite a host of studies into more exotic singular Lewis or Brønsted catalytic systems, they generally offer minimal improvements in ethyl levulinate yields compared to sulphuric acid. This is because the rate of reaction depends on the concentration of the hydrogen cation, regardless of its source.

Many studies suggest the use of heterogeneous catalysts. This is most often rationalised in the context of process improvement, recognising that heterogeneous catalysts are more easily removed from the reaction media and recycled. However, while this may be true for ideal model systems (i.e., glucose, fructose, and cellulose), the ethanolysis of biomass results in the formation of insoluble polymeric materials known as humins which prevent the easy recovery of these catalytic materials [1]. For these reasons, sulphuric acid is the catalyst most widely employed in the literature for the ethanolysis of biomass and is also the catalyst chosen in this work.

When considering the alcoholysis processes that use sulphuric acid as the catalyst, there is a clear absence of a detailed and reliable dataset that establishes the steady state conditions of ethyl levulinate production from pure carbohydrates and real-world biomass. This work addresses this knowledge gap by establishing the steady-state conditions for ethyl levulinate production from glucose, cellulose, and corn cob (5, 10, and 20 mass%) at 150 °C. This data has been cast as a detailed kinetic model that accurately describes the experimental yields of crucial chemical species. Moreover, with optimal reaction conditions established, future work entails a temperature-dependent study on the steady states of ethyl levulinate production from pure carbohydrates and real-world biomass.

Multiple Linear Regression

A detailed literature review was performed on the alcoholysis of glucose to produce ethyl levulinate in ethanol solvent, for various catalysts in a one-pot process. From the data gathered (30 reported yields of ethyl levulinate from glucose), multiple linear regression (MLR) was performed to identify which reaction conditions were statistically significant with regard the production of ethyl levulinate. The independent reaction variables used in the regression were:

1. Feedstock concentration
2. Ethanol concentration
3. Catalyst concentration
4. Catalyst type
5. Reaction temperature
6. Reaction time

From this analysis, no reaction conditions were determined to be statistically significant. The two most common categories of catalyst used were:

1. Inorganic mineral acid and metal salts.
2. Zeolite based catalysts.

A MLR model was separately created for each catalyst type. Within each catalyst type, models were produced for every combination of the independent variables (reaction conditions). The p-value of each coefficient for the reaction conditions were calculated for each model produced. The p-values are indicators that represent how statistically significant an independent variable is and are found using the probability of the observed data occurring by chance. It was found that for both zeolite based and Inorganic mineral acid and metal salt catalysts, both feedstock loading and reaction temperature were statistically significant variables on the yield of ethyl levulinate from glucose. However, there was not enough data to draw any meaningful conclusions. The models produced from MLR are shown in figures 1 and 2.

A literature review on previous ethanolysis kinetic models was carried out and is presented in table 1.

-0.47*Feedstock (mass%) + 0.21*Temperature(°C) = Yield of Ethyl Levulinate (mol%)

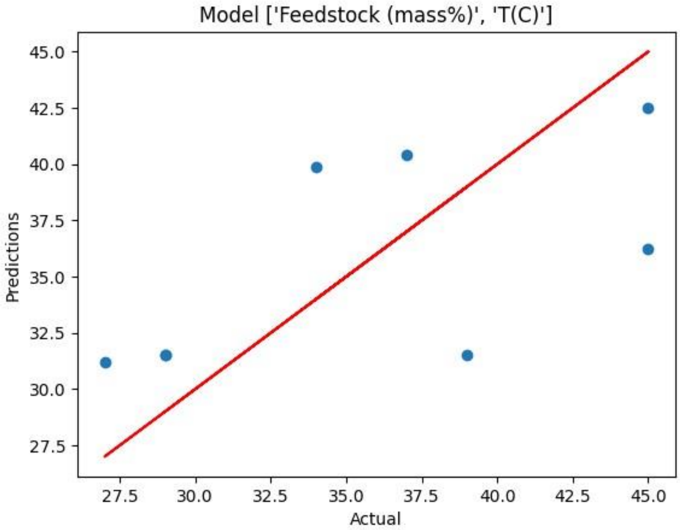

Figure 1. Predicted ethyl levulinate yields (mol%) versus the actual yields (mol%) reported from the literature based on two reaction conditions: feedstock loading (mass%) and reaction temperature (°C). This model only considers glucose as a feedstock and Inorganic mineral acid and metal salts as catalysts. The model's equation is presented above the plot shown.

-3.80*Feedstock (mass%) + 0.29*Temperature(°C) = Yield of Ethyl Levulinate (mol%)

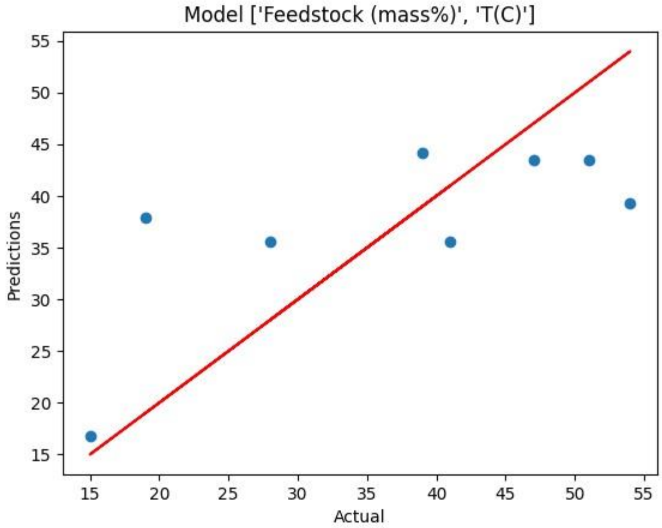

Figure 2. Predicted ethyl levulinate yields (mol%) versus the actual yields reported from the literature based on two reaction conditions: feedstock loading (mass%) and reaction temperature (°C). This model only considers glucose as a feedstock and zeolite based materials as catalysts. The model's equation is presented above the plot shown.

Literature Review of Ethanolysis Kinetic Models

Feedstock	Reaction Time (mins)	Reaction Temperature (°C)	Reaction mechanism	Fidelity	Ref.
Fructose	480	78	$Fructose \xrightarrow{H+} HMF + 3H_2O$ $HMF + Ethanol \xrightarrow{H+} EMF + H_2O$ $EMF\ + 2H_2O \xrightarrow{H+} HMF + Formic\ acid$ $Fructose\ + Ethanol\ \xrightarrow{H+} Ethyl\ glucosides + H_2O$ $Ethyl\ glucosides + H_2O \xrightarrow{H+} fructose\ + Ethanol$	R^2= 0.75	Flannelly et al. [58]
Fructose	250	180	$Fructose \xrightarrow{H+} HMF + 3H_2O$ $HMF + Ethanol \xrightarrow{H+} EMF + H_2O$ $EMF\ + 2H_2O \xrightarrow{H+} HMF + Formic\ acid$ $Fructose\ + Ethanol\ \xrightarrow{H+} Ethyl\ glucosides + H_2O$ $Ethyl\ glucosides + H_2O \xrightarrow{H+} fructose\ + Ethanol$ $Fructose\ \xrightarrow{H+} Unknowns$	R^2= 0.93	Howard at al. [59]
Glucose	1600	180	$Glucose + Ethanol\ \xrightarrow{H+} Ethyl\ glucosides + H_2O$ $Ethyl\ glucosides + H_2O\ \xrightarrow{H+} Glucose + Ethanol$ $Ethyl\ glucosides\ \xrightarrow{H+} Ethyl\ levulinate + Formic\ acid +\ H_2O$ $Glucose\ \xrightarrow{H+} Unknowns\ A$ $Ethyl\ glucosides\ \xrightarrow{H+} Unknowns\ B$	R^2= 0.90	Howard at al. [59]
Glucose	210	160	$Glucose\ \xrightarrow{H+} Ethyl\ levulinate + Ethyl\ acetate$ $Glucose \xrightarrow{H+} Humin + unidentified\ soluble\ products$	R^2= 0.986	Zhu et al. [60]
Glucose	210	180	$Glucose\ \xrightarrow{H+} Ethyl\ levulinate + Ethyl\ acetate$ $Glucose \xrightarrow{H+} Humin + unidentified\ soluble\ products$	R^2= 0.986	Zhu et al. [60]
Glucose	210	200	$Glucose\ \xrightarrow{H+} Ethyl\ levulinate + Ethyl\ acetate$	R^2= 0.986	Zhu et al. [60]

Table 1. Literature review of the kinetic modelling of the ethanolysis of carbohydrates using a sulphuric acid catalyst for a closed homogeneous isothermal reaction system.

Ultimate and Proximate Analysis of Humins

Table 2. Ultimate and Proximate Analysis of humin samples

Reaction Conditions				Elemental Analysis (mass %) *db*										Proximate Analysis (mass %) *db*			HHV (MJ/kg)
Feedstock	Feedstock Loading (mass%)	Reaction Time (mins)	Feedstock /Acid ratio	Carbon		Hydrogen		Nitrogen		Sulphur		Oxygen		VM	FC	Ash	
				Ave	SD	Ave	SD	Ave	SD	Ave	SD	Ave	SD				
Corn cob	20	8000	10	54.99	1.87	3.61	0.41	1.06	0.03	4.03	0.15	26.14	1.33	55.79	34.02	10.18	19.09
Corn cob	20	8000	40	66.67	0.16	5.23	0.03	0.10	0.01	0.80	0.04	21.15	0.08	58.33	35.62	6.05	26.23
Corn cob	20	10000	10	55.51	3.54	4.09	0.24	1.09	0.02	4.71	0.05	25.54	3.76	54.02	36.92	9.06	20.05
Corn cob	20	4000	10	55.48	0.46	3.80	0.10	1.00	0.01	2.58	0.07	28.81	0.45	52.76	38.92	8.32	19.06
Cellulose	20	10000	40	68.45	0.89	4.89	0.08	0.13	0.01	0.48	0.03	19.96	1.00	58.57	35.35	6.08	26.57
Corn cob	20	6000	10	60.32	1.60	4.41	0.38	1.14	0.09	3.32	0.72	21.16	2.79	54.92	35.44	9.65	22.92
Corn cob	20	9000	10	62.47	1.19	4.64	0.10	1.15	0.02	2.41	0.11	19.69	1.42	55.58	34.78	9.64	24.23
Corn cob	20	7000	10	56.20	3.33	4.10	0.35	1.07	0.07	2.28	0.10	27.18	3.85	54.09	36.75	9.17	20.01
Corn cob	10	10000	20	60.64	1.14	4.44	0.10	1.21	0.01	0.85	0.09	23.24	1.13	53.24	37.13	9.63	22.70
Corn cob	20	5000	10	54.58	1.38	3.50	0.47	1.00	0.00	1.72	0.06	29.41	1.91	52.86	37.34	9.80	18.21
Corn cob	20	10000	40	56.50	1.20	6.02	0.25	1.03	0.02	0.49	0.32	25.63	1.29	65.86	23.80	10.34	23.11
Cellulose	20	6000	40	69.25	3.20	4.89	0.23	0.12	0.00	1.08	0.03	18.41	3.46	55.33	38.41	6.25	27.10
Corn cob	20	9000	40	50.91	2.01	5.27	0.11	0.96	0.01	1.28	0.20	32.03	2.33	67.72	22.73	9.55	19.02
Corn cob	20	4000	40	49.20	4.53	5.28	0.55	0.87	0.07	1.11	0.36	33.29	5.51	70.25	19.51	10.24	18.24
Corn cob	20	7000	40	48.03	0.82	5.08	0.08	0.85	0.03	1.13	0.02	34.65	0.95	68.77	20.98	10.25	17.31
Cellulose	20	7000	40	63.84	0.56	4.33	0.07	0.09	0.00	0.92	0.01	25.32	0.63	57.00	37.50	5.50	23.25
Cellulose	20	9000	40	64.21	5.64	4.03	1.07	0.11	0.01	0.82	0.16	30.51	6.88	61.70	37.98	0.32	22.04
Corn cob	20	5000	40	47.85	0.59	5.03	0.03	0.88	0.01	0.76	0.10	40.58	0.53	72.60	22.49	4.90	16.12
Cellulose	20	5000	40	64.65	0.38	4.79	0.00	0.06	0.00	0.88	0.03	28.91	0.34	65.60	33.68	0.72	23.54
Corn cob	20	6000	40	49.92	0.89	4.96	0.12	0.93	0.01	0.69	0.03	38.64	1.06	71.54	23.59	4.87	17.07
Corn cob	20	8000	40	51.55	2.45	5.23	0.29	0.95	0.06	0.96	0.39	36.23	3.19	72.13	22.77	5.09	18.43
Cellulose	20	4000	40	67.44	5.00	4.54	0.63	0.08	0.00	0.76	0.06	26.49	5.58	63.30	36.01	0.69	24.57

db = dry basis, Ave = average, SD = standard deviation, VM = volatile matter, FC = fixed carbon, and HHV = high heating value.

$$HHV\ \left(\frac{MJ}{kg}\right) = \left(0.3383\ \times C_{(db)}\right) + (1.422\ \times (H_{(db)} - \left(\frac{O_{(db)}}{8}\right))$$

Destination of Sulphuric from Acid Catalyst

After alcoholysis, most of the sulphur content is present in the humins (≥93.9 %). This is evidenced by the data below in table 2. Considering the longest reaction time (10000 mintes), and lowest feedstock/acid ratio (10), shown in table 1, the humins produced have a sulphur content of 4.71 mass %. The mass of humins produced from this reaction is 0.65 g, giving 0.031g of sulphuric present in the humins. For this reaction, 2 mass % of sulphuric acid was used in a total reaction system of 5 g, which is the equivalent of 0.1 g of sulphuric acid initially. This gives a sulphur content of 0.033 g.

$$Recovered\ Sulphuric\ Content = \frac{Sulphur\ in\ Humins\ at\ 10000\ minutes\ (g)}{Sulphur\ in\ Acid\ Catalyst\ (g)} \times 100\% = \frac{0.31}{0.33} \times 100\% = 93.9\ \%$$

Considering the inherent mass loss attributed to humins measurements via centrifugation, this is a sufficiently high percentage to conclude that most, if not all the sulphur from the acid catalyst is present in the produced humins after ethanolysis reactions.

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