

Renewable Adipic Acid From the Hydrogenation of *Trans,Trans*-Muconic Acid: Selection of a Three Phases Kinetic Model

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The hydrogenation of muconic acid to adipic acid is studied in a three phases slurry reactor. This is the last step of a novel biotechnological process which, starting from lignocellulosic biomass, allows the production of renewable PA 6,6. A new Pt/C 5% catalyst was selected, which outperformed all the catalysts mentioned in previous literature, and was considered for a more detailed kinetic study. Following an original approach, *trans,trans*-muconic acid was preferred for the hydrogenation, even though the biological transformation of biomass yields only the *cis,cis* isomer. This choice is motivated by the higher stability of *trans,trans* form, which allows to exclude isomerization reactions when studying the mechanism. Also, this isomer is the most likely to be found after the fermentation broth workout and in presence of noble metal catalysts. Preliminary tests identified in 60 °C and 4 bar of hydrogen pressure the mildest conditions to achieve complete conversion to adipic acid in a reasonably short time (1.5 h). The kinetic data collected were used to suggest a plausible reaction pathway and to derive some preliminary kinetic equations. Different models were proposed to interpret the experimental values, developed according to the LHHW theory to consider different adsorption-desorption equilibria. A dual-step hydrogenation mechanism, characterized by hydrogen dissociation on the metal, was hypothesized and validated. These original results provide a first insight on the kinetics of muconic acid hydrogenation and a first reference to further investigations. The purpose is to pave the way for the industrialization of the concept of renewable adipic acid.

1. Introduction

The awareness of the green-house gases impact on climate change and the little predictability oil price have urged industry and scientific research to explore renewable solutions, even for bulk chemicals. This is the case of adipic acid (AA), which has been produced at demonstrative scale starting from sugar and vegetable oil, revolutionizing the traditional benzene chemistry. Several different renewable raw materials can be fermented to achieve adipic acid, following different metabolic pathways (Bart and Cavallaro 2015). Among these, one of the most promising routes exploits either glucose or benzoic acid to produce muconic acid (MA), an intermediate that can be easily purified and can be further hydrogenated to adipic acid (Xie et al. 2014). MA hydrogenation is a chemically catalysed reaction, already investigated in the literature, even though the sole purpose was demonstrating its feasibility. To justify an industrial application of the reaction, an economic (cheap or reusable) catalyst should be found, characterized by high conversion and selectivity for the target product, and able to operate at low temperatures and low pressures. These conditions have not been fulfilled yet (Scelfo et al 2016, a). Furthermore, the reaction mechanism has never been analysed in detail, except for the paper of Vardon et al (2016), which however addressed this problem only cursorily. Another aspect that has been taken into account only recently is the presence of different isomers of muconic acid, which affect the hydrogenation kinetics and complicates the chemical analytics. Biological transformations can only yield the *cis,cis*-MA isomer, which, in virtue of its high steric hindrance, spontaneously evolves into the geometrical

isomer *cis,trans* in acidic environment at temperatures above 30 °C (Frost et al. 2013), conditions that are very likely to be encountered during the workout to purify the fermentation broths. Surprisingly, this aspect has never been considered in previous papers, even though this isomerization increases five times the substrate solubility (Matthiesen et al. 2016). Also, it has been extensively proven that both *cis,cis* and *cis,trans*-muconic acid isomerize to *trans,trans*-muconic acid in presence of noble metals as Pt and Pd (Frost et al. 2013; Matthiesen et al. 2016): these conditions are to be found in the hydrogenation reactor. A new approach was hence followed in this work, using *trans,trans* muconic acid (simply referred as MA) as starting substrate. The use of the most stable isomer allows excluding the isomerization equilibria when modelling the hydrogenation kinetics. This also simplifies the analytical work, given the complexity in characterizing the substrates (Scelfo et al. 2016b; Carraher et al. 2016). The catalyst employed in this study achieved complete conversion and selectivity to AA in mild conditions, which made it a good candidate to proceed with a systematic study of reaction mechanism. This work then provides the first insight of the hydrogenation kinetics of muconic acid in aqueous solutions.

2. Materials and Methods

The substrates were *trans,trans*-muconic acid (Sigma Aldrich, purity 98 %), Pt/C 5 % (Taminco), butanol (Sigma Aldrich, purity >99 %), sulphuric acid 98 % (Sigma Aldrich), Sodium hydroxide (Sigma Aldrich, purity >99 %), Adipic acid (Sigma Aldrich), (2E)-2-Hexenedioic acid (Sigma Aldrich, purity 98 %), dimethyl adipate (Sigma Aldrich, purity ≥99 %). Reagents and solvent were used without further purification.

The hydrogenation of MA was performed on the sodium muconate salt that was obtained adding to the aqueous solution a stoichiometric amount of solid sodium hydroxide. The reaction was carried out in a cylindrical batch autoclave equipped with two different gas lines. Helium was used to clean the reactor and to quench the reaction, while hydrogen was used for catalyst pre-treatment and as reactant for the hydrogenation. The reaction took place in a cylindrical glass tube to avoid that the Nickel contents in the steel could interfere. All the system was heated through an external metal jacket and the temperature was monitored with a thermocouple. The reaction mixture was stirred with a magnetic stirrer at a stirring rate of 500 rpm. The catalyst (0.1 g) pre-treatment occurred in situ at 6 bar of static hydrogen for 3 hours at 200 °C. The hydrogenation reaction was achieved in 10 mL volume of water, with a concentration of 0.7×10^{-2} M. The hydrogenation tests were performed varying temperature (40 and 60 °C) and keeping constant the hydrogen pressure, the amount of catalyst, the agitation speed and the reactor configuration. The reaction tests were performed in batch using a fresh catalyst for all the tests. Sodium muconate conversion was evaluated by UV-Vis analysis. A reaction mixture sample collected after the catalyst filtration was analysed in a spectrophotometer T60 UV-Visible Spectrophotometer PRIXMA from 400 to 190 nm. The maximum absorption was at 264 nm. The calibration of the analysis was performed with sodium muconate prepared from *trans,trans*-muconic acid. The selectivity toward AA and monounsaturated compounds was estimated by GC analyses on derivative methyl esters (Master GC Fast Gas Chromatograph Dani Instrument equipped with an Aldrich Supelcowax 10: 60 m x 0.53 mm id, 1 µL) with TCD detector operating in splitless mode. Butanol was used as internal standard.

The recognition of the reaction intermediates was carried out with GC coupled with mass detector on derivatized esterified products.

3. Kinetic modelling

The studied Pt/C 5 % catalyst outperformed all the others previously tested in terms of conversion and selectivity (>99 %), even at milder pressure (4 bar). Therefore, the reaction was investigated to characterize the kinetic parameters, which represent the basis for the scale up of laboratory data to industry. Since *trans,trans*-muconic acid is a double unsaturated compound, it is reasonable to assume a multi-step reaction, in which mono-unsaturated hexenedioic acid is formed as an intermediate product, and then is hydrogenated to adipic acid. The presence of a solid catalyst in a slurry reactor involves adsorption-desorption equilibria of the reacting species, thus Langmuir-Hinshelwood-Hougen-Watson (LHHW) expressions were used to model the reaction rates (Yang and Hougen 1950; Rostrup-Nielsen 1994). These models, originally developed for gas phase reactions, proved to be effective also for liquid reactions, in which competitive adsorption of hydrogen and organic molecules occurs (Chaudhari and Ramachandran 1980).

The macroscopic performance of a slurry reactor can be affected by the insurgence of mass-transfer resistances between the gas (hydrogen), the liquid (water and reactants dissolved) and the solid (catalyst particles) phases. Even though slurry reactors and the use of a catalyst in fine powder (40 µm) usually minimize transport phenomena issues, the validation of a pure kinetic regime was necessary. Chaudari et al developed some qualitative indexes to assess whether any external or intraparticle mass transfer phenomena

are the rate determining step, taking care, among other aspects, of the initial reaction rate, of the stirring speed, and of the catalyst properties (Chaudhari and Ramachandran 1980; Rajashekharam et al. 1997; Chaudhari et al. 2003). A pure kinetic regime was therefore confirmed. The hydrogen concentration was assumed to be constant throughout the reaction, given the fixed pressure and the exclusion of gas-liquid mass transfer limitation. The nonlinear regression of model parameters, coupled with the solution of the differential equations for the material balances in the reactor, were performed in C++ language applying Bzz-Math libraries (Buzzi-Ferraris and Manenti 2010).

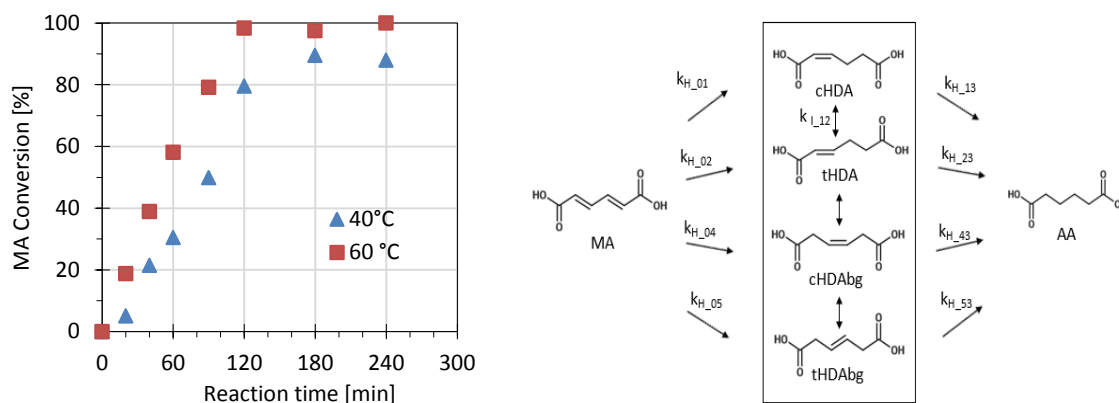


Figure 1: Left: Conversion in time of muconic acid. Right: Reaction scheme with all the possible monounsaturated intermediate isomers. The species reported are *trans,trans*-muconic acid (MA), α,β *cis*-hexenedioic acid (cHDA), α,β *trans*-hexenedioic acid (tHDA), β,γ *cis*-hexenedioic acid (cHDAbg), β,γ *trans*-hexenedioic acid (tHDAbg), adipic acid (AA). In the simplified mechanism, all the intermediates were considered as a single pseudo-component “IN”.

4. Results and discussion

4.1 Preliminary tests and first hypothesized mechanism

Since the main purpose of the study was to demonstrate the feasibility of MA hydrogenation in mild conditions, lower pressures and lower temperatures were studied preferably. As is clear from figure 1 (left), the reaction at 40 °C presents an induction period, and does not achieve full conversion after 4 hours: this denotes too slow kinetics for any practical application. A lag time is often detected in heterogeneous catalytic systems at low temperatures, and it is due to the strong absorption of the organic species on the active sites of the catalyst that gradually are deactivated. Low temperatures are not sufficient to sustain the desorption step, and full conversion cannot be achieved. Vardon et al. (2016) suggested a similar explanation. An increase of temperature to 60 °C eliminated the lag time and allowed complete conversion in only 1.5 hours. The kinetic study was then performed on the data at 60 °C, in line with the suggestions of Scelfo et al. (2016a). Many batches were necessary to provide a sufficient amount of experimental data at different times. Also, the complex and time-demanding workout to characterize the samples limited the number of the available points. To accelerate the data collection, the intermediates were considered initially as a single pseudo-component, referred as “IN” in table 1. Two models based on LHHW adsorption mechanism were evaluated. Model A, considered the dissociation of molecular hydrogen when it is adsorbed on the catalyst, while model B, assumed no dissociation. The reaction rate equations are summarized in table 1. Each hydrogenation step is considered irreversible and rate-determining, if compared to the kinetics of adsorption and desorption of all the species.

In both the cases, the calculations failed to represent properly the experimental data. In particular, the model showed an overestimation of the reactant and the intermediate concentrations. This trend, common in both the models, introduced a doubt on the reliability of the experimental measures, later confirmed by the material balances. A lack of molar quantities up to -20 % was observed during the reaction, which reduced to 0 as long as the reactants were consumed. This peculiar trend could only be explained by some errors in the quantification of the intermediate. After repeating the experiments and increasing the resolution of the gas chromatograph, it was possible to identify two distinct intermediates with different retention times. The analytical technique was then improved, so that all the possible intermediates were considered (table 4) in the successive modelling.

Table 1: Generic equations for the simplified mechanism with intermediate pseudo component. Dual site L-H model according to Yang and Hougen tables, $n=2$ without H_2 dissociation, $n=3$ with dissociation.

Kinetic equation	Reaction step
$R_1 = \frac{\bar{k}_1[\text{MA}][\text{H}_2]}{(1 + K_{MA}[\text{MA}] + K_{H_2}[\text{H}_2] + K_{IN}[\text{IN}] + K_{AA}[\text{AA}])^n}$	MA hydrogenation to IN
$R_2 = \frac{\bar{k}_2[\text{IN}][\text{H}_2]}{(1 + K_{MA}[\text{MA}] + K_{H_2}[\text{H}_2] + K_{IN}[\text{IN}] + K_{AA}[\text{AA}])^n}$	IN hydrogenation to AA

4.2 Refined mechanism and model

Figure 1 (right) shows the possible pathways that the multi-step hydrogenation can follow. Since the hydrogenation catalyst promotes double bond rotation (Frost et al. 2013), all the four isomers are possible. However, the β,γ unsaturated intermediates were not detected in significant amounts, therefore the reaction scheme was simplified.

Three pathways were taken into consideration:

- Model C: Mechanism LHHW without hydrogen dissociation ($n=2$) $T=60$ °C with irreversible isomerization of cHDA to tHDA.
- Model D: Mechanism LHHW with hydrogen dissociation ($n=3$) with irreversible isomerization of cHDA to tHDA
- Model E: Mechanism LHHW with hydrogen dissociation ($n=3$) with isomerization equilibrium between cHDA and tHDA.

Table 2: Generic equations for the refined mechanism with intermediates: dual site L-H model according to Yang and Hougen tables, $n=2$ without H_2 dissociation, $n=3$ with dissociation.

Kinetic equation	Reaction step
$R_{H_01} = \frac{\bar{k}_{_h01}^*[C_1][\text{H}_2]}{(1 + \sum K_i[C_i])^n}$	MA hydrogenation to cHDA
$R_{H_02} = \frac{\bar{k}_{_h02}^*[C_1][\text{H}_2]}{(1 + \sum K_i[C_i])^n}$	MA hydrogenation to tHDA
$R_{H_13} = \frac{\bar{k}_{_h13}^*[C_1][\text{H}_2]}{(1 + \sum K_i[C_i])^n}$	cHDA hydrogenation to AA
$R_{H_23} = \frac{\bar{k}_{_h23}^*[C_2][\text{H}_2]}{(1 + \sum K_i[C_i])^n}$	tHDA hydrogenation to AA
$R_{I_12} = \frac{\bar{k}_{_i12}^*[C_1]}{(1 + \sum K_i[C_i])^n} \quad \text{and} \quad R_{I_21} = \frac{\bar{k}_{_i21}^*[C_2]}{(1 + \sum K_i[C_i])^n}$	Isomerization cHDA \leftrightarrow tHDA

The models of the reaction rates are reported in table 2. Given the higher number of species and reactions with respect to the first modelling attempt, the number of kinetic parameters increases, resulting in different models which all perform a fairly good fitting (R^2 higher than 95% in all the cases). The comparison of the residues of model C and D (figure 2), equivalent in the number of parameters, shows that hydrogen dissociates on the catalyst surface. Model E instead focuses on the isomerization reaction. It considers the reaction from *cis* to *trans* and the opposite isomerization, assuming hydrogen dissociation (the same model without dissociation gave poorer fit, data not included). Theoretically, the *trans* configuration should be favored due to its lower sterical hindrance, however, comparing the two kinetic constants reported in table 3, the reaction seems to move backward. In absence of further experimental evidence, this phenomenon can be explained by the higher reactivity of cHDA, confirmed by the values of k_{H_13} an order of magnitude higher than k_{H_23} . A lower cHDA concentration shifts then the equilibria. The fitting residue of model E is lower than model D, but this could be due to the higher number of parameters. These results therefore serve as an indication, before more experimental data become available. In addition, the kinetic constants show an undue variability,

especially referring to model D. Their values cannot however be compared to other published literature, since no data are available for benchmarking.

Nonetheless, some confirmation on the relative values of the adsorption constants can be found in Chaudhari et al. (2003), who studied the kinetics of hydrogenation of maleic acid to succinic acid in a slurry reactor, a similar system to MA. They observed that the unsaturated acid adsorbs preferably, confirming the relative magnitude of the calculated constants, even though their investigated temperatures were higher than 230 °C.

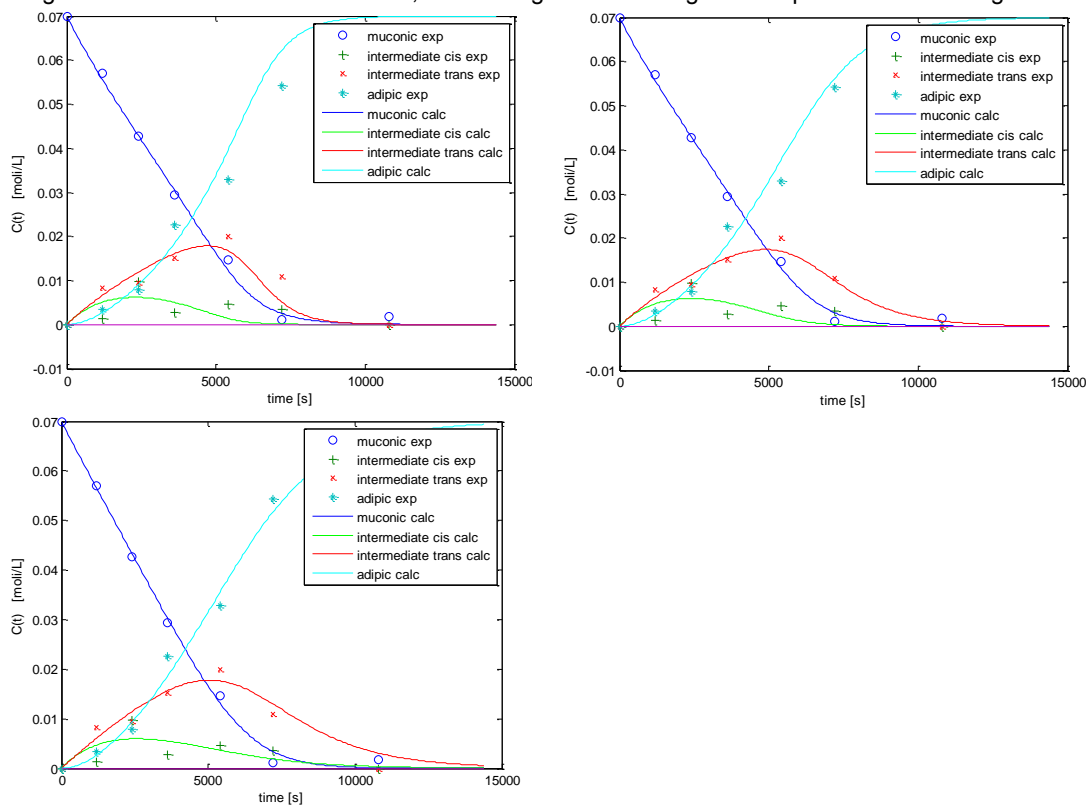


Figure 2: Comparison between experimental points and calculated concentration for model C (top left, residues: 0.0327); model D (top right, residues: 0.0249); model E (bottom left, residues: 0.0226).

Table 3: calculated parameters for the three models, adsorption constants K_i are in $m^3/kmol$

	K_{MA}	K_{CHDA}	K_{THDA}	K_{AA}	K_{H_2}	k_{H_01}	k_{H_02}	k_{H_13}	k_{H_23}	$K_{I_12(I_21)}$
C	67.36	77.17	2.14e-3	2.83	1.75e-1	6.61e-1	5.96e-1	4.60	5.09e-1	1.01e-3
D	15.90	2.60e-1	1.87e-2	3.25	2.33e-2	1.86e-1	1.70e-1	1.28	1.51e-1	1.0e-1
E	12.46	14.91	1.0e-5	2.92e-2	1.08e-2	0.113e-1	9.93e-2	9.52e-1	1.0e-5	2.27e-4 (5.14e-4)

Table 4: concentration of the species during the reaction $T=60$ °C, Pt/C 5 %, $P(H_2)=4$ bar, 500 rpm

Time [min]	C_{MA} [mol/L]	C_{CHDA} [mol/L]	C_{THDA} [mol/L]	C_{AA} [mol/L]
0	7.00E-02	0.00E+00	0.00E+00	0.00E+00
20	5.69E-02	1.36E-03	8.25E-03	3.48E-03
40	4.28E-02	9.79E-03	9.50E-03	7.94E-03
60	2.93E-02	2.85E-03	1.53E-02	2.26E-02
90	1.46E-02	4.69E-03	2.00E-02	3.28E-02
120	1.19E-03	3.52E-03	1.10E-02	5.43E-02
180	1.75E-03	0.00E+00	0.00E+00	6.10E-02
240	1.00E-09	1.00E-09	1.00E-09	7.00E-02

5. Conclusions

This work offers a first insight on the hydrogenation in of *trans,trans*-muconic acid to adipic acid on a new catalyst, which currently allows the highest yields in the mildest conditions. The kinetic data collected have been used to suggest different plausible reaction pathways and to derive some preliminary kinetic equations. Several models have been used to interpret the experimental values, developed according to the LHHW theory, which considers different adsorption-desorption equilibria. In spite of the limited amount of data available, a dual-step hydrogenation mechanism was demonstrated, characterized by hydrogen dissociation on the metal. ttMA is hydrogenated first to cHDA and tHDA, that both undergo to an isomerization reaction, promoted by the double bond activation by the catalyst. The intermediates are further hydrogenated to AA. Further investigation will follow, to improve the model discrimination, to disclose the temperature dependence of the kinetic constants, and to assess the feasibility of a hydrogenation directly on the fermentation broth. A well-characterized and optimized reaction is necessary to demonstrate the scalability of the technology, to exploit the industrial potential of this green approach to adipic acid production.

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