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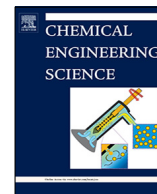
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Reaction mechanism and intrinsic kinetics of sugar hydrogenation to sugar alcohols on solid foam Ru/C catalysts – From arabinose and galactose to arabitol and galactitol



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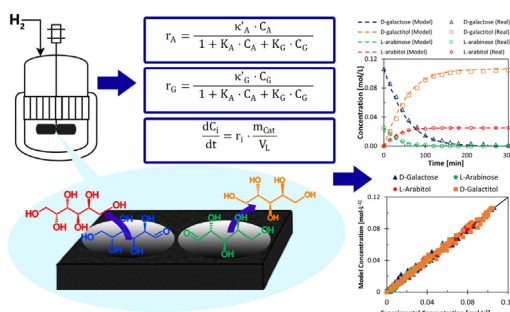
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HIGHLIGHTS

- Selective hydrogenation of sugars to sugar alcohols was successful.
- Ru/C solid foams were used as heterogeneous catalysts.
- Kinetic models based on reaction mechanisms were derived.
- The models described well the individual sugar and mixture hydrogenation.

GRAPHICAL ABSTRACT

Reaction mechanism and intrinsic kinetics of sugar hydrogenation to sugar alcohols on solid foam Ru/C catalysts – From arabinose and galactose to arabitol and galactitol.



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ABSTRACT

Solid foam catalysts have two great benefits: thin catalyst layers guaranteeing a high effectiveness factor and a low pressure drop in continuous operation. The ability of ruthenium-based solid foam catalysts in the hydrogenation of monomeric sugars was illustrated with extensive experiments of L-arabinose and D-galactose hydrogenation at 90–120°C and 20 bar hydrogen pressure. Kinetic experiments were carried out with individual sugars and binary sugar mixtures at different D-galactose-to-L-arabinose molar ratios to reveal the molecular interactions in the presence of the solid foam catalyst. High conversion of sugars and high selectivity to sugar alcohols were achieved in the isothermal and isobaric laboratory-scale reactor which operated under intrinsic kinetic control.

The sugar hydrogenation process was considered from a viewpoint of elementary steps on the catalyst surface. By assuming plausible surface reaction mechanisms, it was possible to derive rate equations for the formation of sugar alcohols, both in case of individual sugars and binary sugar mixtures. The kinetic model based on the non-competitive adsorption of sugars and hydrogen on the ruthenium surface gave a very good description of the hydrogenation kinetics and product distribution on the solid foam catalysts.

The work opens a perspective to the selective and very effective hydrogenation of several sugars to valuable sugar alcohols in the presence of open foam Ru/C catalysts, both in batch and continuous operation modes.

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Nomenclature

A'_s	Pre-exponential factor	k''_s	Merged reaction parameter at constant hydrogen concentration for sugar s
C^*_H	Hydrogen concentration on active sites **	K_{si}	Adsorption constant for component i
C^*_s	Sugar concentration on active sites *	m_{cat}	Mass of catalyst
C'_0	Total concentration on active sites **	Q	Objective function, residual sum of squares (RSS)
C_0	Total concentration on active sites *	R^2	Coefficient of determination in regression analysis
C_A	Concentration of L-arabinose in liquid phase	r_i	Reaction rate of component i
C_{AOH}	Concentration of L-arabitol in liquid phase	r_s	Reaction rate of sugar s
C_{cacli}	Estimated concentration of component i	T	Temperature
C_{expi}	Experimental concentration of component i	V_L	Reaction volume, liquid volume in the reactor
C_G	Concentration of D-galactose in liquid phase	α	Relative reactivity of sugars
C_{GOH}	Concentration of D-galactitol in liquid phase	κ'_A	Merged parameter of L-arabinose in sugar mixture modeling at a constant hydrogen concentration
C_H	Atomic hydrogen concentration in liquid phase	κ'_G	Merged parameter of D-galactose in sugar mixture modeling at a constant hydrogen concentration
C_{mean}	Mean concentration	κ_A	Merged parameter of L-arabinose in sugar mixture modeling
C_S	Sugar concentration in liquid phase	κ_G	Merged parameter of D-galactose in sugar mixture modeling
E_s	Activation energy of sugar s	ρ_B	Bulk density of catalyst
K_A	Adsorption constant for L-arabinose		
K_G	Adsorption constant for D-galactose		
K_H	Adsorption constant for hydrogen		
k_s	Reaction rate constant of the surface reaction between hydrogen and sugar		
k'_s	Merged reaction parameter		

1. Introduction

Reduction of sugar monomers to sugar alcohols is one of the classical and well-established processes in chemical and alimentary industries. Sugar alcohols have a widespread use as health-promoting sweeteners as well as ingredients in pharmaceuticals (Grembecka 2015) and they are important platform chemicals for biorefineries (Werpy et al. 2004, Ruppert et al. 2012). A long time ago it was discovered that the reduction of the carbonyl group in the open form of a sugar monomer can be done with molecular hydrogen, provided that a selective heterogeneous catalyst is available. Sponge nickel – often called Raney nickel according to M. Raney (1926) (Cabrera and Grau 2008) – is an active catalyst for sugar hydrogenation, for instance, in the production of sorbitol from glucose and xylitol from xylose (Wisniak et al. 1979, Mikkola et al. 1999, Van Gorp et al. 1999). However, this well-established industrial catalyst suffers from serious disadvantages because sponge nickel is poisonous, pyrophoric and subject to deactivation. Therefore, extensive scientific efforts have in the recent years been focused on discovering more safe and durable catalysts for sugar hydrogenation. After extensive screening of various metals, it has been evidenced that ruthenium is a very suitable metal for the hydrogenation of sugars to sugar alcohols (Kuusisto et al. 2008, Sifontes Herrera et al. 2011, Simakova et al. 2016). Ruthenium is active and selective, but strongly structure sensitive: an optimal ruthenium nanoparticle size of ca. 3 nm is required to achieve the best possible activity and selectivity (Simakova et al. 2016). Ruthenium nanoparticles deposited on activated carbon supports work very well for the hydrogenation of carbonyl groups as has been evidenced by several independent investigators (e.g., Gallezot et al. 1998, Crezee et al. 2003, Kuusisto et al. 2008, Aho et al. 2015).

Is this scientific and technological issue fully clarified? The answer is definitely 'no', because in heterogeneous catalysis, chemistry and physics are closely coupled to the catalyst and reactor technologies. The history of sugar hydrogenation technology has been like an Odyssey between Skylla and Kharybdis. Conventional slurry technology with finely dispersed catalyst particles (diameters < 100 μm) results in relatively high hydrogenation rates, but the approach is limited to batch and semibatch

processes, which represent an inefficient discontinuous production technology. The use of very small catalyst particles is impossible in continuous packed beds, because the pressure drop increases tremendously for small catalyst particles. On the other hand, the use of large catalyst particles (1–10 mm) in continuous hydrogenation processes results in heavy internal mass transport limitations in the catalyst pores which implies a low overall performance because only the outer layers of the catalyst particles are in an efficient use. This negative effect has been illustrated by detailed numerical simulations of the concentration profiles in conventional catalyst particles used for sugar hydrogenation (Salmi et al. 2008, Sifontes Herrera et al. 2012).

There is, however, a way out from this dilemma. Structured catalysts, such as monoliths, fibres, solid foams and structures created by 3D printing allow deposition of thin catalyst layers and a low pressure drop, combining the benefits of the conventional slurry and packed bed technologies (e.g., Nijhuis et al. 2001, Vergunst et al. 2002, Cybulski and Moulijn 2005, Pangarkar et al. 2008, Wenmakers et al. 2010, Tronconi et al. 2014, Lali et al. 2015a,b, Najarnezhadmashhadi et al. 2020, Najarnezhadmashhadi et al. 2021).

Based on this reasoning, we have initiated a research effort on sugar hydrogenation on a particular structured catalyst, an open foam containing ruthenium (Najarnezhadmashhadi et al. 2021, Araujo-Barahona et al. 2022). A surface of a commercial aluminium foam was exposed to anodic oxidation, coated with polyfurfuryl alcohol (PFA), pyrolyzed and activated in oxygen to get a carbon layer on which ruthenium nanoparticles were deposited with the incipient wetness impregnation method. The structures of the foam catalysts at the different stages of the preparation procedure are displayed in Fig. 1.

The foam catalyst was tested in a laboratory-scale autoclave operated at elevated but constant hydrogen pressures. Hydrogen was fed continuously into the reactor autoclave to keep the hydrogen pressure constant. The catalyst foams were fixed to the impeller of the reactor, hydrogenation experiments were conducted, liquid-phase samples were withdrawn at different reaction times and analyzed by high-performance liquid chromatography (HPLC). The hydrogenation results became a success: this Ru/C catalyst turned out to be very active, selective and durable in the hydro-

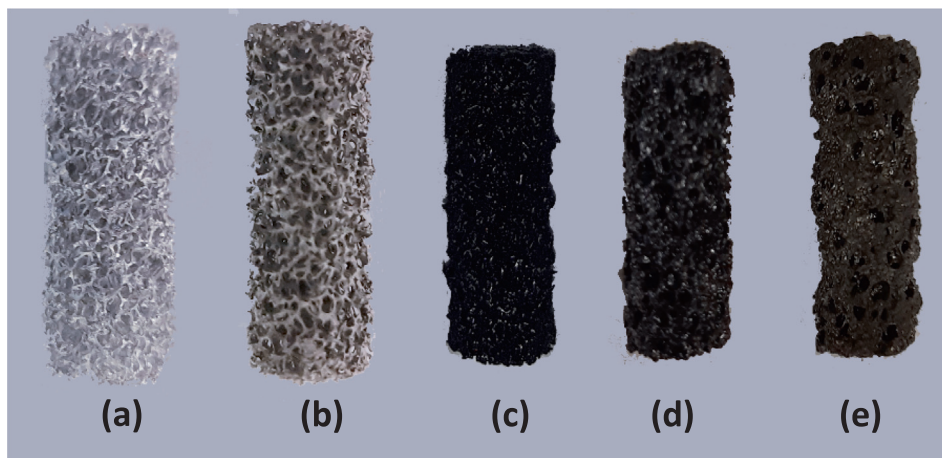


Fig. 1. Preparation stages of Ru/C open-cell foam catalyst: (a) untreated Al foam, (b) anodized Al foam, (c) Al foam coated with PFA, (d) pyrolyzed/oxygen treated carbon-coated foam, (e) carbon-coated, Ru impregnated and reduced catalyst.

genation of two model molecules of sugars, L-arabinose and D-galactose. High yields and selectivities (>95%) of the desired sugar alcohols, arabitol and galactitol were obtained (Araujo Barahona et al. 2021).

The selection of these model molecules for the hydrogenation experiments is relevant, because they appear in the hemicellulose arabinogalactan, which can be obtained from the *Larix* softwood. These trees are among the dominant species in the arctic and subarctic areas of the Northern hemisphere, from the huge Siberian taiga to North American forests. Acid-catalyzed hydrolysis of arabinogalactan under moderate conditions (90°C or less) in the presence of a homogeneous (HCl, H₂SO₄, CF₃COOH) or heterogeneous catalyst (cation exchange resin with sulfonic acid groups) gives a mixture of arabinose and galactose molecules (Salmi et al. 2014).

The endeavor of this research work is to demonstrate the power of kinetic modeling in the description of the performance of the new solid foam catalysts for sugar hydrogenation. This fundamental work elucidating the intrinsic kinetics of sugar hydrogenation on foam catalysts opens the pathway for future industrial applications of solid foams in efficient and selective sugar hydrogenation to sugar alcohols.

2. Experimental

The kinetic experiments were carried out in a 0.3 L laboratory-scale semi-batch reactor (Parr 4561) in which two Ru/C catalyst foam pieces equivalent to a carbon mass of approximate 1 g and a Ru content of about 1.1 wt% based on carbon were mounted in the endpoint of the mechanical agitating shaft to work as the stirrer at 600 rpm. Two set of experiments were conducted with a 0.13 M sugar solution—one for individual sugar hydrogenation and one for sugar mixtures, in each set a pair of foam catalyst as the described above were utilized.

The individual kinetic experiments were carried out with L-arabinose and D-galactose at 90, 100, and 120 °C and a constant hydrogen pressure of 20 bar. On the other hand, to study the interaction of the sugars during the hydrogenation reaction, a series of experiments was also conducted using binary mixtures of D-galactose and L-arabinose, varying the initial molar ratio of D-galactose to L-arabinose (G:A ratios, 0.5, 1, and 5) at the same temperature and pressure conditions of the individual set.

A detailed description of the catalyst preparation and experimental conditions is reported in a previous article from our group (Araujo Barahona et al., 2022).

3. Reaction mechanism and kinetic modelling

3.1. Reaction mechanism of sugar hydrogenation

Regarding the kinetic model of sugar hydrogenation, reaction mechanisms have been suggested in previous references according to which the reactants (sugars and hydrogen) are adsorbed on the active sites of the catalyst. Afterwards, the adsorbed sugar molecules react with hydrogen on the surface of the catalyst to form the correspondent products, which are desorbed. Generally, it is inferred that the reaction between the adsorbed sugar species and the adsorbed hydrogen is the rate determining step, while the adsorption of the reactants and the desorption of products are rapid (Salmi et al. 2004, Kuusisto et al. 2008, Salmi et al. 2008, Sifontes Herrera et al. 2011, Najarneshadmashhadi et al. 2021)

Other aspects concerning a plausible mechanism are still a matter of debate, such as the mode of the hydrogen adsorption i.e., in molecular or dissociated forms. Moreover, the simultaneous adsorption of sugar and hydrogen, species of very different sizes, raises the question whether the adsorption is of competitive or non-competitive nature (Mikkola et al. 1999, Salmi et al. 2004, Cabrera and Grau 2008)

Competitive and non-competitive adsorption models have been proposed and implemented to describe the hydrogenation of several sugar molecules to sugar alcohols (Mikkola et al. 1999, Kuusisto et al. 2008, Sifontes Herrera et al. 2011). Because of the huge size differences between sugar molecules and hydrogen, it is reasonable to envisage a completely non-competitive adsorption, even though this approach is only an approximation from a mechanistic viewpoint (Salmi et al. 2004).

In this sense, an alternative semi-competitive mechanism has been proposed by Mikkola et al. (1999) and Salmi et al. (2004). The idea behind this concept is that the larger molecules (sugar molecules) are adsorbed on the primary sites of the catalyst surface, leaving some accessible interstitial sites for small species such as hydrogen (whether in atomic or molecular form). The semi-competitive adsorption concept is illustrated in Fig. 2, assuming dissociative adsorption of hydrogen. An overview and a further

extension of the semi-competitive adsorption model is provided by Cabrera and Grau (2008).

3.2. Modelling of individual sugars and binary mixtures

3.2.1. Model hypotheses

The kinetic experiments were conducted in an isothermal semi-batch reactor with a fixed mass of catalyst, where hydrogen was continuously added in such a way that the pressure and the concentration of the dissolved hydrogen can be assumed constant, and therefore the mass balance of hydrogen can be discarded.

The reactions were inferred to be in the kinetic regime, in the absence of mass transfer limitations due to the high stirring speed (600 rpm) and very thin catalyst layers ($\ll 100 \mu\text{m}$) of the solid foam. The operation in the regime of intrinsic kinetics was ensured by comparing the reaction and diffusion rates according to the criterion of Weisz and Hicks (1962). Because the change of the liquid volume during the reaction is minor, the volume of the reaction medium was considered constant.

Regarding the reaction kinetics and thermodynamics, sugar hydrogenation is known to be an irreversible reaction in practice (Mikkola et al. 1999) – sugar alcohols are not reacting back to sugars, but complete conversion is achieved on durable catalysts. The amount of by-products depends on the particular sugar monomer being hydrogenated, but in general, monomeric sugars give much less by-products than dimeric sugars (Kuusisto et al. 2008, Sifontes Herrera et al. 2011). Negligible amounts of by-products were observed in our experimental data on arabinose and galactose hydrogenation. Therefore, the reactions were assumed to proceed towards the exclusive formation of the sugar alcohols arabitol and galactitol.

Although various reaction mechanisms have been proposed for the hydrogenation of sugars to sugar alcohols, for the sake of simplicity, a non-competitive adsorption model was used. Dissociative adsorption of hydrogen was considered in the model, but hydrogen was maintaining its molecular identity in the sense that two atoms of hydrogen react with the adsorbed sugar to form the reaction product.

Since the adsorption affinity of sugar alcohols has been shown to be lower than that of the corresponding sugar monomers (Sifontes Herrera et al. 2011), the adsorption of the reaction products was neglected. The catalyst surface was assumed ideal so that the adsorption model of Langmuir was applied and the surface reaction between the adsorbed sugar species and the adsorbed hydrogen was presumed as the rate determining step in the catalytic process.

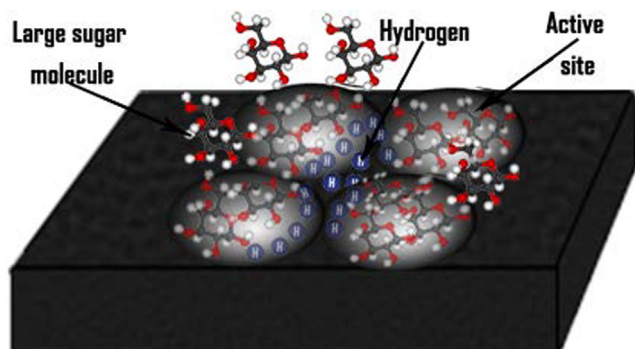


Fig. 2. Illustration of the semi-competitive sugar and hydrogen adsorption concept – hydrogen is adsorbed in dissociated form on the interstitial sites between the sugar molecules.

3.2.2. Hydrogenation rate expressions

The reaction mechanism based on the hypotheses presented in the previous section is shown in Fig. 3, where * denotes an active site devoted to sugar adsorption (L-arabinose or D-galactose), whilst *' is a site for hydrogen adsorption.

Consequently, the adsorption quasi-equilibria for L-arabinose, D-galactose and hydrogen are expressed as follows,

$$C_{*A} = K_A \cdot C_A \cdot C_* \quad (1)$$

$$C_{*G} = K_G \cdot C_G \cdot C_* \quad (2)$$

$$C_{*H} = \sqrt{K_H \cdot C_H} \cdot C_{*' } \quad (3)$$

The site balances for sugar and hydrogen adsorption can be written as

$$C_{*A} + C_{*G} + C_* = C_0 \quad (4)$$

$$C_{*H} + C_{*' } = C'_0 \quad (5)$$

where C_0 and C'_0 denote the total concentrations of the adsorption sites available for sugar and hydrogen, respectively. Substituting the quasi-equilibrium expressions (1)–(3) in the site balances (4)–(5) gives the concentrations of vacant sites,

$$C_* = \frac{C_0}{1 + K_A \cdot C_A + K_G \cdot C_G} \quad (6)$$

$$C_{*' } = \frac{C'_0}{1 + \sqrt{K_H \cdot C_H}} \quad (7)$$

Considering that the surface reactions between the adsorbed sugar molecules and hydrogen are the rate determining steps, the rate equations for L-arabinose (r_A) and D-galactose, (r_G) become

$$r_A = k_A \cdot C_{*A} \cdot C_{*' }^2 \quad (8)$$

$$r_G = k_G \cdot C_{*G} \cdot C_{*' }^2 \quad (9)$$

The expressions for C_* and $C_{*' }$ are inserted in the rate equations, which yields

$$r_A = \frac{k_A \cdot K_A \cdot K_H \cdot C_0 \cdot C'_0{}^2 \cdot C_A \cdot C_H}{(1 + K_A \cdot C_A + K_G \cdot C_G) \cdot (1 + \sqrt{K_H \cdot C_H})^2} \quad (10)$$

$$r_G = \frac{k_G \cdot K_G \cdot K_H \cdot C_0 \cdot C'_0{}^2 \cdot C_G \cdot C_H}{(1 + K_A \cdot C_A + K_G \cdot C_G) \cdot (1 + \sqrt{K_H \cdot C_H})^2} \quad (11)$$

The following merged parameters are defined as

$$\kappa_A = k_A \cdot K_A \cdot K_H \cdot C_0 \cdot C'_0{}^2 \quad (12)$$

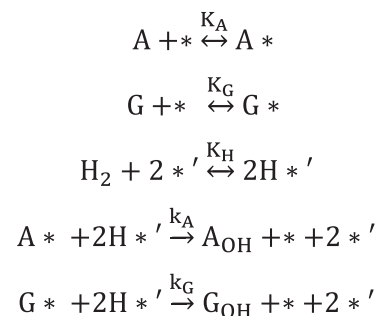


Fig. 3. Presumed surface reaction mechanism for the hydrogenation of binary sugar mixtures of L-arabinose and D-galactose.

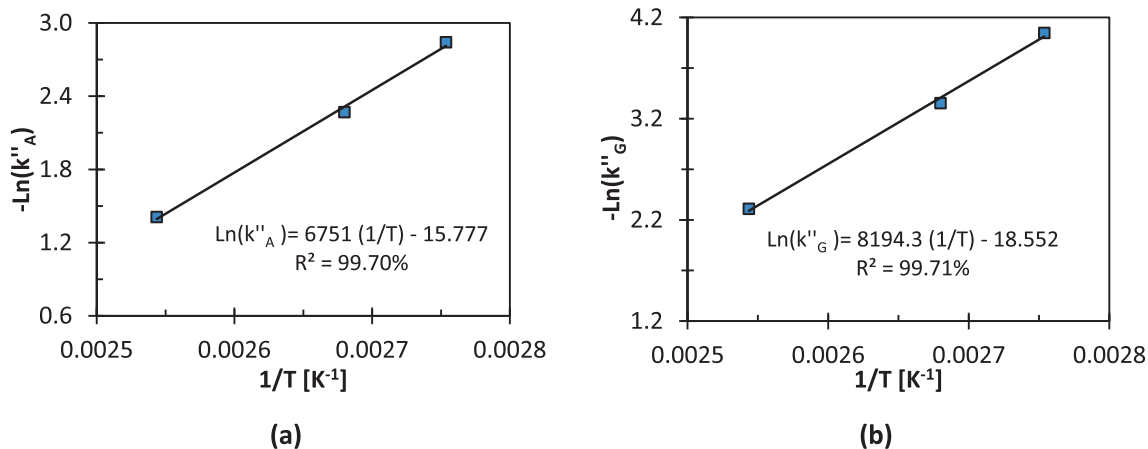


Fig. 4. Logarithmic plots for the rate parameters for individual hydrogenation of L-arabinose (a) and D-galactose (b).

Table 1
Kinetic parameters determined by linear regression (Fig. 4).

Sugar	A_s' [L·g ⁻¹ ·min ⁻¹ ·mol ⁻¹]	E_s [kJ·mol ⁻¹]
L-arabinose	$7.11 \cdot 10^6$	56.1
D-galactose	$1.14 \cdot 10^8$	68.1

$$\kappa_G = k_G \cdot K_G \cdot K_H \cdot C_0 \cdot C_0'^2 \quad (13)$$

The rate equations obtain the operative forms

$$r_A = \frac{\kappa_A \cdot C_A \cdot C_H}{(1 + K_A \cdot C_A + K_G \cdot C_G) \cdot (1 + \sqrt{K_H \cdot C_H})^2} \quad (14)$$

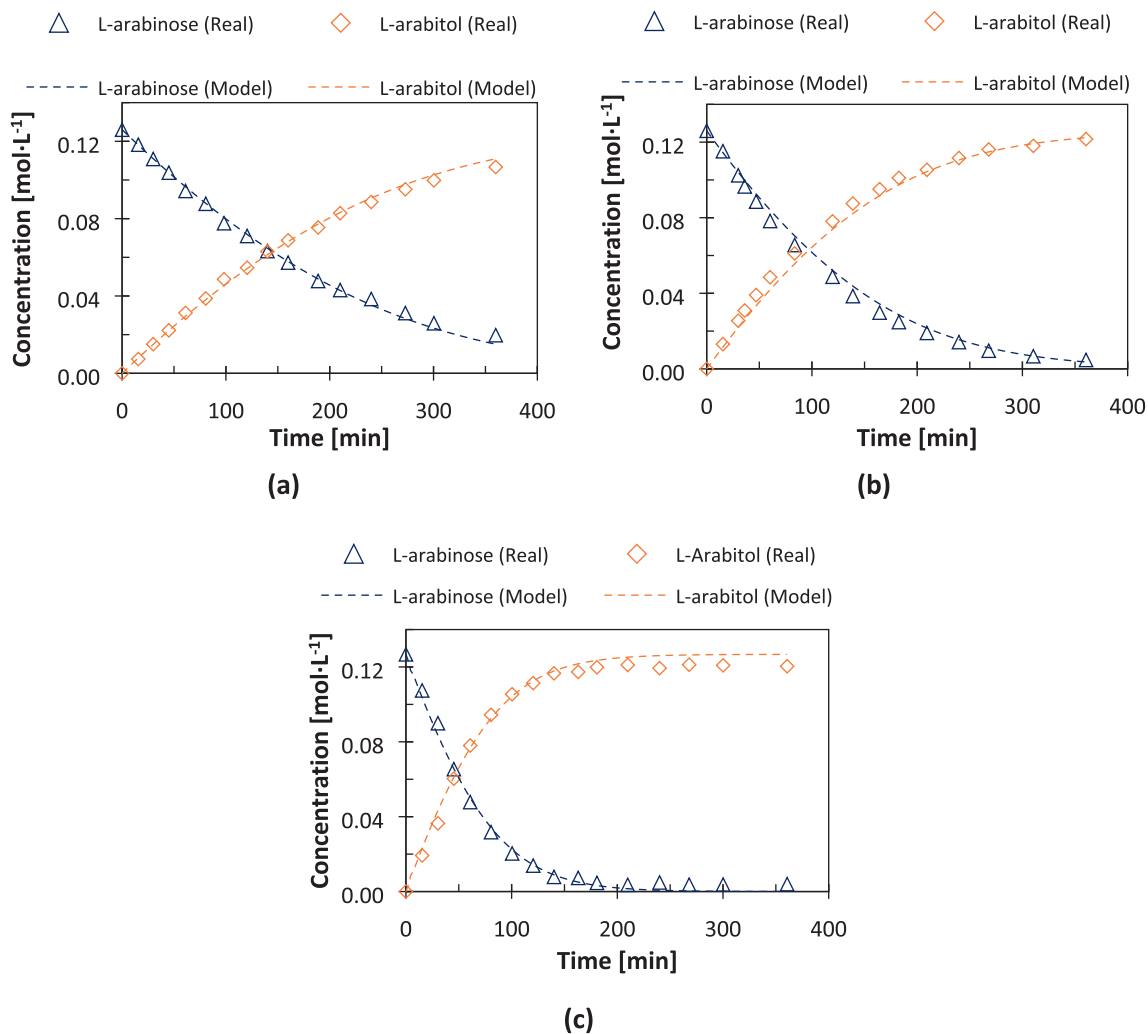


Fig. 5. Modeling results for L-arabinose hydrogenation to arabinitol at 20 bar hydrogen and different temperatures: (a) 90C, (b) 100C and (c) 120C.

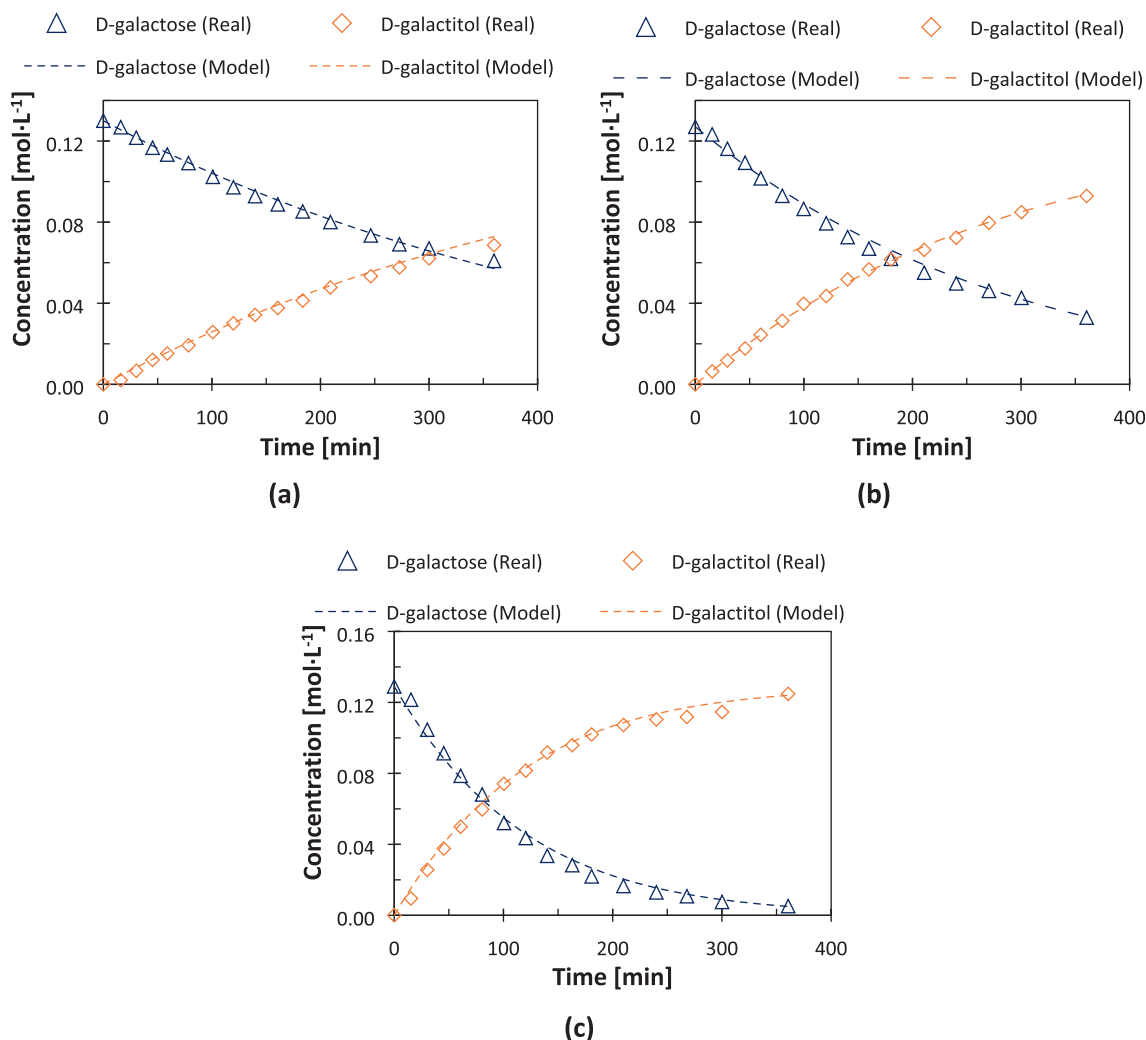


Fig. 6. Modeling results for D-galactose hydrogenation to galactitol at 20 bar and different temperatures: (a) 90C, (b) 100C and (c) 120C.

Table 2

Kinetic parameters estimated for L-arabinose and D-galactose in individual hydrogenation experiments.

	A_s' [L·gRu ⁻¹ ·min ⁻¹ mol ⁻¹]	E_s [kJ·mol ⁻¹]	K_s [L mol ⁻¹]	R^2 [%]	Q (SRS) ¹ [mol ² ·L ⁻²]
L-arabinose	181,390	44.22	8.78	99.8	0.0008
D-galactose	663,000	51.74	1.56	99.9	0.0006

¹ Sum of the residual squares.

$$r_G = \frac{\kappa_G \cdot C_G \cdot C_H}{(1 + K_A \cdot C_A + K_G \cdot C_G) \cdot (1 + \sqrt{K_H \cdot C_H})^2} \quad (15)$$

Furthermore, since the hydrogen pressure was maintained constant during all the experiments, the term $\frac{C_H}{(1 + \sqrt{K_H \cdot C_H})^2}$ was constant in each individual experiment, which implies that equations (14) and (15) can be simplified to

$$r_A = \frac{\kappa'_A \cdot C_A}{(1 + K_A \cdot C_A + K_G \cdot C_G)} \quad (16)$$

$$r_G = \frac{\kappa'_G \cdot C_G}{(1 + K_A \cdot C_A + K_G \cdot C_G)} \quad (17)$$

If the rate and equilibrium constants are presumed to follow the laws of Arrhenius and van't Hoff, the temperature dependences of the merged parameters can be expressed as

$$\kappa'_A = A'_A \cdot e^{-\frac{E_A}{RT}} \quad (18)$$

and

$$\kappa'_G = A'_G \cdot e^{-\frac{E_G}{RT}} \quad (19)$$

3.3. Liquid-phase mass balances

The reactions took place in a constant liquid volume (V_L) with a fixed mass of catalyst (m_{Cat}) in the well stirred reactor vessel. Therefore, the mass balance for the implied chemical species in the liquid phase can be expressed by equation (20), where C_i denotes the concentration of the component i .

$$\frac{dC_i}{dt} = r_i \cdot \frac{m_{Cat}}{V_L} \quad (20)$$

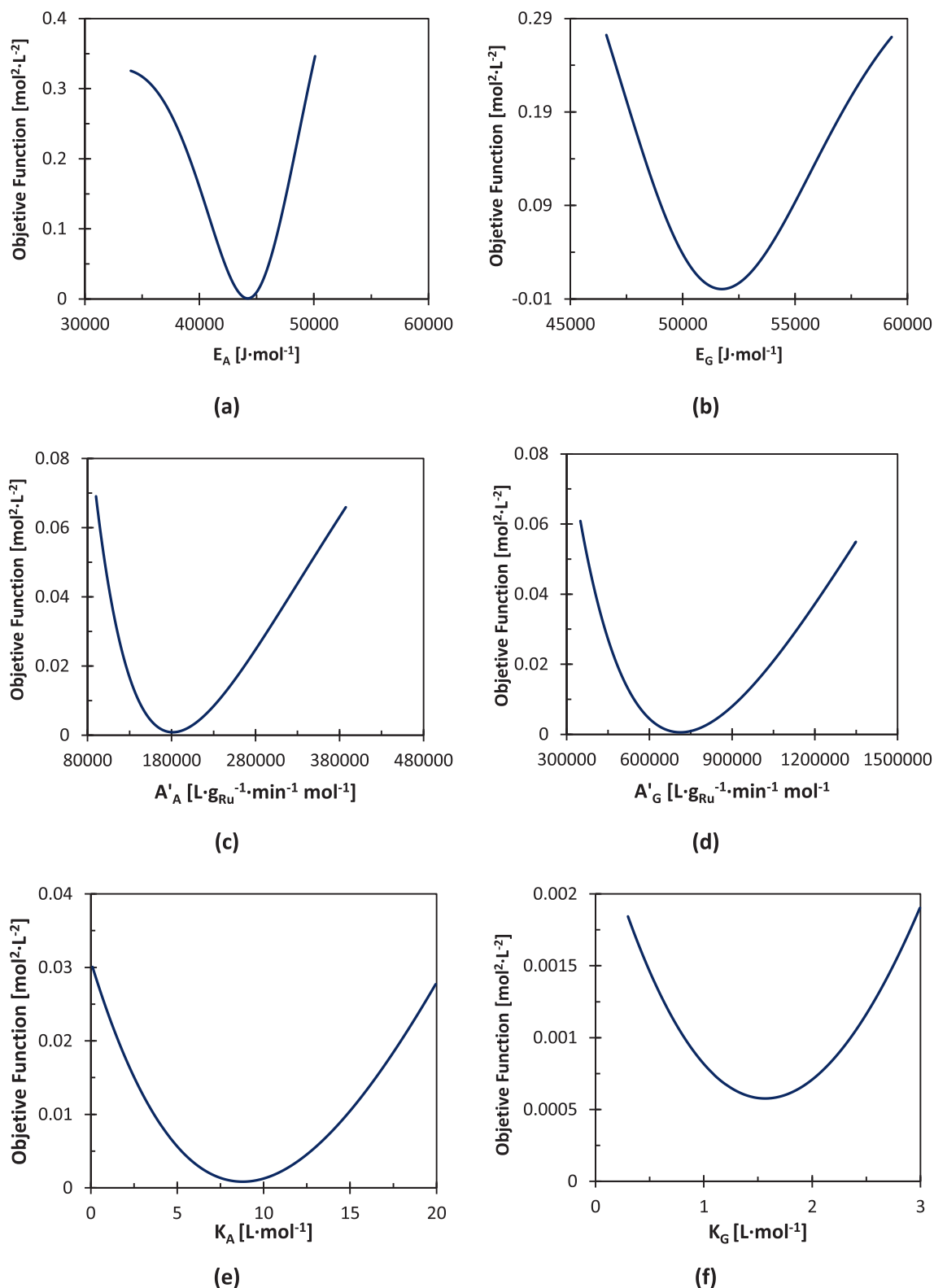


Fig. 7. Sensitivity analysis of estimated parameters: (a) E_A , (b) E_G , (c) A'_A , (d) A'_G , (e) K_A , (f) K_G .

The hydrogenation reactions proceeded by consuming the sugar ($S = A$ or $S = G$) to form the corresponding sugar alcohol (S_{OH}); consequently the mass balances for the participating species are given by equations (21)–(24), where $A = L$ -arabinose, $G = D$ -galactose, $A_{OH} = L$ -arabitol, $G_{OH} = D$ -galactitol, and the catalyst bulk density is defined as $\rho_B = \frac{m_{Cat}}{V_L}$.

$$\frac{dC_A}{dt} = -\Gamma_A \cdot \rho_B \quad (21)$$

$$\frac{dC_{A_{OH}}}{dt} = \Gamma_A \cdot \rho_B \quad (22)$$

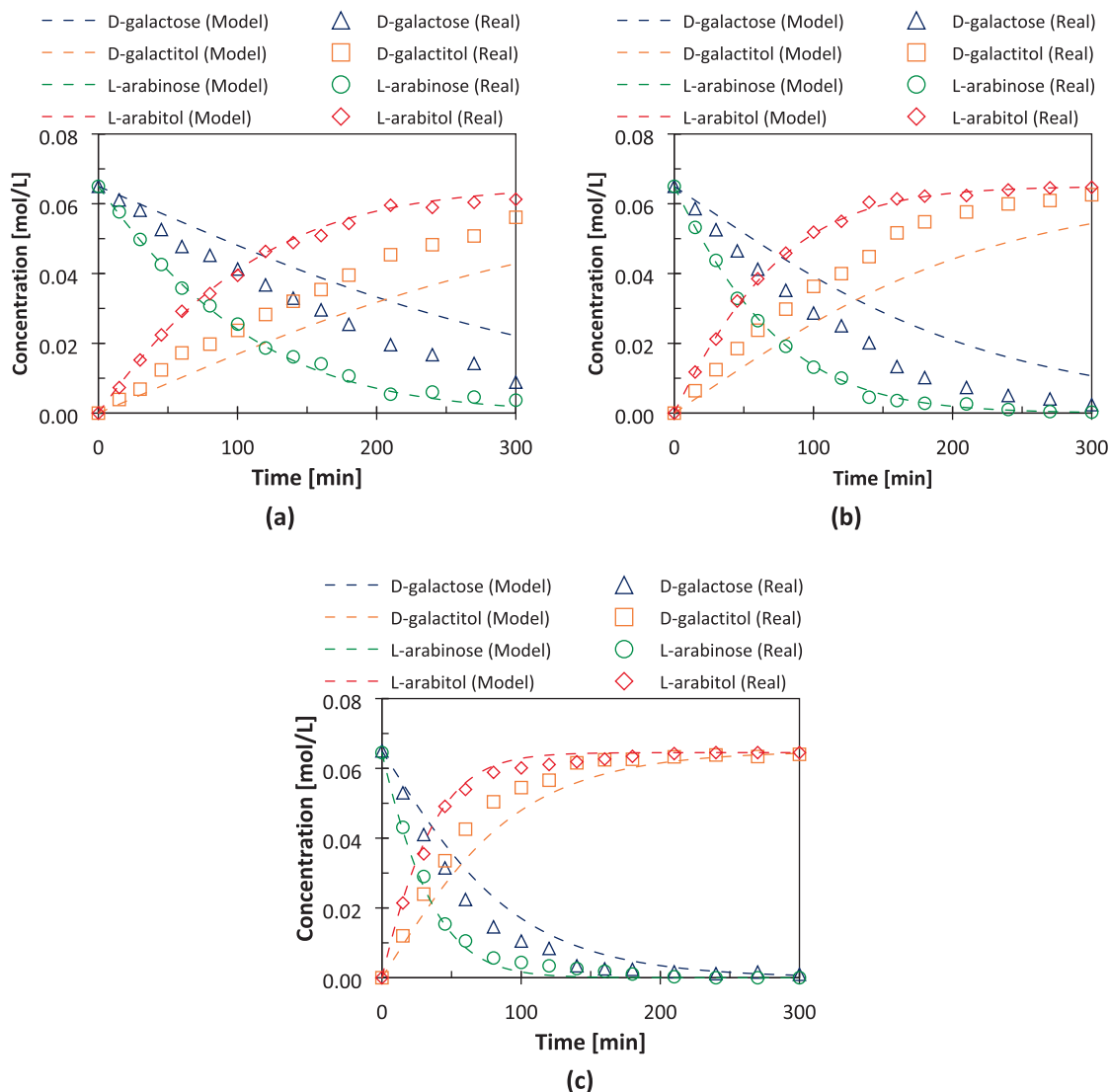


Fig. 8. Modeling of sugar mixture hydrogenation data, G:A ratio = 1: a) 90C, b) 100C and (c) 120C.

Table 3

Kinetic parameters estimated for L-arabinose and D-galactose in mixture experiments.

Parameter	A_s' [L·gRu ⁻¹ ·min ⁻¹ ·mol ⁻¹]	E_s [kJ·mol ⁻¹]	K_s [L·mol ⁻¹]	R^2 [%]	Q (SRS) mol ² ·L ⁻²
L-arabinose	61,559	40.91	8.72	99.4	0.002
D-galactose	93,346	44.10	2.39		

$$\frac{dC_G}{dt} = -r_G \cdot \rho_B \quad (23)$$

$$\frac{dC_{G_{OH}}}{dt} = r_G \cdot \rho_B \quad (24)$$

3.4. Parameter estimation strategy

The parameters were estimated by minimizing the objective function (Q), i.e. sum of residual squares as defined in equation (25) by using the Nelder-Mead optimization method (Nelder and Mead 1965). The underlying ordinary differential equations (ODEs) (21)–(24) were solved in Python with the aid of the LSODA solver originally created at Lawrence Livermore Laboratory for accurate

numerical solution of stiff ordinary differential equations (Hindmarsh 1983). The ODEs were solved repeatedly until the minimum of the objective function was found,

$$Q = \sum_{i=1}^n (C_{Exp,i} - C_{Calc,i})^2 \quad (25)$$

From the parameter estimation results, the coefficient of determination (R^2) for the model was computed from equation (26), which compares the model performance with the simplest possible model, i.e. the average of all concentrations. The coefficient varies between 0 and 100%.

$$R^2 = \left(1 - \frac{\sum_{i=1}^n (C_{Exp,i} - C_{Calc,i})^2}{\sum_{i=1}^n (C_{Exp,i} - C_{mean})^2} \right) \cdot 100 \quad (26)$$

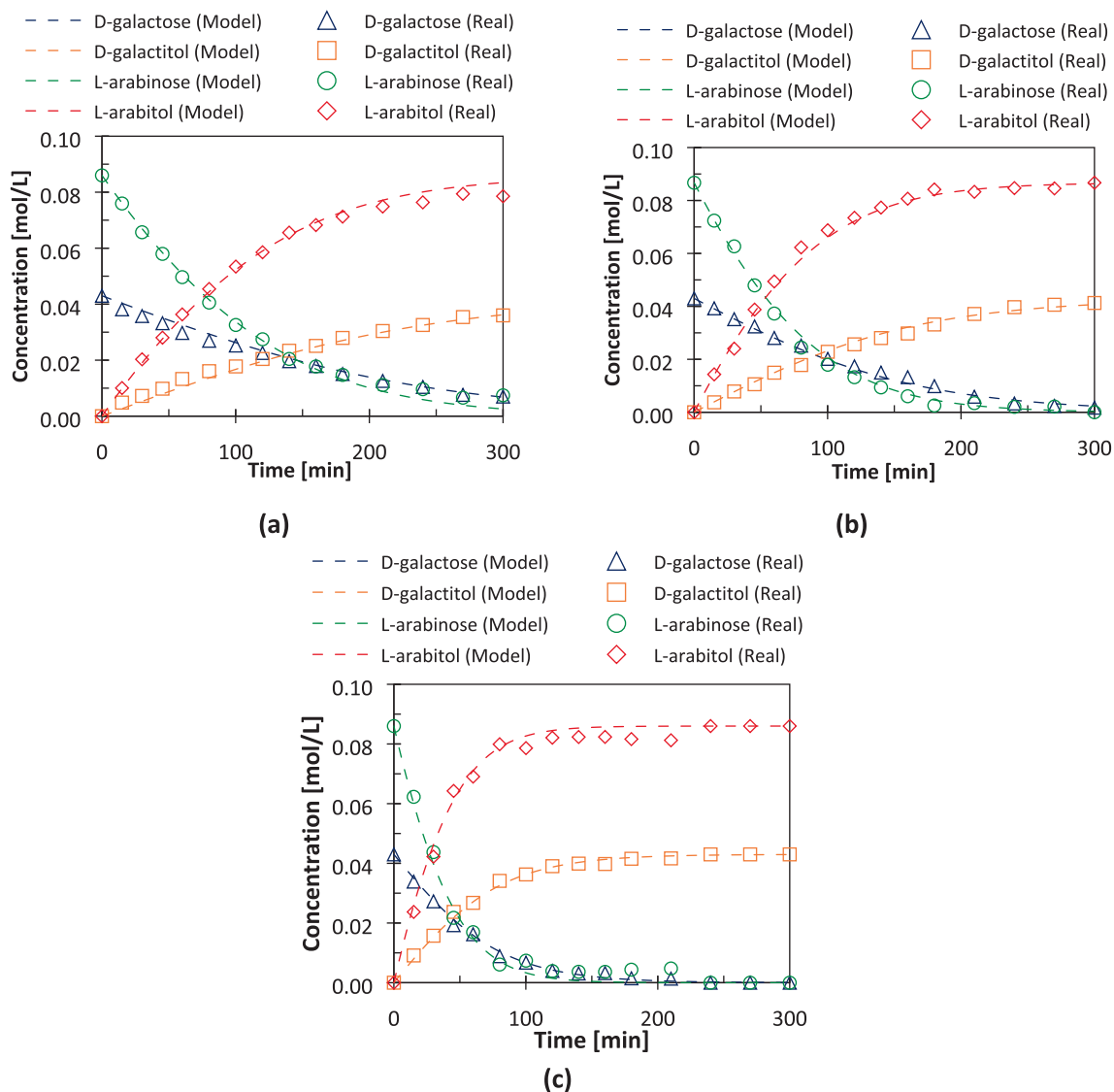


Fig. 9. Modeling of sugar mixture hydrogenation data, G:A ratio = 0.5: a) 90C, b) 100C and (c) 120C.

3.5. Modelling results and discussion

3.5.1. Hydrogenation of single sugars

As the first approach, the parameters included in equations (16) and (17) were estimated individually for the experimental temperatures (90C, 100C and 120C). The logarithmic Arrhenius plots for L-arabinose and D-galactose are displayed in Fig. 4.

High coefficients of determination (R^2) for both sugars were obtained resulting in a very good description of the experimental data. Consequently, Arrhenius law can accurately describe the effect of the temperature on these reactions, as documented in Table 1 and Fig. 4. The apparent activation energies for the hydrogenation of L-arabinose and D-galactose were determined to 56 kJ/mol and 68 kJ/mol, respectively.

The parameters obtained from the linear regression analysis were used as initial values for the simultaneous optimization of the parameters from the experimental data obtained at different temperatures. The coefficient of determination for the model was computed from equation (26) and the values of R^2 were very high, around 99%.

The model fitting results are displayed in Figs. 5 and 6, demonstrating how the proposed model very successfully describes the

experimental concentration profiles recorded during the hydrogenation of individual sugars on the prepared Ru/C foam catalyst at different temperatures.

The parameters for the L-arabinose and D-galactose hydrogenation obtained from the regression analysis are listed in Table 2. High values of R^2 and small values of the objective function were obtained in both cases, which confirms the very good performance of the model.

The apparent activation energies obtained in this work are in the order of magnitude of the values reported in previous research (Sifontes Herrera et al. 2011, 2012). The adsorption constant was clearly higher for L-arabinose than for D-galactose, which was expected due to the smaller molecular size of L-arabinose compared to D-galactose.

The sensitivities of the estimated parameters were evaluated by plotting the parameter values against the corresponding objective function (Q) while keeping the other values constant and equal to best-fitted from the model. The sensitivity plots of the objective function for the parameters A_S' , E_S , and K_S are shown in Fig. 7. The presence of sharp valleys in these graphs confirms that the parameters are well-defined, and all of them have an important contribution to the model.

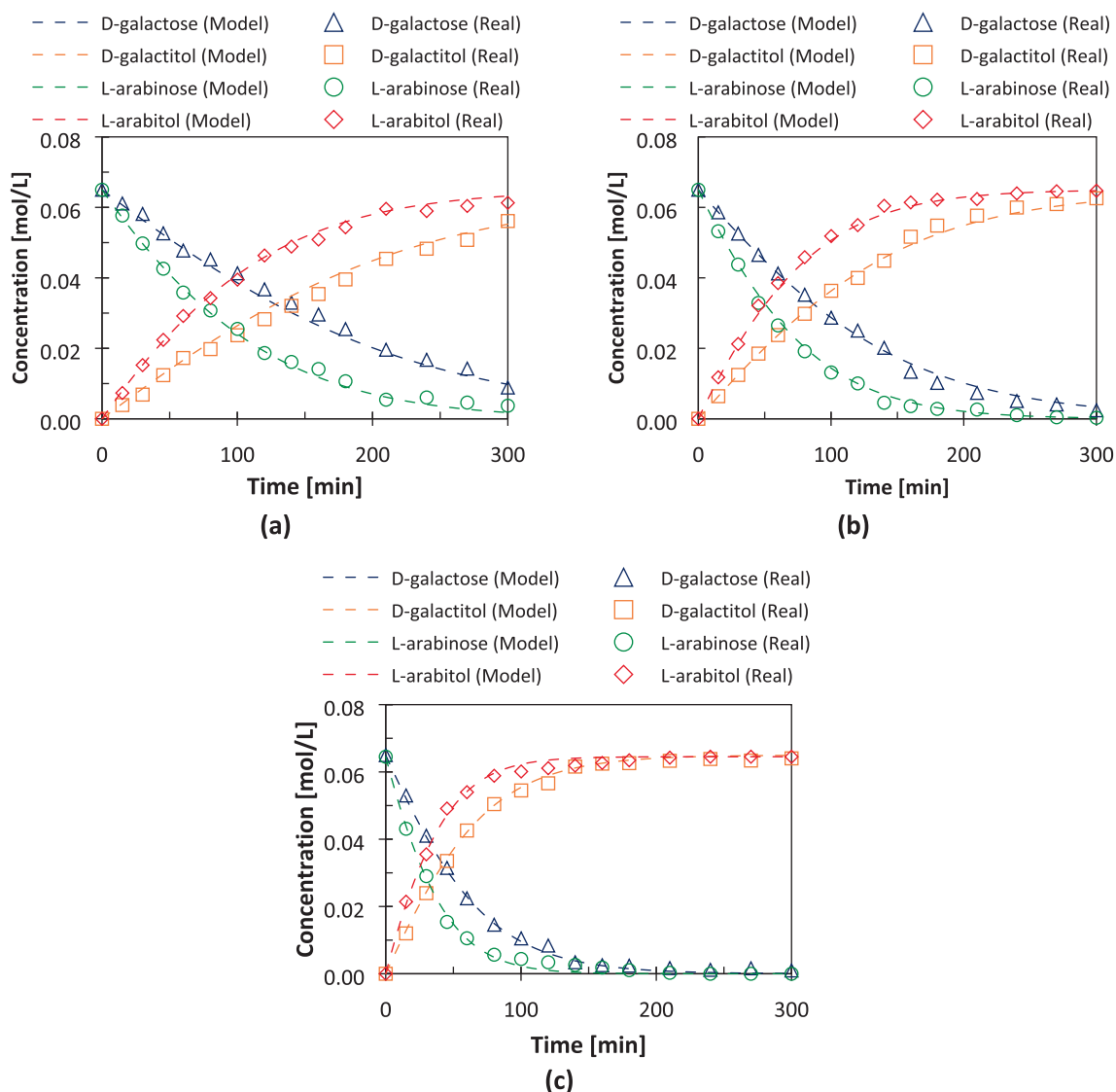


Fig. 10. Modeling of sugar mixture hydrogenation data, G:A ratio = 1: a) 90C, b) 100C and (c) 120C.

3.5.2. Binary sugar mixtures

The first attempt to describe the kinetics of the binary sugar mixtures was based on the use of the rate parameters obtained from experiments conducted with individual sugar solutions (Table 2). The parameters were taken from the table and used to simulate the behavior of binary mixtures under the experimental conditions. The experimental data and the model predictions are displayed in Fig. 8. By looking at the figure, the conclusions are very clear: the behavior of arabinose kinetics is well described with the parameters obtained from the pure arabinose experiments, but the description of the galactose concentration is not satisfactory, because too low concentrations are predicted by the parameters from pure galactose hydrogenation. Evidently the presence of arabinose enhances the hydrogenation of galactose, which is a very interesting observation. A hypothesis could be that the co-existence of two sugar molecules affect their adsorption state, particularly the adsorption geometry on the catalyst surface. This kind of interaction has been previously observed for organic reactions. For instance, Toukoniitty et al. (2013) has shown that the adsorption state

shifts from ‘flat’ state of the molecule to a tilted one, as the amounts of organic molecules on the surface increase.

Anyway, this exercise confirms that a separate parameter estimation for the sugar mixtures is a necessity, in such a way that all the data from the mixtures are merged and the model is solved repeatedly until the minimum of the least sum of squares, the objective function (Q) is reached.

The simultaneously estimated parameters for the binary mixtures are listed in Table 3. As can be observed from the table, a higher value was obtained for the objective function compared with the estimations conducted with individual sugars.

Figs. 9-11 display the concentration profiles of the reagents and products obtained from the model compared with the experimental data for the hydrogenation of mixtures of L-arabinose and D-galactose at 120C and 20 bar and different D-galactose to L-arabinose molar ratios. The results revealed that the model rather well follows the experimental data.

The sensitivity plots of the kinetic parameters are shown in Fig. 12. The prominent minima in the sensitivity plots confirm that

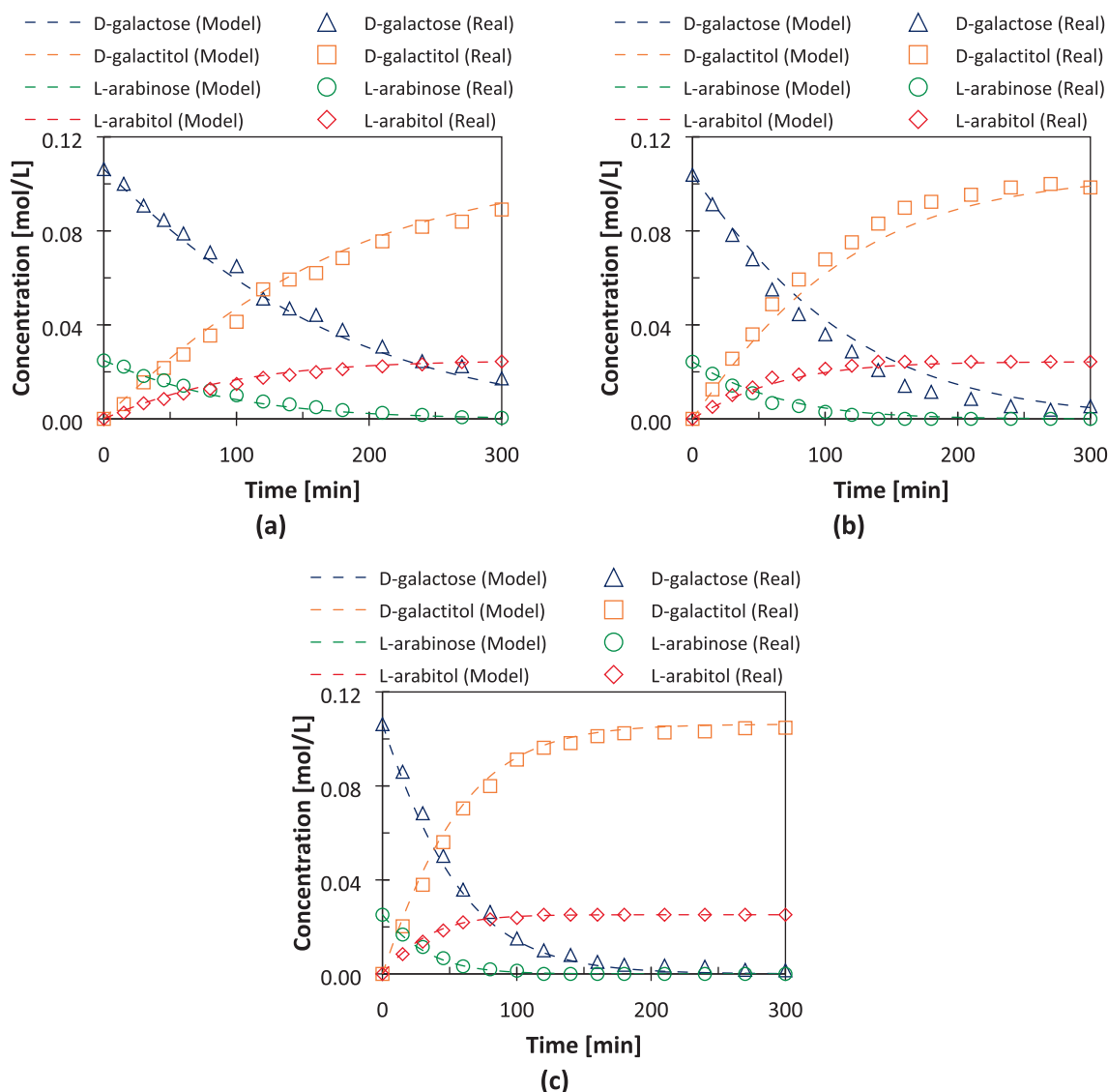


Fig. 11. Modeling of sugar mixture hydrogenation data, G:A ratio = 5: a) 90C, b) 100C and (c) 120C.

the parameters are very well identified, indicating the reliability of the estimated parameters.

The parity plot of all the data from the hydrogenation of binary mixtures is shown in Fig. 13. The parity plot demonstrates the overall very good description of the experimental data by the kinetic model. The correlation coefficient of the plot is practically 1.

A simultaneous catalytic process of molecules, which follow identical reaction mechanisms can be investigated with double logarithmic plots of the reactant concentrations. This kind of plots are used to confirm the correspondence of simultaneous reactions with a common mechanism (Wauquier and Jungers 1956, 1957). The basic idea is that the ratio of the reaction rates of the competing components is proportional to the ratio of their concentrations. Thus, if the mixture behavior obeys the supposed reaction mechanism on an ideal surface, a double logarithm plot of the concentrations would result in a straight line.

In case of L-arabinose and D-galactose competing for hydrogen on the surface of the catalyst, dividing equations (14), (15), (21) and (23) yields

$$\frac{r_A}{r_G} = \frac{dC_A}{dC_G} = \frac{k'_A \cdot C_A}{k'_G \cdot C_G} \quad (27)$$

The relative reactivity of the components is denoted by the parameter α

$$\alpha = \frac{k'_A}{k'_G} \quad (28)$$

Separation of variables and integrating equation (27) with the limits $[C_{A0}, C_A]$ and $[C_{G0}, C_G]$ gives

$$\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \alpha \cdot \int_{C_{G0}}^{C_G} \frac{dC_G}{C_G} \quad (29)$$

Solving the integrals and inserting the integration limits gives the logarithmic relationship,

$$-\ln\left(\frac{C_A}{C_{A0}}\right) = -\alpha \cdot \ln\left(\frac{C_G}{C_{G0}}\right) \quad (30)$$

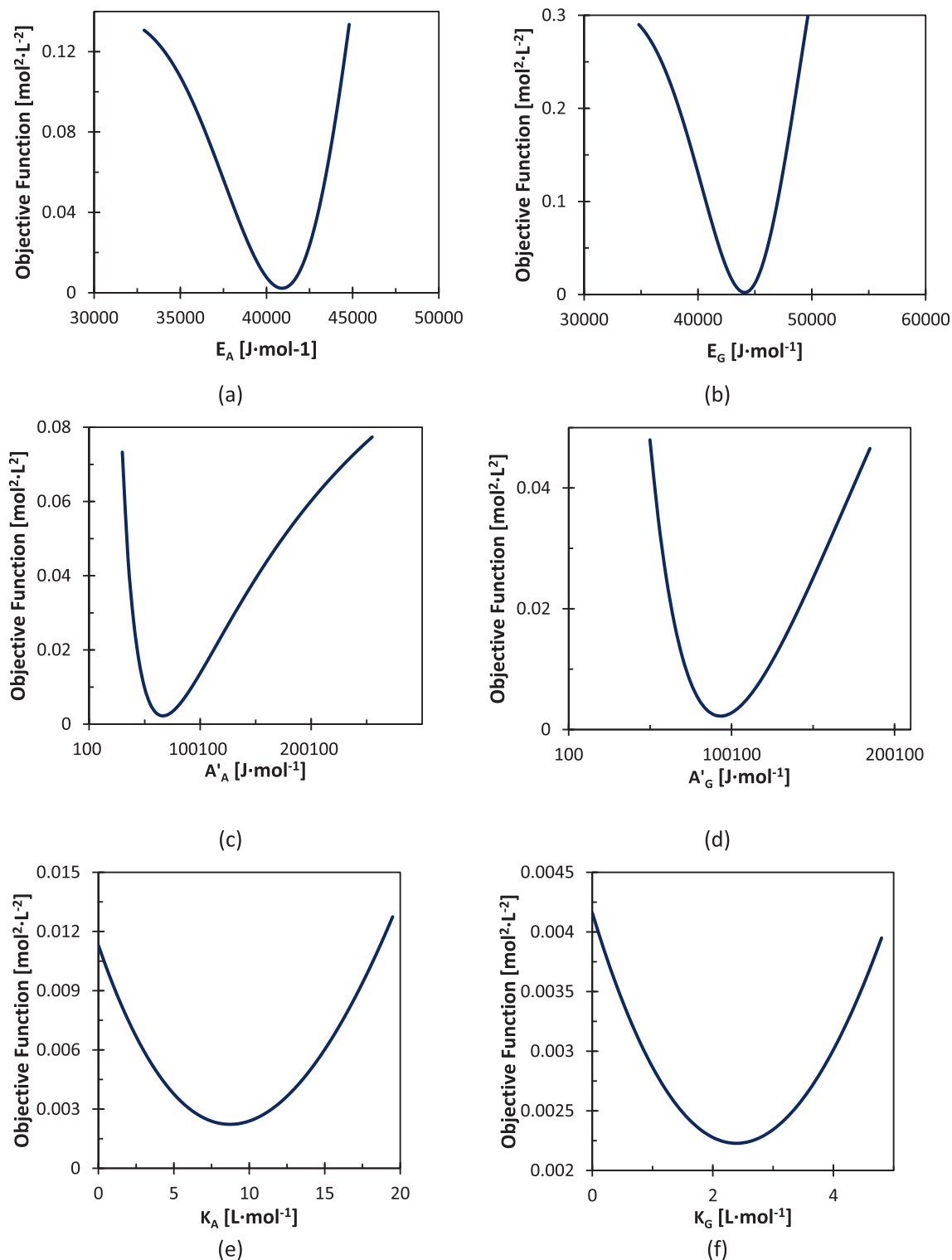


Fig. 12. Sensitivity analysis of estimated parameters for binary mixtures: (a) E_A , (b) E_G , (c) A'_A , (d) A'_G , (e) K_A , (f) K_G .

The logarithm $-\ln\left(\frac{C_A}{C_{A0}}\right)$ was plotted against $-\ln\left(\frac{C_G}{C_{G0}}\right)$ for the data obtained from the mixture experiments. In case of ideal mixtures, the expression (30) predicts a linear relation, from which the relative reactivity α can be evaluated. The value of α is temperature dependent but independent of the initial concentrations of the reactants. The double logarithmic plots are shown in Figs. 14–16,

and the results suggest that both sugars follow similar kinetics, i.e. chemically analogous reaction mechanisms.

As shown by Table 4, the reactivity of L-arabinose is higher than that of D-galactose for all the initial ratios of the sugars. However, the relative reactivity varied with the initial molar ratio, indicating some non-ideality in the adsorption behavior. Sifontes et al. (2011) have obtained similar results for the

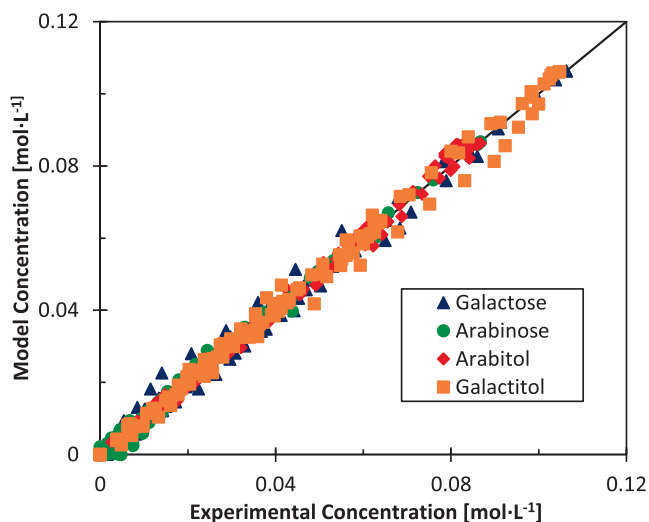
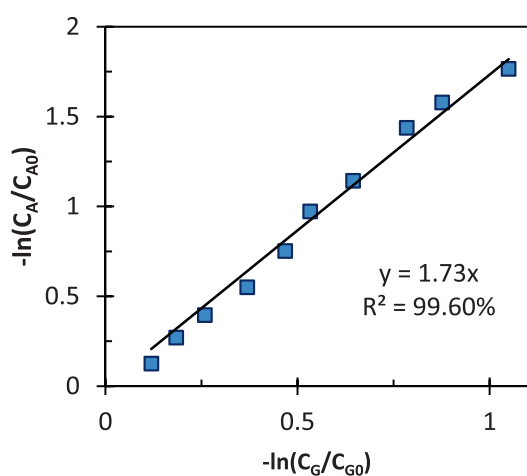


Fig. 13. Parity plot for the modelling results of binary mixtures.

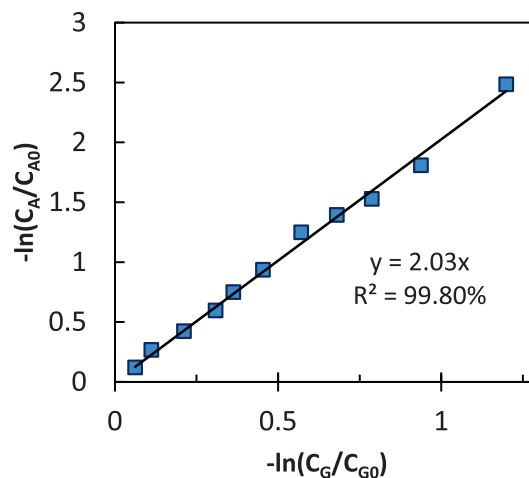
hydrogenation of binary sugar mixtures in the presence of a commercial Ru/C powder catalyst.

4. Conclusions

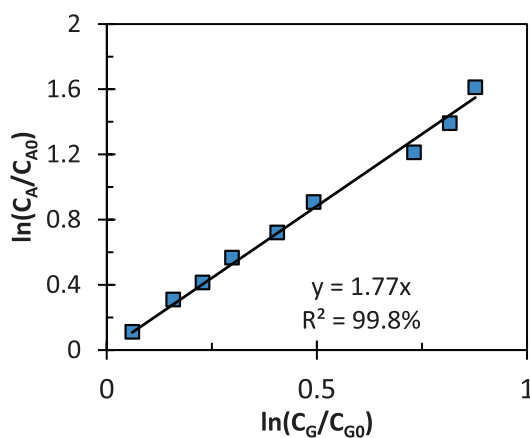
The intrinsic kinetics of hydrogenation of two monomeric sugars, L-arabinose and D-galactose on Ru/C solid foam catalysts was modelled mathematically. The model was based on hypotheses at the molecular level, on elementary steps on the Ru nanoparticles. Non-competitive adsorption behavior between the sugar molecules and hydrogen was presumed and the corresponding rate expressions were derived. The model was fitted to the experimental data obtained from the laboratory-scale semibatch reactor at 90–120°C and 20–40 bar of hydrogen pressure. A very successful description of the concentration profiles and the effect of the reaction temperature was achieved for the data obtained from the hydrogenation of individual sugars and binary sugar mixtures. The sensitivity analysis of the estimated parameters revealed that all the parameters were well-defined, and they had a significant impact on the model.



(a)



(b)



(c)

Fig. 14. Double logarithmic plots of sugar mixtures at 90°C and 20 bar: (a) D-galactose: L-arabinose = 0.5, (b) D-galactose: L-arabinose = 1, (c) D-galactose: L-arabinose = 5.

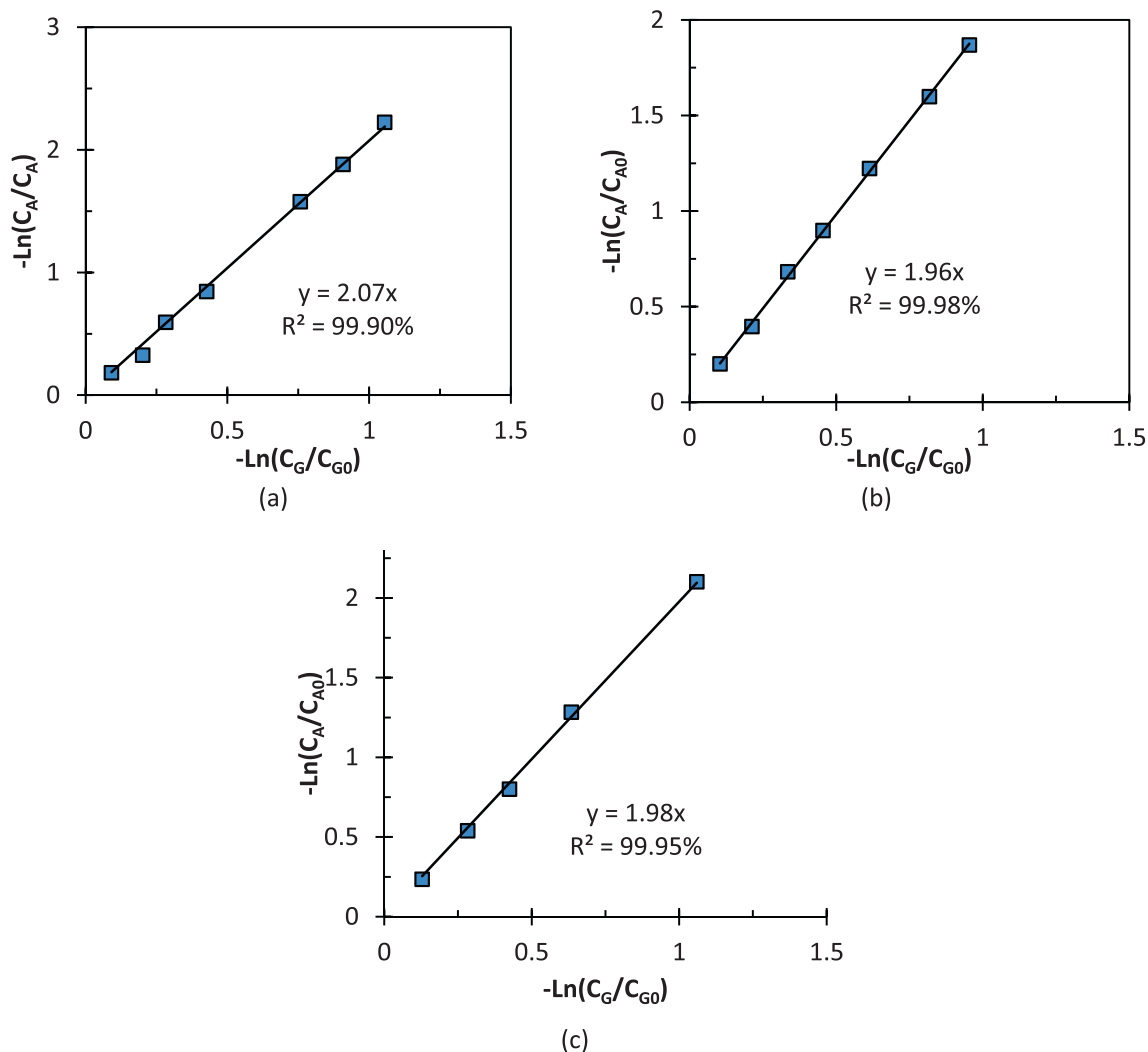


Fig. 15. Double logarithmic plots of sugar mixtures at 100C and 20 bar: (a) D-galactose: L-arabinose = 0.5, (b) D-galactose: L-arabinose = 1, (c) D-galactose: L-arabinose = 5.

The experimental data of the hydrogenation of mixtures at 90–120C and 20 bar and different molar ratios of D-galactose to L-arabinose were evaluated through double logarithmic plots, which indicated that both sugars followed a common reaction mechanism since the logarithmic plots resulted in straight lines. Nevertheless, the relative reactivity varied slightly with the initial molar ratio of the sugars, suggesting that there is a mutual influence of adsorbed sugars.

Table 4
Relative reactivities for different initial molar ratios of D-galactose to L-arabinose.

Molar Ratio (D-galactose to L-arabinose)	Relative Reactivity (α)		
	90C	100C	120C
0.5	1.73	2.07	1.67
1	2.03	1.96	1.70
5	1.77	1.98	1.78

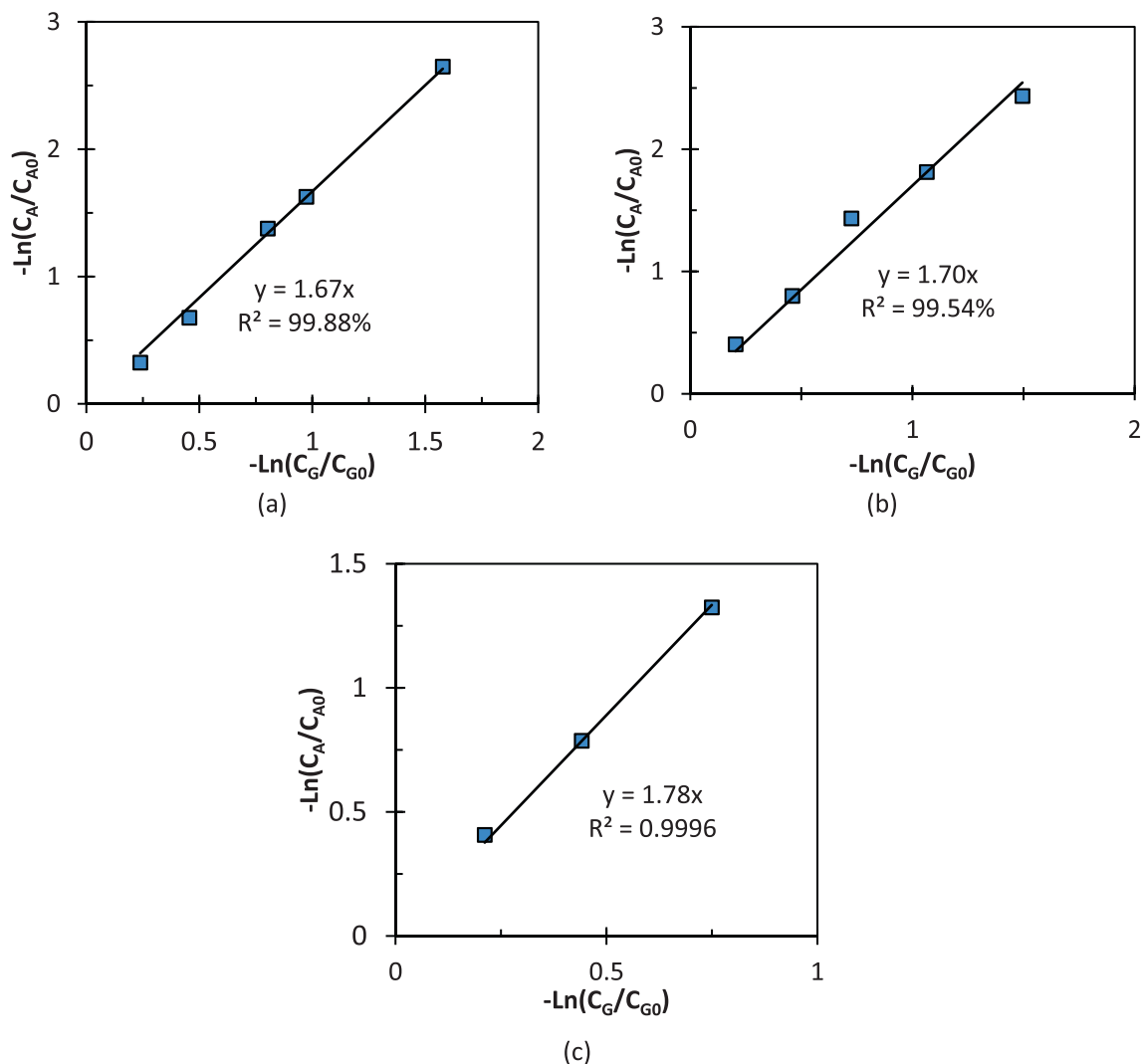


Fig. 16. Double logarithmic plots of sugar mixtures at 120C and 20 bar: (a) D-galactose: L-arabinose = 0.5, (b) D-galactose: L-arabinose = 1, (c) D-galactose: L-arabinose = 5.

CRedit authorship contribution statement

German Araujo-Barahona: Conceptualization, Methodology, Formal analysis, Software, Writing – original draft, Writing – review & editing. **Kari Eränen:** Conceptualization, Methodology, Resources, Project administration, Supervision. **Dmitry Murzin:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision. **Juan García-Serna:** Conceptualization, Methodology, Formal analysis, Writing – original draft, Resources, Funding acquisition, Supervision. **Tapio Salmi:** Conceptualization, Methodology, Formal analysis, Writing – original draft, Writing – review & editing, Resources, Project administration, Supervision.

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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