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Erny Encarnacion Munoz [a], Daniele Di Menno Di Bucchianico [a,b], Christine Devouge-Boyer [d], Julien Legros [d], Christoph Held [e], Jean-Christophe Buvat [a], Valeria Casson Moreno [c], Sébastien Leveneur [a,*]

[a] INSA Rouen Normandie, Univ Rouen Normandie, Normandie Univ, LSPC UR 4704, Rouen F-76000, France
[b] Dipartimento di Ingegneria Chimica, Civile, Ambientale e dei Materiali, Alma Mater Studiorum—Università di Bologna, via Terracini 28, Bologna 40131, Italy
[c] Department of Civil and Industrial Engineering, University of Pisa, Largo Lucio Lazzarino n. 1, Pisa 56126, Italy
[d] Univ Rouen Normandie, INSA Rouen Normandie, CNRS, Normandie Univ, COBRA, Rouen F-76000, France
[e] Laboratory of Thermodynamics, Department of Biochemical and Chemical Engineering, TU Dortmund University, Emil-Figge. Str.70, Dortmund 44227, Germany

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ABSTRACT

In the context of cellulose valorization, we studied the kinetics of levulinates synthesis via the solvolysis of 5-HMF by alcohol over Amberlite IR-120. The alcohol plays a double role; it is a reactant and acts as the solvent. In the literature, kinetic models were developed for each type of alcohol, but there were no models combining the dual effect of alcohol alkyl group substituent (ROH) as a reactant and solvent. Such global kinetic models can save time and optimize a process by considering the solvent effect. This effect was taken into account via the Kamlet–Abboud–Taft and Taft equations, using Bayesian inference. We studied the kinetics of levulinate production from 5-HMF in a reaction mixture made of alcohol and GVL within a temperature range from 80 to 115 °C. The following alcohols were used: methanol, ethanol, propanol, butanol, pentanol, and hexanol. It was found that the rate of alkyl levulinate production increases faster in alcohol reaction medium compared to water reaction medium, and increases when increasing the alkyl group substitution ($r_{ML}^{Methanol} > r_{EL}^{Ethanol} > r_{PL}^{Propanol} > r_{BL}^{Butanol} > r_{PeL}^{Pentanol} > r_{HeL}^{Hexanol} > r_{LA}^{Water}$). Among the global kinetic models developed in this study, the one that neglects the side reaction of humins was found to be the most reliable.

1. Introduction

Valorization of biomass contributes to decreasing our dependency on fossil raw materials. There are mainly three different technology approaches, which are pyrolysis (Gogoi et al., 2023; Ayub et al., 2023), gasification (Ayub et al., 2023; Verma et al., 2023; Yan et al., 2021) or chemical and enzymatic valorization (Ning et al., 2021), also known as hydrolysis. For the chemical and enzymatic routes, the sugar fraction (cellulose or hemicellulose) or simple sugars (glucose, fructose, etc.) are the most valorized, and can lead to several chemicals and platform molecules like 5-(hydroxymethyl) furfural (5-HMF), sorbitol, alcohol (ethanol, butanol, etc.) or levulinic acid or alkyl levulinates (Takkellapati et al., 2018; Wu et al., 2023). The production of any of these platform molecules depends on the operating conditions, solvent and catalyst.

In the valorization of cellulose or hemicellulose, solvent plays several fundamental roles in depolymerization stages, sugar solubilization, and as reactant. It is the case for the production of 5-(hydroxymethyl) furfural (5-HMF)/levulinic acid (LA) or 5-(alkoxymethyl) furfural (RMF) or alkyl levulinates (RL). The alcohol (ROH) or water influences the solubility of simple sugars like fructose or glucose but also orients the final product, i.e., methyl levulinate if methanol is used, ethyl levulinate if ethanol is used, and so on (Di Menno Di Bucchianico et al., 2022a).

Alkyl levulinates are promising platform molecules identified as potential biofuels and fuel additives (Chen et al., 2019; Karnjanakom et al., 2021; Chithra and Darbha, 2020; Yu et al., 2019; Flannelly et al., 2015; Sajid et al., 2021; Ahmad et al., 2022; Delidovich et al., 2014). They could also be used in the food industry because the combination of LA and sodium dodecyl sulfate is a promising antimicrobial agent (Zhou

* Corresponding author.
E-mail address: sebastien.leveneur@insa-rouen.fr (S. Leveneur).

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Notation

Ea_i	activation energy of reaction *i* [J mol^{-1}]
k_i	Rate constant of reaction *i*
r_i	Rate of generation or comsuption of a species i
R_i	reaction rate *i* [mol L min^{-1}]
R	gas constant [J K^{-1} mol^{-1}]
R^2	coefficient of determination [%]
T	temperature [K]
w_i	weight percent
y_{iu}	experimental observablemean value of the experimental observables
$\widehat{y_{iu}}$	observable simulated by the model
MSD	Mean squared deviation

Greek letters

δ_i	sensitivity factor of a reaction series to steric effects
σ_i^*	near-quantitative measure of the polar effect of a substituent i
ρ	mass density [$kg.m^{-3}$]
ρ_i^*	sensitivity factor of a reaction series to polar effects
ψ	resonance effect between the substituent & the reaction center
ω	weight factor
$\omega_{Cat.}$	catalyst loading [$kg.m^{-3}$]

Subscripts and superscripts

Ref	reference

Abbreviations

5-HMF or HMF	5- (hydroxymethyl) furfural
5-RMF or RMF	5- (alkoxymethyl) furfural
BF	Butyl formate
BL	Butyl levulinate
BMF	5-(Butoxymethyl) furfural
BuOH	Buthanol
EF	Ethyl formate
EL	Ethyl levulinate
EMF	5-(Ethoxymethyl) furfural
EtOH	Ethanol
FA	Formic acid
FID	Flame ionization detector
GVL	γ-valerolactone
HeMF	5-(Hexoxymethyl) furfural
HeOH	Hexanol
HF	Hexyl formate
HL	Hexyl levulinate
KAT	Kalmet-Abboud-Taft
LA	Levulinic acid
LFER	Linear Free Energy Relationships
MeOH	Methanol
MF	Methyl formate
ML	Methyl levulinate
MMF	5-(Methoxymethyl) furfural
ODE	Ordinary differential equation
OF	Objective function
PeF	Pentyl formate
PeL	Pentyl levulinate
PeMF	5-(Penthoxymethyl) furfural
PeOH	Pentanol
PF	Propyl formate
PL	Propyl levulinate
PMF	5-(Propoxymethyl) furfural
PrOH	Propanol
ROH	Alcohol group i.e methanol, ethanol, etc

et al., 2020a). Besides, levulinic acid and alkyl levulinates can be hydrogenated into γ-valerolactone (GVL), an essential intermediate for fuel production (Yan et al., 2015; Bond et al., 2010) and as solvent biomass valorization for its dissolution properties (Raj et al., 2021; Lu et al., 2023; Ahmed et al., 2020; Xue et al., 2016).

One of the first studies on the production of alkyl levulinates using different alcohols from glucose was conducted by Brown et al (Brown et al., 1982).: they tested other alcohols but did not show any kinetic profiles. Several studies demonstrate that the production goes through 5-HMF for levulinic acid and 5-(alkoxymethyl) furfural (5-RMF) for alkyl levulinates (Di Menno Di Bucchianico et al., 2023, 2022a; Zheng et al., 2017; Jung et al., 2021; Ramli and Amin, 2016; Wang and Chen, 2016; Wang et al., 2022).

The development of biomass processes is complex because several time-consuming stages are needed to find appropriate target molecules, the efficient catalyst, and develop kinetic and thermodynamic models for scaleup and process optimization. Besides, solvent or co-solvent screening is also vital in biomass valorization (Liu et al., 2021; Soh and Eckelman, 2016; Meng et al., 2023). The solvent choice is guided by its role in chemical kinetics and process separation (Caron, 2011; Zhou et al., 2020b).

For instance, Mellmer et al. show the benefits of polar aprotic solvents in acid-catalyzed biomass conversion (Mellmer et al., 2014). Yiin et al. reviewed different green solvents for hydrothermal liquefaction of lignin (Yiin et al., 2022). Zula et al. studied the acid-catalyzed depolymerization of lignin by evaluating different solvents, and found that nucleophile presence in solvent and nucleophile strength in solvent significantly impact the kinetics (Žula et al., 2023). Zhang et al. tested different deep eutectic solvents to produce 5-HMF (Zhang et al., 2020). Capecci et al. found the benefits of using γ-valerolactone (GVL) solvent compared to butanol (BuOH) and butyl levulinate (BL) solvents for the hydrogenation of BL (Capecci et al., 2021). Baco et al. used the Kamlet-Abboud-Taft equation to establish a relationship between the kinetics of levulinic acid esterification in different solvents (Baco et al., 2022).

These articles show the need to develop kinetic models, including the solvent effect. However, the consideration of solvent effect in kinetics is challenging because of complex interactions, non-ideality or quantum mechanical effects. The literature shows that the technique to consider the solvent effect can be divided into implicit solvation models, explicit solvation models or quantum mechanical/molecular mechanical methods (QM/MM).

The implicit solvation models are particularly useful when the solvent-solute interaction is weak. Examples are the conductor-like screening model (COSMO), conductor like screening model for real solvents (COSMO-RS) or polarizable continuum model (PCM) (Sure et al., 2021; Gerlach et al., 2022; Saidi et al., 2020; Alibakhshi and Hartke, 2021).

In the explicit solvation models, the solvent molecules are treated explicitly, i.e., they are represented as individual molecules in the simulation. Examples are the Monte Carlo simulation (MC) and the molecular dynamics models (MD) (Tanoury et al., 2023; Chen et al., 2021). QM/MM simulations are to evaluate the structure and property data of molecular structures, and they are essentially used in drug design or protein understanding (Kulkarni et al., 2021).

All these methods can be computationally expensive and time-consuming (Sure et al., 2021; Xu and Coote, 2019, 2022). In the 70 s, Kamlet, Abboud, and Taft developed an empirical approach to consider the solvent effect, named Kamlet-Abboud-Taft equation (KAT), also known as Kamlet-Taft solvatochromic parameters (Kamlet et al., 2007).

From the linear solvation energy relationships (LSERs), they developed a quantitative measure of solvent polarity effect by considering three parameters: solvent capacity to donate hydrogen bonds, solvent capacity to accept hydrogen bonds, and solvent capacity to stabilize or destabilize charges and dipoles.

As mentioned, in the case of RL and 5-RMF production from simple sugar solvolysis by alcohol, alcohol (ROH) plays a double role: solvent and reactant. The motivation of our study was to develop kinetic models considering the dual role of alcohol reaction medium. Our study started with the solvolysis of 5-HMF (Fig. 1) to avoid interference from the complex fructose or glucose dissolution mechanism. The KAT relationships were used to describe the solvent effect, and the Taft equation was used to explain the reactant effect between the substituent R- and the kinetics (Kamlet et al., 2007; Taft, 1952a, 1952b, 1953a, 1953b). Taft showed three main contributions of the substituent R- on the reaction center: the polar, steric and resonance effects. The use of the Taft equation in kinetic modeling has successfully been applied in several reactions, such as esterification (Lilja et al., 2002; Vojtko and Tomčík, 2014) or hydrogenation (Wang et al., 2019).

To the best of our knowledge, it is the first time that a kinetic model includes the solvent effect via the KAT equation and the substituent R- effect via the Taft equation. Such an approach could save time for the kinetic modeling stage by combining substituent and solvent effects on kinetics. A previous study of our group shows that Amberlite IR-120 is an efficient catalyst for this reaction system, and using GVL as a co-solvent is beneficial for this reaction system (Di Menno Di Bucchianico et al., 2023, 2022a, 2022b). In this study, kinetic models of the 5-HMF solvolysis over Amberlite IR-120 in a reaction medium constituted of 70 wt% of alcohol and 30 wt% of GVL were developed. Di Menno Di Bucchianico et al (Di Menno Di Bucchianico et al., 2022b). showed that this alcohol/GVL ratio gave the best results from a kinetic standpoint. Water and different alcohols such as methanol, ethanol, propanol, n-butanol, pentanol and hexanol were used.

2. Experimental section

2.1. Chemicals

All the chemicals used as reagents and solvents are listed in Table 1, along with their purity and supplier. The Amberlite IR-120 H+ form (ion-exchange resin, 94 % of particle have a native particle size range (μm): 300–1180 μm) commercial catalyst was purchased from Thermo Scientific. Nitrogen gas (N_2, purity > 99.999 vol %) came from Linde.

Table 1
List of chemicals used in this work as reagents and solvents.

Chemicals	Acronym	Purity, wt%	Supplier
5-(hydroxymethyl) furfural	5-HMF	96	Apollo Scientific
5-(ethoxymethyl) furfural	EMF	97	Sigma-Aldrich
levulinic acid	LA	≥97	Sigma-Aldrich
γ-valerolactone	GVL	≥99	Sigma-Aldrich
methanol	MeOH	≥ 99.8	Merck
ethanol	EtOH	≥99.5	Merck
1-propanol	PrOH	≥99.7	Merck
1-butanol	BuOH	≥99.5	Merck
1-pentanol	PeOH	≥99	Merck
1-hexanol	HeOH	≥98	Merck
methyl levulinate	ML	≥98.0	Sigma-Aldrich
ethyl levulinate	EL	≥ 99	Sigma-Aldrich
propyl levulinate	PL	≥95	Sigma-Aldrich
butyl levulinate	BL	≥98	Sigma-Aldrich
methyl formate	MF	≥ 97	Sigma-Aldrich
ethyl formate	EF	≥ 97	Sigma-Aldrich
propyl formate	PF	≥ 97	Sigma-Aldrich
butyl formate	BF	≥ 97	Sigma-Aldrich
acetone	-	≥99.9	Sigma-Aldrich

All chemicals were employed without further purification.

2.2. Analytical methods

Reaction samples were diluted in acetone and analyzed by a gas chromatograph Scion 456 GC, equipped with a VF-1701 ms Agilent column (60.0 m length × 250 μm inner diameter × 0.25 μm film thickness) and a flame ionization detector (FID). The injector was set with a temperature of 250 °C, injection volume of 1 μL, and a split ratio of 1:20. Helium (>99.999 vol %) is used as the carrier gas at a constant flow rate of 1.0 ML/min to transfer the sample from the injector through the column and into the FID detector, whose temperature was set to 250 °C. The oven temperature was programmed from 40 to 240 °C with 20 °C/min of ramp rate. Reference samples with standard solutions of pure 5-HMF, LA, EMF and the corresponding alkyl levulinate were used as standards to prepare daily calibration curves. EMF and BL were used as the standard for concentrations of 5-(methoxymethyl) furfural (MMF), 5-(propoxymethyl) furfural (PMF), 5-(butoxymethyl) furfural (BMF), 5-(pentoxymethyl) furfural (PeMH), 5-(hexoxymethyl) furfural (HeMF), hexyl levulinate (HL), pentyl levulinate (PeL) and propyl levulinate (PL) due to their commercial unavailability. Each sample was measured three times on the GC, the standard deviation of the measured concentrations

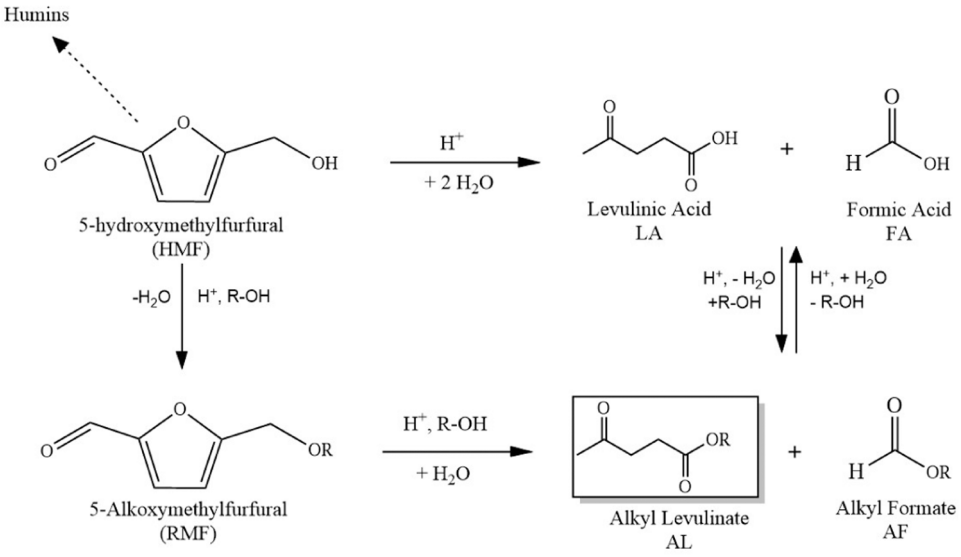

Fig. 1. Pathway for 5-HMF conversion to levulinic acid and alkyl levulinates.

was around 0.03 mol/L.

2.3. Kinetic experiments

Kinetic experiments were performed under isobaric and controlled-temperature conditions in a 300 ML stainless steel batch reactor. The reactor was equipped with an electrical heating jacket, a cooling coil, and a thermocouple capable of measuring the reaction temperature and communicating with the temperature controller. The presence of a gas entrainment impeller (diameter 2.5 cm) with a hollow shaft provided a uniform mixing of the mixture.

As shown in Table 2 for each experiment, the reactor was loaded with 5-HMF initial mass varying between 4 and 5 g, a catalyst loading varying between 2.5 and 4 g and a fixed volume with a ratio of 70/30 %wt alcohol/GVL were used (Di Menno Di Bucchianico et al., 2022a). The rotation speed was set to 800 rpm, since previous studies by Di Menno Di Bucchianico et al. (2022b). on fructose butanolysis using Amberlite IR120 in the same apparatus have demonstrated the negligibility of external and internal mass transfer limitations by using the native catalyst particle size distribution (≥94 %, particle diameters between 300 and 1180 μm) at this agitation speed (Di Menno Di Bucchianico et al., 2022b). For each kinetic experiment (Table 2) fresh catalyst was used; before its use the catalyst was washed with distilled water and then with the pure corresponding alcohol, then dried in an oven for 5 h (Di Menno Di Bucchianico et al., 2022b).

After loading the reaction mixture, catalyst and assembling the reactor, the system was pressurized with nitrogen at 20 bars to avoid any vaporization of the reaction mixture. Then, the temperature heater and rotation stirrer were switched on, and it was defined at time zero. It is essential to stress that when the rotation stirrer was switched on, the time to reach the desired temperature could vary between 15 and 20 minutes. This temperature variation was considered in the modeling, and samples were collected at ambient temperature, 60 °C, 90 °C, then when the desired temperature was reached a sample was taken, and then every hour up to 7 h.

In kinetic experiments, the temperature was set between 80 and 110 °C, without exceeding 120 °C. In fact, active sulfonic sites from Amberlite IR-120 can leach for temperatures higher than 120 °C (Di Menno Di Bucchianico et al., 2023).

2.4. Structure reactivity relationships

For the Taft equation, the substituent Me- is the reference one. Thus, we needed to express all relationships towards this substituent and in the methanol reaction medium.

2.4.1. Taft equation

Based on linear free-energy relationships (LFER), this equation allows predicting kinetic or thermodynamic constants of a chemical reaction based on reactant structure. The LFER is used for a congeneric series of compounds that share the same reaction center or functional group for a specific reaction; such groups can be −SH, −COOH and −CO, etc (Leveneur, 2017). In our system, alcohols share the same functional group −OH, meaning we can use the LFER to relate their reactivity and structure for different reactions.

$$\log\frac{k_{X,-R}^{MeOH}(T)}{k_{X,-Me}^{MeOH}(T)} = \rho_X^{*,MeOH} \bullet \sigma^*(-R) + \delta_X^{MeOH} \bullet E_s(-R) + \Psi_X^{MeOH} \quad (1)$$

where, $k_{X,-R}^{MeOH}(T)$ is the rate constant at a temperature T of a reaction X involving the substituent $-R$ in methanol reaction medium. The terms $k_{X,-Me}^{MeOH}(T)$ is the rate constant of reaction X at the same temperature T of the same reaction but involving the reference substituent in methanol reaction medium, which is the methyl group (CH_3-) for Taft equation. The term $\sigma^*(-R)$ represents the net polar effect of the substituent $-R$ on the functional group or reaction center. It measures the inductive electron-withdrawing or –donating towards the functional group or reaction center. The term $\rho_X^{*,MeOH}$ measures the importance of the polar effect on a given reaction series X in methanol reaction medium. The term $E_s(-R)$ represents the total steric effect due to the substituent $-R$ on the functional group or reaction center. The term δ_X^{MeOH} evaluates the importance of steric effect for a given reaction series. The term Ψ_X^{MeOH} describes the resonance effect between the substituent and the reaction center. In this study, there is no resonance between the selected substituents and reaction center/functional group. The Taft substituent parameters ($E_s(-R)$ and $\sigma^*(-R)$) and the Taft reaction ($\rho_X^{*,MeOH}$, δ_X^{MeOH} and Ψ_X^{MeOH}) parameters were supposed to be temperature-independent, because the temperature range was relatively small.

2.4.2. KAT equation

There is a distinction between non-specific and specific solute-solvent interactions in the KAT approach. The latter interaction, i.e., the solute-solvent specific interactions, comprises solvent Lewis-acidity and solvent Lewis-basicity interactions. The relationship between the rate constant in a solvent $k_X^{Solvent}$ and the solvent properties is expressed in Eq. (2) (Kamlet et al., 2007; Weiß et al., 2021; Nikolć et al., 2010).

$$\ln\left(k_X^{Solvent}\right) = A_{0,X} + s_X \bullet \pi^{*,Solvent} + a_X \bullet \alpha^{Solvent} + b_X \bullet \beta^{Solvent} \quad (2)$$

where, $\pi^{*,Solvent}$, $\alpha^{Solvent}$ and $\beta^{Solvent}$ are solvatochromic solvent pa-

Table 2
Experimental matrix with initial conditions.*

Run	Temp (°C)	mHMF$_0$ (g)	mROH$_0$ (g)	mGVL$_0$ (g)	m$_{dried\ cat}$ (g)	[GVL]$_0$ (mol/L)	[ROH]$_0$ (mol/L)	[HMF]$_0$ (mol/L)	Alcohol
1	100	5	83.71	35.88	4	2.27	16.58	0.28	MeOH
2	110	5	83.71	35.88	4	2.27	16.58	0.27	MeOH
3	100	5	83.6	35.8	4	2.27	11.51	0.30	EtOH
4	110	5	83.6	35.8	4	2.27	11.51	0.27	EtOH
5	100	5	84.67	36.29	4	2.31	8.99	0.26	PrOH
6	110	5	84.67	36.29	4	2.31	8.99	0.28	PrOH
7	100	5	85.22	36.53	4	2.33	7.34	0.26	n-BuOH
8	110	5	85.22	36.53	4	2.33	7.34	0.27	n-BuOH
9	100	5	85.22	36.53	4	2.33	6.17	0.26	n-PeOH
10	110	5	85.22	36.53	4	2.33	6.17	0.26	n-PeOH
11	90	5	83.71	35.88	4	2.27	16.58	0.34	MeOH
12	100	5	83.6	35.8	4	2.27	11.51	0.28	EtOH
13	90	5	83.6	35.8	4	2.27	11.51	0.28	EtOH
14	90	5	85.22	36.53	4	2.33	6.17	0.25	n-PeOH
15	85	4	83.71	35.88	3.5	2.29	16.72	0.22	MeOH
16	80	4	85.22	36.53	2.5	2.33	7.34	0.20	n-BuOH
17	100	5	85.54	36.66	4	2.36	5.39	0.26	n-HeOH
18	110	5	85.54	36.66	4	2.36	5.39	0.25	n-HeOH

* [RMF]$_0$ and [RL]$_0$ initial concentrations are zero in every Run.

rameters, assumed to be temperature-independent. The parameter $\alpha^{Solvent}$ measures the hydrogen-bond donor (HBD) acidity of a solvent. The parameter $\pi^{*,Solvent}$ is a solvent index representing its ability to stabilize a charge via the dielectric effect. The solvatochromic parameter $\beta^{Solvent}$ measures the solvent hydrogen-bond acceptor (HBA) basicity.

The term $A_{0,X}$ is the regression value, representing the rate constant in methanol reaction medium. The regression coefficients (a_X, b_X, and s_X) present the relative susceptibilities of the solvent dependence of $\ln\left(k_X^{Solvent}\right)$ to the solvent parameters. Table 3 displays the solvatochromic solvent parameters for each solvent/environmental condition used in this study (Wang et al., 2019; Islam et al., 2020; Brändström, 1999; MacPhee et al., 1978; Dubois et al., 1980; Panaye et al., 1980; Jessop et al., 2012).

From Table 3, one can notice that all these alcohols have similar abilities to donate hydrogen bonds ($\beta^{Solvent}$). However, their abilities to accept hydrogen bonds ($\alpha^{Solvent}$) vary, with methanol and ethanol showing higher values than the longer-chain alcohols. Additionally, polarizability ($\pi^{*,Solvent}$) tends to decrease as the carbon chain length increases.

The reaction rate of 5-HMF by ROH reactant in an alcohol reaction medium can be expressed as

$$\ln\left(k_{X,-R}^{ROH}\right) = A_{0,X} + s_X \bullet \pi^{*,ROH} + a_X \bullet \alpha^{ROH} + b_X \bullet \beta^{ROH} \quad (3)$$

The reaction rate of 5-HMF by ROH reactant in methanol reaction medium by using KAT relationships is

$$\ln\left(k_{X,-R}^{MeOH}\right) = A_{0,X} + s_X \bullet \pi^{*,MeOH} + a_X \bullet \alpha^{MeOH} + b_X \bullet \beta^{MeOH} \quad (4)$$

In Eqs. (3) and (4), the term A_0, s_X, a_X and b_X are the same, and by subtracting both relationships, we get

$$\ln\left(k_{X,-R}^{ROH}\right) - \ln\left(k_{X,-R}^{MeOH}\right) = s_X \bullet \left(\pi^{*,ROH} - \pi^{*,MeOH}\right) + a_X \bullet \left(\alpha^{ROH} - \alpha^{MeOH}\right) + b_X \bullet \left(\beta^{ROH} - \beta^{MeOH}\right) \quad (5)$$

The kinetic terms $\ln\left(k_{X,-R}^{MeOH}\right)$ can be determined from Taft equation, i.e., Eq. (1):

$$k_{X,-R}^{MeOH} = k_{X,-Me}^{MeOH} \bullet 10^{\rho_X^{*,MeOH}\bullet\sigma^*(-R)+\delta_X^{MeOH}\bullet E_s(-R)} \quad (6)$$

Combination of Eqs. (5) and (6) leads to

$$\ln\left(k_{X,-R}^{ROH}\right) = \ln\left(k_{X,-Me}^{MeOH}(T) \bullet 10^{\rho_X^{*,MeOH}\bullet\sigma^*(-R)+\delta_X^{MeOH}\bullet E_s(-R)}\right) + s_X \bullet \left(\pi^{*,ROH} - \pi^{*,MeOH}\right) + a_X \bullet \left(\alpha^{ROH} - \alpha^{MeOH}\right) + b_X \bullet \left(\beta^{ROH} - \beta^{MeOH}\right) \quad (7)$$

Table 3
Taft and solvatochromic parameters (Wang et al., 2019; Islam et al., 2020; Brändström, 1999; MacPhee et al., 1978; Dubois et al., 1980; Panaye et al., 1980; Jessop et al., 2012).

Alkyl substituent	$\sigma^*(-R)$	$E_s(-R)$	α	β	π	Alcohol
CH_3-	0	0	0.98	0.7	0.6	Methanol
CH_3-CH_2-	-0.1	-0.07	0.86	0.8	0.54	Ethanol
CH_3-CH_2-CH_2-	-0.115	-0.36	0.84	0.85	0.53	n-Propanol
CH_3-$(CH_2)_2$-CH_2-	-0.13	-0.39	0.79	0.84	0.47	n-Butanol
CH_3-$(CH_2)_3$-CH_2-	-0.15	-0.4	0.84	0.86	0.4	n-Pentanol
CH_3-$(CH_2)_4$-CH_2-	-0.124	-0.44	0.80	0.84	0.4	n-Hexanol

3. Experimental results and discussion

3.1. Phenomenological description

The solvolysis of 5-HMF to alkyl levulinates was performed in (H_2O, MeOH, EtOH, PrOH, BuOH, PeOH, HeOH) reaction medium, keeping an alcohol/GVL system of 70/30 wt% ratio over different temperature conditions, initial concentration and catalyst loading. The normalized concentration profiles of each species (Fig. 2) are displayed, except for formic acid (FA). Due its high volatility and low stability, it was not possible to track the concentration of FA.

Kinetic results from Runs 1, 2, 3, 5, 7, 9, and 17 were compared for this section.

Fig. 2A shows that the consumption rate of 5-HMF with short carbon chain alcohols is the most rapid, notably for methanol and ethanol. Nevertheless, there is no explicit relationship between the number of carbon and the consumption rate; for instance, the 5-HMF generation rate is slightly faster for hexanol than propanol. One must observe that the consumption rate of 5-HMF in water reaction medium is very slow compared to that of other alcohol reaction medium in the same operating conditions. For example, after 420 minutes of reaction, ca. 20 % of the initial 5-HMF is converted into water reaction medium compared to almost 100 % for the other alcohol reaction medium.

From Fig. 2B, one can determine the generation rate for 5-RMF, intermediate produced from 5-HMF etherification, which is a balance between its rate of formation and consumption. From this figure, one can observe that the generation rate evolves in the following order: $r_{MMF}^{MeOH} > r_{EMF}^{EtOH} > r_{PMF}^{PrOH} > r_{BMF}^{BuOH} > r_{PeMF}^{PeOH} > r_{HeMF}^{HeOH}$, showing a relationship between the number of carbon and the kinetics. The etherification of 5-HMF with HeOH, PeOH, BuOH produces a high yield of HeMF, PeMF and BMF compared to MMF, EMF, PMF. This is due to the higher thermal stability of HeMF and PeMF.

Fig. 2C shows the production rate of RL, and these rates evolve in the following order $r_{ML}^{MeOH} > r_{EL}^{EtOH} > r_{PL}^{PrOH} > r_{BL}^{BuOH} > r_{PeL}^{PeOH} > r_{HeL}^{HeOH} > r_{LA}^{H2O}$. This order agrees with the ones for the generation rate of 5-RMF.

In 5-HMF hydrolysis (Fig. 2A) we observe that the 5-HMF conversion with water is quite slow as well the production of LA (Fig. 2C). This result agrees with the ones obtained by Di Menno Di Bucchianico et al. with butanol (Di Menno Di Bucchianico et al., 2022a, 2022b). They reported that the mix of butanol/water did not result in a great conversion of fructose nor a better production of butyl levulinate (BL). The production of LA from the solvolysis of 5-HMF can be considered negligible under the studied experimental conditions since no water is added or present in the reaction system. Hence, the LA production from 5-HMF was neglected during experiments in alcohol reaction medium in the developed models.

From Fig. 2, one can also observe no explicit relationships between the carbon chain from the alcohol and the solvolysis kinetics. Hence, it is necessary to test the Taft equation corrected by the KAT equation to consider the solvent effect.

4. Kinetic modeling

The reaction mechanism of 5-HMF solvolysis remains elusive and is still under debate, essentially from the ring-opening step of 5-HMF or 5-RMF to LA or RL. The first proposed pathway consists of the 5-HMF etherification to RMF and its further conversion to alkyl levulinates; according to some publications on quantum chemical simulations, this route is considered the thermodynamic and kinetic primary way in the solvolysis of hexoses sugar monomers (glucose, fructose) (Wang et al., 2021). The second one requires the hydrolysis of 5-HMF to produce LA, FA and further esterification to alkyl levulinates. Previous studies from our group show that the production of LA is mainly favored by the presence of water (Di Menno Di Bucchianico et al., 2022b).

For the kinetic modeling of the 5-HMF solvolysis, a combination of

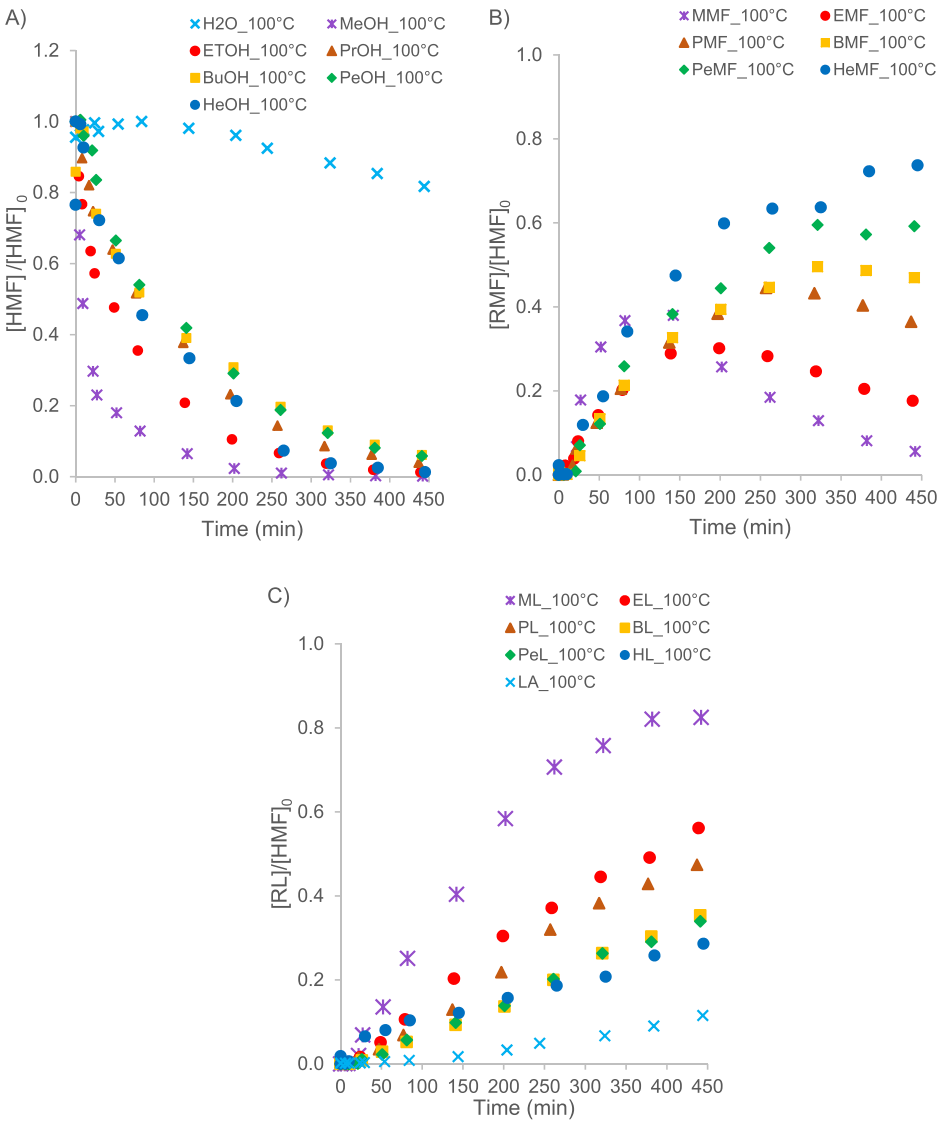

Fig. 2. Reaction medium effect on the solvolysis of 5-HMF at 100°C.

Taft and KAT equations was applied in one model to aid the kinetic prediction in different reaction medium and substituents. Methanol was used as a reference reaction medium and substituent.

From our experimental results, we noticed that the production of LA can be neglected during experiments carried out in alcohol reaction medium. The experimental concentrations of 5-HMF, 5-RMF and RL were used as observables.

Based on some recent publications (Wang et al., 2021; Guo et al., 2020), the first reaction is the protonation of the alcohol by the acid catalyst, and then the hydroxyl group from 5-HMF performs a nucleophile substitution.

In the developed models, we omitted the solvolysis in water reaction medium of 5-HMF into LA and FA, because the reaction steps could differ. Indeed, the literature mentions that the first step is the protonation of the hydroxyl group, leading to dehydration for the 5-HMF solvolysis by water.

Another challenge is the kinetic description of humins production from 5-HMF (Liu et al., 2022). We did not track the humins concentration analytically, but from the mass balance, its presence varied from 0 % to 25 % according to the solvent nature (Table S1 of the Supplementary Data). The reaction steps explaining the humins production are also unclear, but it is linked to the reactivity of the hydroxyl group of 5-HMF, which does not exist in 5-RMF (Sun et al., 2020; Guo et al., 2017; Karnjanakom et al., 2019). Thus, humins production comes solely from the degradation of 5-HMF.

Hence, we developed four global kinetic models. Fig. 3. shows the reaction pathway for Models 1 and 2. Model 1 excludes the presence of humins, and Model 2 includes the production of humins. Model 2 results are displayed in Supplementary Data (Section S3). Model 3 assumed that there are no intermediates (Section S4 of the Supplementary Data). Model 4 proposed an intermediate between 5-RMF and RL (Section S5 of the Supplementary Data).

The developed global Model 1 gave the best statistical results, so we presented its results in the main document. In Fig. 3, the species Int1 is a hypothetical intermediate.

Global kinetic models were carried out using the commercial software Athena Visual Studio (Stewart and Caracotsios, 2008, 2010). The ordinary differential equations (ODEs), i.e., Eqs. (11)-(12), derived from material balances were solved out by DDAPLUS solver using a modified Newton algorithm. Athena Visual Studio uses a Bayesian framework. Literature shows that Bayesian framework is better for a multiresponse system than the non-linear least squares one (Kopyscinski et al., 2012; Stewart et al., 1992). Box and Draper found a way to minimize the determinant criterion used as an objective function (OF), Eq. (8), in

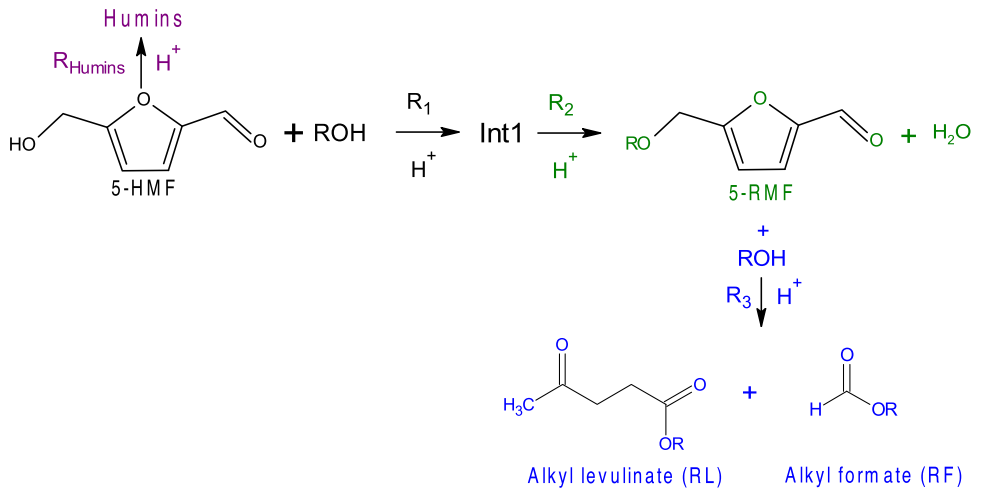

Fig. 3. Reaction steps for the solvolysis of 5-HMF in alcohol reaction medium (Models 1 and 2).

Bayesian framework for multiresponse chemical systems (Box and Draper, 1965; van Boekel, 2020). Athena Visual Studio implemented the GREGPLUS subroutine, which minimizes the OF. GREGPLUS also calculates the credible intervals for each estimated parameter and the normalized parameter covariance.

$$OF = (\gamma + \zeta + 1) \bullet \ln(|\nu|) \tag{8}$$

where $|\nu|$ is the determinant of the covariance matrix of the responses, γ is the number of responses, and ζ is the number of events in response.

Each element of this matrix is as follows:

$$\nu_{ij} = \sum (y_{iu} - \widehat{y_{iu}}) \bullet (y_{ju} - \widehat{y_{ju}}) \tag{9}$$

where y_{iu} is the experimental concentration or temperature and $\widehat{y_{iu}}$ is the estimated value for response i and event u; and y_{ju} the experimental data and $\widehat{y_{ju}}$ the estimated value for response j and event u.

The minimization of the OF is done via successive quadratic programming. The credible intervals of the estimated parameters were evaluated by the marginal highest posterior density (HPD).

A modified Arrhenius equation was used as suggested by Buzzi-Ferraris (Buzzi-Ferraris, 1999)

$$\ln(k_i(T)) = \ln\left(k_i\left(T_{Ref}\right)\right) + \frac{E_{a,i}}{R \bullet T_{ref}} \bullet \left(1 - \frac{T_{Ref}}{T}\right) \tag{10}$$

where, $E_{a,i}$ is the activation of reaction i, R is the universal gas constant, T_{ref} is a reference temperature and T is the reaction temperature. The use of Eq. (10) decreases the correlation between the rate constant and activation energy.

4.1. Kinetics for Model 1

Rate expression for steps 1–3 were expressed as

$$R_1^{ROH} = k_1^{ROH}[H^+][5HMF][ROH] \tag{11}$$

$$R_2^{ROH} = k_2^{ROH} \quad [H^+][Int1] \tag{12}$$

$$R_3^{ROH} = k_3^{ROH}[H^+][RMF][ROH] \tag{13}$$

$$R_{Humins}^{ROH} = k_{Humins}^{ROH}[H^+][5HMF] \tag{14}$$

Rate constants k_1^{ROH}, k_2^{ROH} and k_3^{ROH} were expressed via Eq. (7).

The humins production does not incorporate the alcohol ROH or other R- species in its expression, thus, Eq. (5) was used to express the rate constant of humins in different alcohol reaction medium.

$$\ln\left(k_{Humins}^{ROH}\right) = \ln\left(k_{Humins}^{MeOH}\right) + s_{Humins} \bullet \left(\pi^{*,ROH} - \pi^{*,MeOH}\right) + a_{Humins} \bullet \left(\alpha^{ROH} - \alpha^{MeOH}\right) + b_{Humins} \bullet \left(\beta^{ROH} - \beta^{MeOH}\right) \tag{15}$$

All the reaction steps were considered irreversible. The reaction steps were considered catalyzed by the Amberlite IR-120 H^+, in which a pseudo-homogeneous approach was used to model the proton catalytic activity (Di Menno Di Bucchianico et al., 2023). The proton concentration was evaluated based in the acid capacity of the Amberlite IR-120 H^+, i.e., 4.4 meq of protons per dried catalyst mass.

In the non-linear regression stage, the following parameters were estimated: $\ln\left(k_{X,-R}^{MeOH}(T_{ref})\right)$; $\frac{E_{a,X}^{MeOH}}{R \bullet T_{ref}}$; $\rho_X^{*,MeOH}$; δ_X^{MeOH}; s_X; a_X; b_X; $\ln\left(k_{Humins}^{MeOH}(T_{ref})\right)$ and $\frac{E_{a,Humins}^{MeOH}}{R \bullet T_{ref}}$

4.2. Material balance for Model 1

Ideal flow conditions were assumed to be. Thus, material balances for each species can be derived as follows:

$$\frac{d[5HMF]}{dt} = -R_1^{ROH} \tag{16}$$

$$\frac{d[RMF]}{dt} = R_1^{ROH} - R_2^{ROH} \tag{17}$$

$$\frac{d[Int1]}{dt} = R_2^{ROH} - R_3^{ROH} \tag{18}$$

$$\frac{d[RL]}{dt} = R_3^{ROH} \tag{19}$$

$$\frac{d[RF]}{dt} = R_3^{ROH} \tag{20}$$

$$\frac{d[ROH]}{dt} = -R_1^{ROH} - R_3^{ROH} \tag{21}$$

4.3. Kinetic modeling results

Fig. 4. shows the fit of Model 1 to experimental concentrations for different reaction medium. In general, Model 1 can fit the experimental concentration correctly. Model 1 can correctly fit the experimental 5-HMF concentration in different reaction medium, except for methanol, that could be due to the fast reaction of 5-HMF consumption in this reaction medium. For the species 5-RMF, the fit is good for species and slightly lower for 5-MMF, which could be linked to faster kinetics

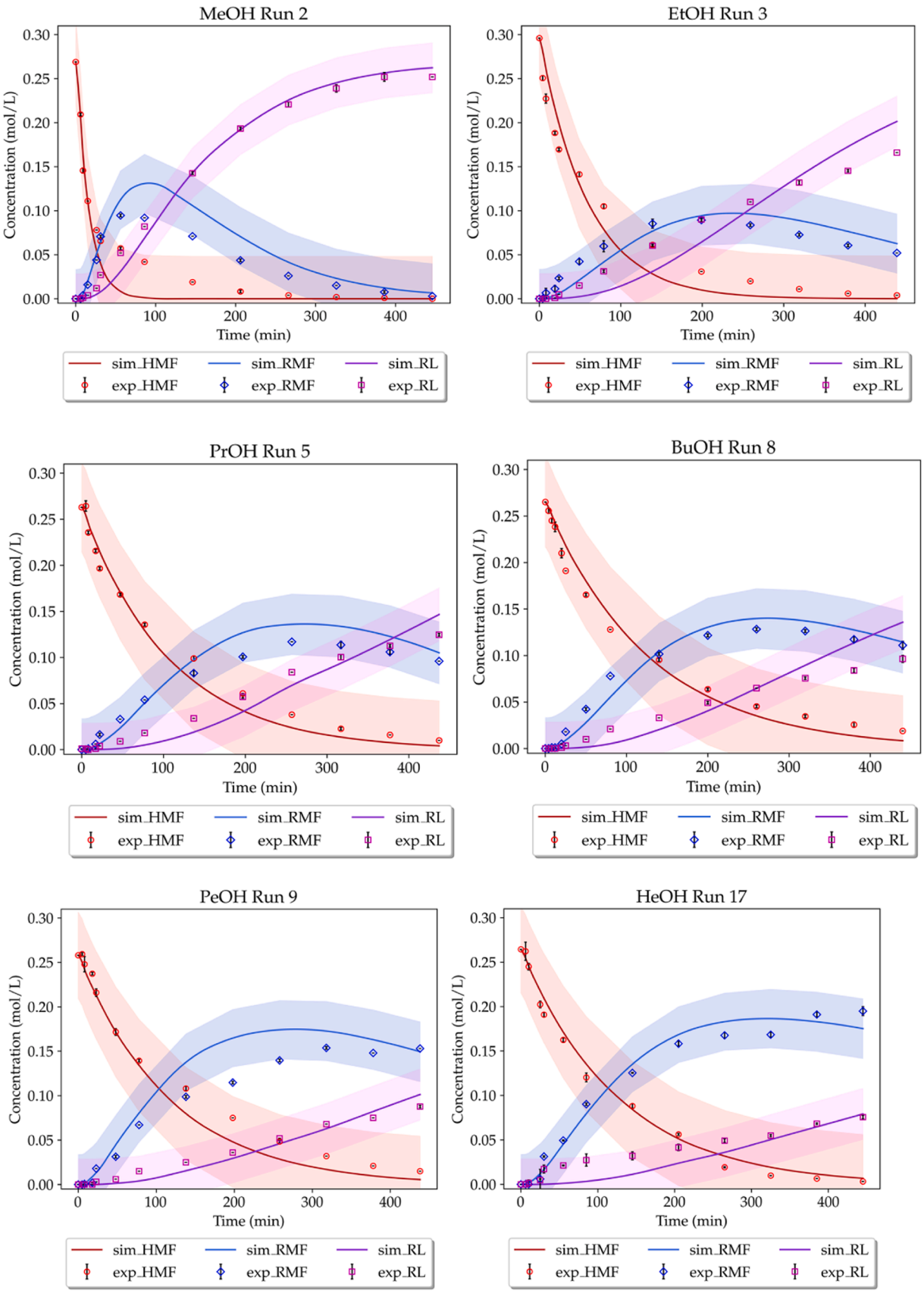

Fig. 4. Fit of Model 1 to experimental concentrations with ± 95 % prediction intervals.

compared to the other reaction media. Model 1 can correctly fit experimental levulinate concentrations, even if in the case of ethanol, propanol and butanol, there are some slight overestimations at the end, which could be linked to side reactions (e.g., production of humins or ether). Fig. 4 shows that all experimental concentrations are within the 95 % prediction intervals bands (Smith, 2013). It indicates that the observed data are consistent with the model predictions.

Fig. 5 shows the parity plot for each species, showing the excellent agreement of the kinetic model and experimental data. The main difficulty comes from the prediction of the intermediate RMF, which is slightly lower compared to 5-HMF and RL.

Fig. 6. shows the normal probability plots, and one can observe that the relationships between residuals and normal order of statistic median is linear. This linearity proves that the residuals are normally distributed, so Model 1 is appropriately expressed.

Table 4 displays the estimated kinetic constant values and the HPD values, i.e., credible intervals, in percentage. In general, one can notice that credible intervals for KAT parameter (a_X,b_X and s_X) and Taft reaction parameter in methanol reaction medium ($\rho_X^{*,MeOH} and \delta_X^{MeOH}$) are wider than the other. These wider credible intervals could be explained by the fact that temperature effect on KAT and Taft substituent and reaction parameters was assumed to be negligible, and the effect of GVL on the solvatochromic parameters was not considered (Table 3). Besides, the solvatochromic parameters $\alpha^{ROH}, \beta^{ROH} and \pi^{*,ROH}$ of the used alcohols (Table 3) are quite similar, making the estimation of a_X, b_X and s_X more challenging.

For reactions 1 and 2, the substituent polar effect is more critical than the steric effect, because the Taft reaction parameters $\rho_1^{*,MeOH}$ and $\rho_2^{*,MeOH}$ are higher than δ_1^{MeOH} and δ_2^{MeOH}. Nevertheless, in reaction 1, the substituent polar effect decreases reaction kinetics 1; in reaction 2, the polar substituent effect increases the kinetics of reaction 2. In reaction 1, if σ_{R-}^* increases, then the substituent R- could stabilize the species R-$(OH_2)^+$ decreasing the kinetics of etherification.

For reaction 3, the steric effect governs the series of transformation of the intermediate to RL and RF in methanol reaction medium. The value of δ_3^{MeOH} is negative, meaning that the higher the substituent group, the faster is reaction 3.

The reader should keep in mind that the estimated Taft reaction parameters, $\rho_X^{*,MeOH}$ and δ_3^{MeOH}, for reactions 1–3 were done in methanol reaction medium.

We need to analyze the KAT parameters. In general, the kinetics of reactions 1, 2 and 3 are mainly affected by the hydrogen-bond donator aspect of the solvent, i.e., a_X. For reactions 1 and 3, the value a_X is negative meaning that solvent with high ability to donate protons decreases the rate constants k_1^{ROH} and k_3^{ROH}. This is undoubtedly due to the fact that the protons stabilize the intermediates and thus decrease the kinetics, as observed in the article of Mellmer et al (Mellmer et al., 2014).

In Supplementary Data, in section S2, the normalized covariance

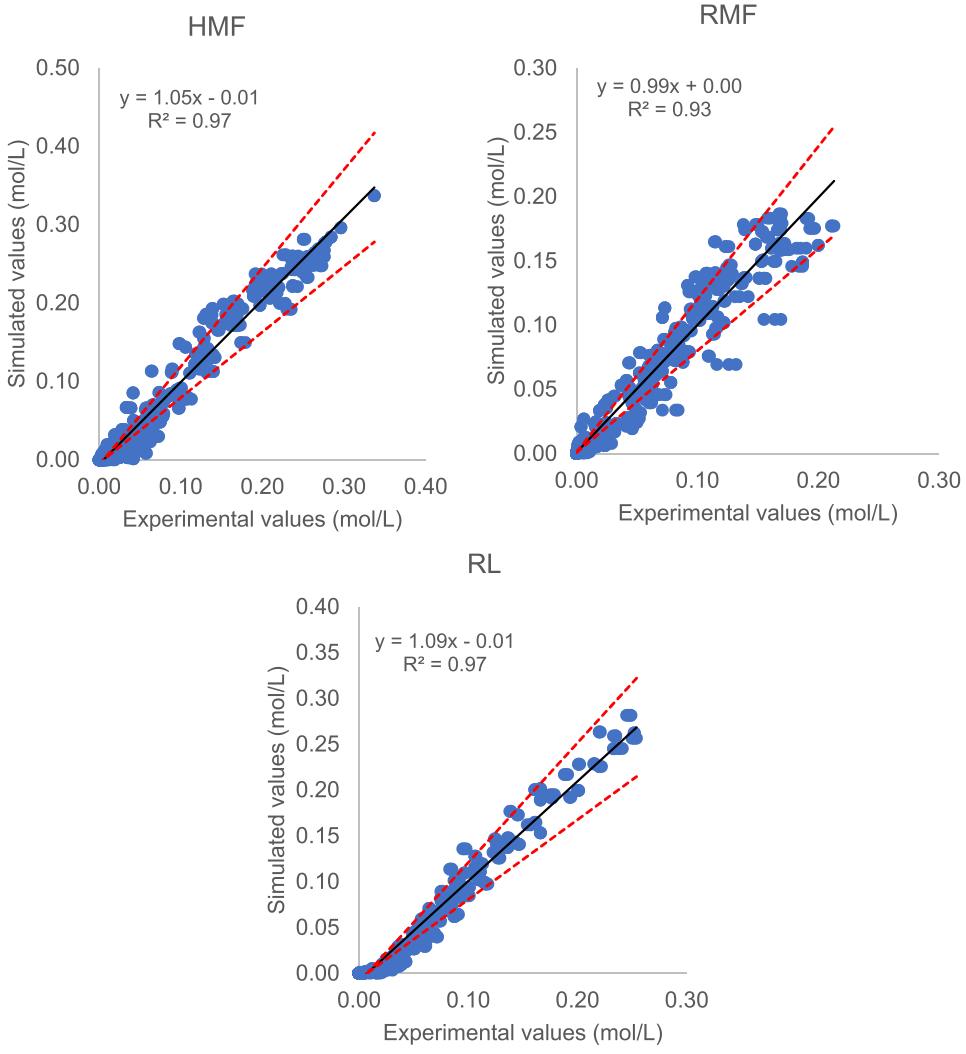

Fig. 5. Parity plots from Model 1 with error lines ± 20 % (in red).

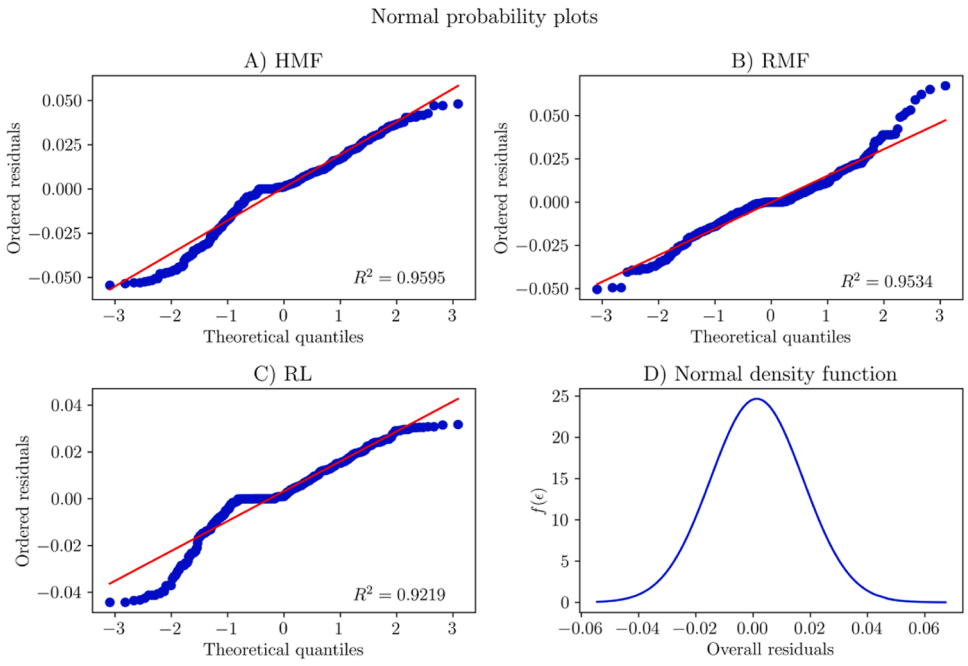

Fig. 6. Normal probability plots for Model 1.

Table 4
Estimated kinetic constants and HPD values and T_{ref} = 105 °C.

Parameters	Estimate	Units	95 % HPD in %
$\ln(k_{1,Me-}^{MeOH}(T_{ref}))$	-6.036	$\frac{mol^{-1}L^2}{\min \bullet g_{dried\ cat}}$	8.22
$\frac{E_{a,1,Me-}^{MetOH}}{RT_{ref}}$	2.421	$\frac{J.mol^{-1}}{J.mol^{-1} \bullet K^{-1} \bullet K}$	40.28
$\ln(k_{2,Me-}^{MeOH}(T_{ref}))$	-7.802	$\frac{\min^{-1}L}{g_{dried\ cat}}$	19.18
$\frac{E_{a,2,Me-}^{MeOH}}{RT_{ref}}$	10.197	$\frac{J.mol^{-1}}{J.mol^{-1} \bullet K^{-1} \bullet K}$	16.34
$\ln(k_{3,Me-}^{MeOH}(T_{ref}))$	-4.032	$\frac{mol^{-1}L^2}{\min \bullet g_{dried\ cat}}$	12.32
$\frac{E_{a,3,Me-}^{MeOH}}{RT_{ref}}$	12.853	$\frac{J.mol^{-1}}{J.mol^{-1} \bullet K^{-1} \bullet K}$	8.11
$\rho_1^{*,MeOH}$	3.399	-	84.06
δ_1^{MeOH}	0.393	-	82.32
$\rho_2^{*,MeOH}$	-2.612	-	>100
δ_2^{MeOH}	-2.010	-	41.36
$\rho_3^{*,MeOH}$	-0.174	-	>100
δ_3^{MeOH}	0.963	-	32.56
s_1	2.050	-	62.13
s_2	10.672	-	41.76
s_3	-1.660	-	73.98
a_1	-4.690	-	30.11
a_2	-4.789	-	91.80
a_3	2.121	-	68.36
b_1	-0.806	-	>100
b_2	-9.339	-	>100
b_3	2.865	-	>100

matrix was displayed. One can observe that in the majority the correlation could be assumed negligible, because absolute values were lower than 0.95 in absolute value (Toch et al., 2015). The correlation was found to be strong between some KAT and Taft substituent parameters, namely b_1 and $\rho_1^{*,MeOH}$; and b_2 and $\rho_2^{*,MeOH}$.

5. Conclusions

This manuscript deals with the kinetic study of 5-(hydroxymethyl) furfural (5-HMF) solvolysis by different alcohols into different alkyl levulinates. Experiments were performed using Amberlite IR-120 as a catalyst and the reaction medium made of alcohol (70 wt%) and GVL (30 wt%). We tested water and the following alcohols: methanol, ethanol, propanol, butanol, pentanol, and hexanol. Preliminary experiments showed that the transformation of 5-HMF to levulinic acid (LA) in water reaction medium was the slowest transformation compared to the other alcohol reaction medium. These preliminary experiments show that the production of 5-HMF and LA is negligible in an alcohol reaction medium. Experimentally, it was found that the rates of alkyl production follow the order: $r_{ML}^{Methanol} > r_{EL}^{Ethanol} > r_{PL}^{Propanol} > r_{BL}^{Butanol} > r_{PeL}^{Pentanol} > r_{HeL}^{Hexanol} > r_{LA}^{Water}$.

Global kinetic models were developed by considering solvent effect, via Kamlet-Abboud-Taft (KAT) equation, and substituent effect, via Taft equation. An experimental matrix was used by varying reaction medium, 5-HMF concentration from 0.20 to 0.30 mol/L, an alcohol concentration from 5.39 to 16.58 mol/L, a catalyst amount from 2.50 to 4.00 g and a reaction temperature from 85 to 110 °C. The developed global kinetic models can predict the experimental concentration of 5-HMF, 5-RMF and RL in alcohol reaction medium. The polar and steric effects characterizing the substituent effect and hydrogen-bond acceptor or donator and solvent polarity provides a better understanding of kinetics, and how to predict the kinetics of the solvolysis of 5-HMF in alcohol reaction medium at different reaction temperature from the knowledge of the kinetics of 5-HMF solvolysis in methanol reaction medium.

This work can be considered as the first brick in this field. A perspective of this work is the evaluation of temperature dependence of the Taft substituent parameters and KAT solvatochromic parameters.

The development of such model considering the solvent effect could ease the process optimization from an economic, environmental and risk standpoints.

CRediT authorship contribution statement

Jean-Christophe Buvat: Writing – original draft, Supervision, Software, Conceptualization. **Julien Legros:** Writing – original draft, Investigation, Conceptualization. **Christoph Held:** Writing – original draft, Methodology, Conceptualization. **Daniele Di Menno Di**

Bucchianico: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Christine Devouge-Boyer:** Writing – original draft, Methodology. **Erny Encarnacion Munoz:** Writing – original draft, Validation, Methodology, Formal analysis, Data curation. **Valeria Casson Moreno:** Writing – original draft, Supervision, Formal analysis, Conceptualization. **sebastien leveneur:** Writing – review & editing, Writing – original draft, Supervision, Resources, Investigation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cherd.2024.03.040.

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