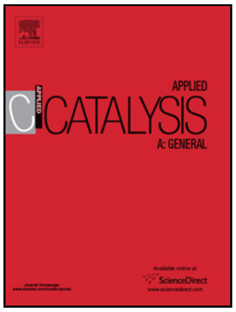

Hydroconversion of xylose derived ketals: a key strategy for producing a broad range of green-hydrocarbons suitable as fuels and petrochemicals

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Hydroconversion of xylose derived ketals: a key strategy for producing a broad range of green-hydrocarbons suitable as fuels and petrochemicals.

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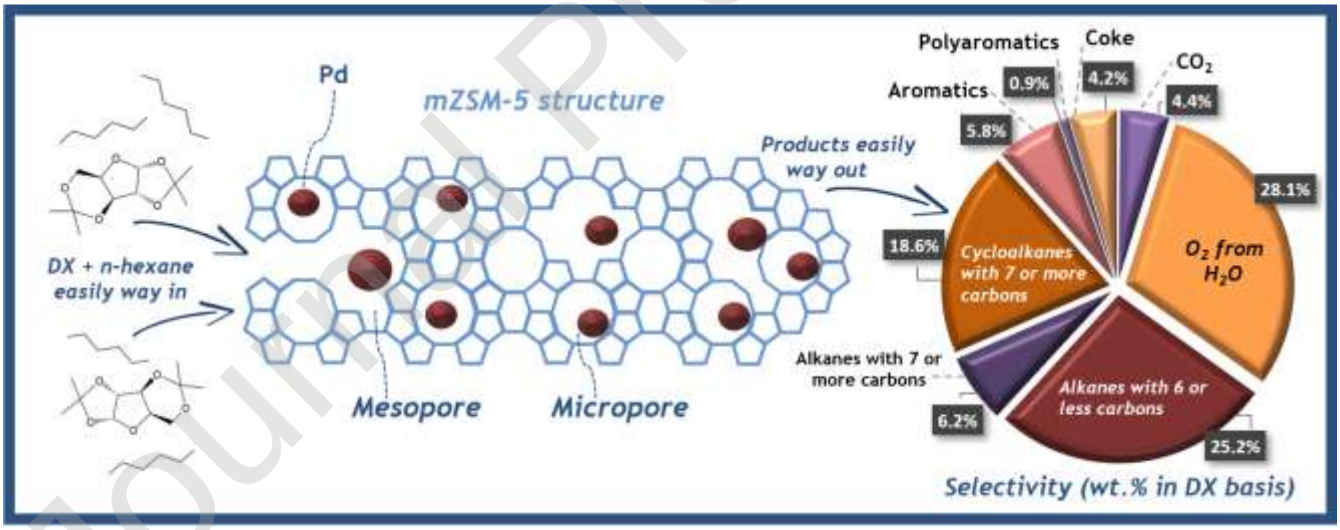


Highlights

- Hydro-conversion of sugar –acetal was explored in fixed and batch reactors.
- Sugar-acetal showed remarkably high green-hydrocarbon yields.

- Obtention of Green iso-paraffin, cyclo-alkanes, and aromatic hydrocarbon.
- Pd/ZSM-5 was the best catalysts used.

Abstract

Recently, sugarcane bagasse was transformed by ketalization reaction into a biocrude with physical-chemical properties adequate for further conversion in typical refining processes. Herein, a representative compound of this biocrude, 1,2:3,5-di-O-isopropylidene-α-D-xylofuranose, DX, in n-hexane was hydro processed in the presence of several palladium-catalysts. Screening in a flow reactor andamong Pd supported on SiO_2, γ-Al_2O_3, HUSY, HY, HBEA and HZSM-5, Pd/HZSM-5 showed the least susceptibility to coke deposition and good deoxygenation capacity, yielding significant amounts of hydrocarbons containing seven or more carbons. Additionally, in a batch and milder conditions, this catalyst was highly selective towards hydrocarbons with high carbon yield and remarkably low coke, i.e., 86 % and <5 % of carbon from DX, respectively. Water was the major product of deoxygenation. The hydrocarbon products included branched and linear alkanes, cycloalkanes and aromatics, whose distribution was sensitive to the catalyst properties, such as support's mesoporosity.

Keywords: green-hydrocarbons, hydro-conversion, ZSM-5, palladium, biomass, sugar.

1 Introduction

The massive use of fossil fuels for hydrocarbons and energy generation led to several concerns in the last decades. Beyond environmental and health hazards, the depletion of petroleum sources and unstable oil prices, have negatively affected economies worldwide. Global population growth and the increasing energy demand required for the many human beings activities are at the center of this problem.

Transportation is one of the activities dependent on fossil fuels, representing a large consumption of primary energy, approximately 28% [1]. Nowadays, renewable energy represents a relatively small portion of the total energy demand, particularly comparing to the photosynthesis potential [2, 3]. Thus, biofuels production from biomass is a promising alternative that can reduce carbon footprint [4].

Among all types of biomass, lignocellulosic biomass is emerging as the main source for biofuels production. Lignocellulosic biomass is the most abundant renewable source on earth, is available worldwide, and can be be a carbon-neutral source [5]. The great complexity of lignocellulosic biomass structure has presented a significant challenge to developing processes capable of promoting its conversion to chemicals and fuels [6, 7]. Fast pyrolysis is the most commonly used technique for the production of second-generation biofuels [8]. Despite the simple structure and flexibility to process different biomass sources, biomass pyrolysis produces a bio-oil with several negative points, including high instability, acidity and oxygen contents, making its transformation into hydrocarbons challenging.

The removal of heteroatoms, like oxygen, from feedstocks, is often achieved by hydrotreating processes or hydroprocessing (HDP) [5, 9]. For instance, catalytic upgrading for oxygen removal has been carried out in pyrolysis bio-oil [10], in oxygenated compounds pure or mixed with hydrocarbons [11, 12]. The catalysts used for bio-oil hydroconversion are quite diverse. However, it has been proven that noble metal catalysts like (Ru, Rh, Pt and Pd) present a better performance regarding oil yield and hydrodeoxygenation degree [13]. γ-alumina is the most commonly used support for hydroprocessing catalysts. However, in recent years, different porous materials such as activated carbon and zeolites have been studied. These catalysts have already shown potential in various processes of refining and hydroprocessing [14-16]. Zeolites are used in several processes due to their high specific area, adsorption capacity and the possibility of tailor-making the number and type of acid sites and textural properties. Also, the pore structures (the size and connectivity of channels and cavities) can control the conversion of molecules involved in the various chemical processes [13].

An alternative approach to biofuel production based on second-generation biomass was proposed in two steps [17]. Firstly, sugarcane bagasse was successfully transformed into a bio-crude by combining acid-catalyzed hydrolysis with organic reactions, like ketalization and acetylation under mild reaction conditions, i.e. temperature between 60-150 °C and pressure up to 12 bar [18-21]. The biocrude, produced from the ketalization of the sugarcane cellulose and hemicellulose sugars with acetone, is mainly composed of isopropyl-ketals, such as 1,2:3,5 -di-O-isopropylidene-α-D-xylofuranose (DX) and 1,2:5,6- di-O-isopropylidene-α-D-glucofuranose (DG), and represented up to 40 wt.% of the total composition [20]. Our group has recently developed a method for full biomass conversion into biocrude using a continuous flow reactor [22]. This method proposed that first hemicellulose is converted, followed by amorphous and crystalline cellulose with 25 substances being found, incluiding and molecules with up to five O-isopropylidene units such as Tetrapentose pentacetonide – m/z 764.37 were identified. Additionally, we demonstrated that this type of biocrude and its representative components, DX and DG, can be converted into green hydrocarbon using simple catalytic tests. Further study, with ^{13}C labeled DX revealed a significant contribution of carbohydrates to the hydrocarbons formation [23]. Indeed, a mixture of DX mixture in n-hexane up to 50 wt.% was recently converted into aromatics in fluidized catalytic cracking (FCC), and carbon from DX conversion into hydrocarbons was estimated to be higher than 70% [24-26].

Herein, DX was used as a representative compound of this new biocrude. DX was mixed and processed with n-hexane under hydroprocessing conditions. Pd supported on γ-alumina, silica-alumina and zeolites (HUSY, HY, HBEA, HZSM-5) were first compared using a fixed-bed flow reactor (350 ºC, 50 bar H_2). Then, the Pd/HZSM-5 was studied in further detail in a batch reactor at different reaction conditions (250 ºC, 40 bar H_2). The obtained results were also compared with those obtained with mesoporous ZSM-5 support. n-hexane hydroconversion under similar conditions was carried out for comparison.

2 Experimental

2.1 Catalyst preparation

The γ-alumina, silica, and the zeolites (Y, USY, BEA and ZSM-5) used as catalyst supports were supplied by Petrobras. The acid form of the zeolites was obtained by ion exchange using a $(NH_4)_2SO_4$ 1M solution at 70 ºC for 1 h in a 50 mL/g zeolite proportion. This procedure was performed four times. After the ionic exchange, the samples were dried at 120 ºC overnight and then calcined in air at 450 ºC for 4 h.

Pd was introduced into the support by incipient wetness impregnation using $Pd(NO_3)_2.2H_2O$ (Sigma-Aldrich) as a precursor. The amount of precursor was estimated to obtain 0.5 wt% of Pd. Then, the samples were dried at 120 °C overnight and calcined in air at 450 °C for 3 h. The catalysts were named Pd/γ-Al_2O_3, Pd/SiO_2, Pd/HUSY, Pd/HY, Pd/HBEA and Pd/HZSM-5.

ZSM-5 (SAR = 41) was treated by an alkaline treatment using a NaOH 0,5 M solution. The mixture (ZSM-5 and NaOH) was heated until 70 ºC and remained at this temperature for 20 min under agitation. Then, the sample was filtered and washed with $(NH_4)_2SO_4$ 1M solution. After this step, the sample was washed with deionized water at 60ºC. Finally, the sample was dried at 120 ºC overnight and calcined at 450 ºC for 3 h. Based on the zeolite yield after alkaline treatment, the SAR was estimated to be 14. The catalyst was named Pd/m-HZSM-5.

2.2. Catalyst characterization

Nitrogen adsorption and desorption process were carried out in a Micromeritics ASAP 2020 apparatus. Firstly, the catalysts were pretreated at 220 °C under vacuum for 4 h. After that, the nitrogen adsorption-desorption isotherms were performed at -196 ºC. The specific surface area (S_{BET}) and external surface area (S_{ext}) were determined by the Brunauer–Emmett–Teller (BET) and *t*-plot method, respectively. The total volume of pores was determined at 0.98 P/P_0 and the micropore volume by the *t*-plot method.

X-ray powder diffraction (XRD) patterns were obtained using a Rigaku X-ray diffractometer with a nickel-filtered CuKα1 radiation source (λ= 0.15406 nm) and a graphite monochromator. XRD profiles were collected by scanning with 0.02° increments (counting 1 s between each increment) in the 2θ angle region between 5° and 80°.

Energy dispersive X-ray spectrometry (EDX) analyses were performed on a Shimadzu EDX-720 spectrometer under vacuum (<30 Pa) to evaluate the chemical composition of the calcined palladium catalysts. Also for these catalysts, SAR is represented by SiO_2/Al_2O_3 molar ratio, which divided by two gives the Si/Al molar ratio.

X-ray photoelectron spectroscopy (XPS) analysis was performed with a Thermo Scientific ESCALAB 250Xi spectrometer (Al-Kα X-ray source, 1486,7 eV). During analysis, the pressure was kept around 10^{-8} mbar inside the analysis chamber. Charging effects were minimized with low energy electron flood gun. XPS data were calibrated using the C 1s peak (284.6 eV) as reference.

NH_3-TPD analysis was performed on a Micromeritics AutoChem II 2920 equipment. Before the analysis, the samples were dried at 150 °C under He flow and reduced at 450 °C for 2 hours. The samples were then purged with He at 450 °C and then cooled to 70 °C to adsorb NH_3. The excess NH_3 in the the samples was removed by purging with He. NH_3 desorption profile was carried out at a constant flow of He from 70 °C to 900 °C with a heating rate of 10 °C.min^{-1}.

The coke loading in the spent catalysts was determined by thermogravimetric analysis in a Netzsch TG-IRIS apparatus. The samples were dried under nitrogen flow at 250 °C for 30 min at a heating rate of 10 °C.min^{-1}. Afterward, the sample was heated

10 °C.min^{-1} up to 700 °C under airflow. The coke loading corresponded to the sample weight loss under airflow.

2.3 Hydroprocessing

Firstly, hydroprocessing was performed in a fixed-bed reactor. For each test, 1 g of catalyst was loaded into the reactor. Before reaction, the catalyst was reduced by flowing H_2 (100 mL.min^{-1}) heating from room temperature to 450 ºC at a rate of 10 ºC.min^{-1} and remained at this temperature for 60 min. The reaction was performed for 2 h at 350 ºC under 50 bar of hydrogen pressure, using hydrogen flow (100 mL.min^{-1}) measured at the condenser exit and atmospheric pressure. DX liquid, 20 wt.% in n-hexane, was admitted with a flow rate of 0.1 mL.min^{-1} using an HPLC pump. For comparison, pure n-hexane hydroconversion was performed under the same conditions for relevant catalysts.

The hydroconversion of DX in the batch reactor was performed in a stirred 450 mL autoclave fabricated by Parr Instrument Company. Before reaction, the catalyst was reduced at 300 ºC for 3 h with an H_2 flow of 50 mL/min. Then, a mixture of the desired amount of DX (15 to 30 g) and 90 g of n-hexane was admitted to the reactor. The reactor was flushed three times with H_2 and then filled with 40 bar H_2. The reactor temperature was increased from room temperature to 250 ºC while the feed was stirred at a rate of 300 rpm. Finally, at this final temperature and pressure the reaction was carried out for 24 h.

Two sets of DX/catalyst ratios were used. First, the amount of DX (in grams) was explored (30, 20, and 15 g), keeping constant the mass of the catalyst (5 g). These experiments were named as T30/5, T20/5, T15/5, respectively. Second, the DX mass was fixed at 15 g and the catalyst amount varied (5, 10, and 15 g). Finally, we explored the effect of improving the mesopores of the ZSM-5, preparing an additional catalyst.

Gas products were analyzed on-line during the fixed-bed reaction and at the end of the hydroconversion reaction by using a MicroGC (Agilent Technologies

MicroGC 490). Liquid products, both organic and aqueous, were collected by condensation (0 ºC), under pressure, with a condenser placed right after the reactor exit. The liquid yield was obtained by the weight of the liquid fraction recovered in the condenser. Then, the liquid phase was frozen at -20 ºC, and the frozen aqueous fraction was measured by weighing after separation from the organic fraction. The organic fraction was analyzed by using GC-MS (Agilent Technologies, 7890A and 5975C) for product identification and by using GC-FID (Agilent Technologies 7890A coupled with FID detector) for product quantification, as described in Supplementary Information. Selectivity was determined by wt.% of carbon. The same equipment estimated oxygenates, their yield were underestimated as they derived from carbon intensity without correction of the weight of oxygen in these components. Thus, values represent an estimated amount. Still, for the the tests where no oxygenates were observed, namely T15/15, the selectivity is in wt.%.

The amount of coke in the spent catalysts was determined by thermogravimetric analysis (Netzsch TG-IRIS). The samples were heated from 308 to 523 K at a rate of 10 °C min^{-1} under N_2 atmosphere. The temperature was kept at 523 K for 30 min, after which the atmosphere was changed to synthetic air (20.9% O_2 in N_2) and the temperature increased to 973 K at a rate 10 K min^{-1} and then maintained at 973 K for 30 min. The amount of coke in the catalyst corresponded to the weight loss at temperatures higher than 523 K. The coke yield was estimated comparing this value (considering the amount of catalyst in each reaction) to the total feed introduced into the reactor.

Conversion, yield, and selectivity were estimated by the equation 1, 2 and 3, respectively.

$$\text{Conversion (\%)}=\frac{\text{initial wt. of reactant-final wt. of reactant}}{\text{initial wt. of reactant}}\text{ x }100 \tag{1}$$

$$\text{Yield (wt.\%)}=\frac{\text{wt. of product}}{\text{initial wt. of reactant}}\text{ x }100 \tag{2}$$

$$\text{Selectivity of product } i\,(\text{wt.\%}) = \frac{\text{wt. of product } i}{\text{wt. of total products}} \times 100 \qquad (3)$$

Relative selectivity to liquid and gas phase, when applied, is defined by equation 4.

$$\text{Selectivity in liq or gas phase}\,(\%) = \frac{\text{Carbon intensity of liq or gas product i in GC-FID or Micro GC}}{\text{Carbon intensity of total liq or gas products}} \times 100 \qquad (4)$$

2.4 Synthesis of 1,2:3,5-di-O-isopropylidene-α-D-xylofuranose (DX)

DX used in the reaction was synthesized as described elsewhere [12][23]. Further informations are presented in Supplementary Information. After the synthesis, pure DX was dissolved in *n*-hexane to obtain the desired mixture used in the reactions. The purity of the final mixture was verified after each synthesis by using GC-MS. It is important to observe that DX can be produced from biomass as recently demonstrated[22].

Results and discussion

3.1 Catalyst support screening in a flow reactor

A mixture of 20 wt.% of DX in n-hexane was converted at 350 ^oC and 50 bar of hydrogen in the presence of Pd/γ-Al_2O_3, Pd/SiO_2, HZSM-5 + Pd/SiO_2, Pd/HUSY and Pd/HZSM-5. The coke and liquid yield and produtct selectivity in the liquid phase (by carbon intensity, %) are presented in Table 1. It was difficult to quantify the gas products under continuous flow, and consequently, a good weight balance could not be attained. Thus, this fraction was not considered. Nevertheless, it was considered that the weight balance could be completed by the gas collected and the light compounds dissolved in the liquid phase, which vaporized during the collection of the liquid from the condenser and were not captured.

Table 1: Hydroconversion of 20% DX in n-hexane with Pd based catalysts in a fixed bed reactor. Coke and liquid yield (wt.% of the feed) and distribution of the products in the organic liquid phase (by carbon intensity), A_{6-} are branched hydrocarbons containing six carbons and hydrocarbon with 5 carbons or less, CyA_{6+} are naphthenics containing cyclopentane and cyclohexane with 6 or more carbons, A_{7+} are hydrocarbons with 7 carbons or more.

	Pd/γ-Al_2O_3	Pd/SiO_2	HZSM-5 + Pd/SiO_2	Pd/HUSY	Pd/HZSM-5
			Yield (wt.%)		
Coke	11.6	19.4	16.3	4.1	0.8
Organic Liquid	62.8	69.9	76.4	66.9	76.2
Aqueous phase				3.2	1.0
Selectivity in the liquid phase (organic compounds in carbon intensity wt.%)					
	−	−	−		
A_{6-}	6.2	1.2	18.7	74.4	66.0
CyA_{6+} + A_{7+}	0.4	−	3.8	16.3	23.5
Oxigenates and non-identified	93.4	98.8	77.5	3.2	8.1

When γ-Al_2O_3 and SiO_2 were used as support a considerable amount of coke was produced. Oxygenates was the major product and hydrocarbons were formed in very small amounts in the liquid phase. With a mixture of HZSM-5 + Pd/SiO_2 catalysts oxygenates slightly decreased, and a corresponding increase in hydrocarbons was observed. Also hydrocarbons containing seven and more carbons were observed. Coke yield remained high. Contrarily, when Pd/HUSY and Pd/HZSM-5 catalysts were used coke yield and oxygenates in the liquid phase drastically decreased. Notably, hydrocarbons were the primary products and a substantial increase of hydrocarbons containing seven or more carbons was observed. Besides, an aqueous phase was observed on both tests.

After the initial tests, a screening of different zeolites supports in flow conditions was carried out. This included previous tested catalysts Pd/HZSM-5 and Pd/HUSY and also Pd/HBEA and Pd/HY. The catalysts were tested with 20% DX in n-hexane and compared with pristine n-hexane at the same conditions. The results are presented in Table 2.

Table 2: Hydroconversion of 20% DX in n-hexane with Pd/zeolite catalysts in a fixed bed reactor. n-Hexane and DX conversion (%). Coke and liquid yield (wt.% of the feed). Liquid products selectivity (wt.% of carbon). A_{5-} are hydrocarbons with 5 carbons or less, branched A_6 are branched hydrocarbons containing six carbons, CyA_{6+} are naphthenics containing cyclopentane and cyclohexane with 6 or more carbons, A_{7+} are hydrocarbons with 7 carbons or more.

	Pd/HUSY		Pd/HY		Pd/HBEA		Pd/HZSM-5	
	nA_6	+ DX	nA_6	+ DX	nA_6	+ DX	nA_6	+ DX
DX conv. (%)	−	100	−	97	−	100	−	100
n-hexane conv. (%)	79	24	51	28	62	29	65	19
Yield (wt.%)								
Coke	0.1	3.3	0.1	1.7	0.1	0.7	0.1	0.6
Organic Liquid	67.8	67.4	72.6	63.2	75.1	69.0	67.5	73.4
Aqueous phase	−	2.8	−	2.0	−	2.6	−	1.6
Selectivity (by carbon intensity in wt.%)								
A_{5-}	0.5	8.5	0.9	4.0	0.2	6.0	0.6	11.9
branched A_6	58.8	3.9	45.6	0.7	58.3	18.3	46.7	4.85
CyA_{6+}	−	2.1	−	1.2	−	2.4	−	3.7
A_{7+}	−	1.4	−	0.8	−	1.7	−	2.1
Oxygenates	−	0.2	−	0.3	−	0.3	−	0.8
Aromatics	−	−	−	−	−	−	−	0.1

All Pd/zeolite catalysts were active for n-hexane conversion. The activity follows: USY > ZSM-5 ≈ BEA > Y. This sequence will be further discussed in the next section of zeolite characterization. The presence of DX reduced the n-hexane conversion in 70% for both Pd/HUSY and Pd/HZSM-5 and 50% for both Pd/HBEA and Pd/HY. For all tests, DX was fully converted. Both the higher molecular weight and the presence of reactive bonds such as the C-O links could be responsible for the more successful occupation of the active sites (both acidic or metallic) by the DX molecule and oxygen intermediates as compare to n-hexane. This could explain the decrease in the activity of n-hexane with the presence of DX in the mixture.

The liquid fraction was the major fraction (yield between 65 and 75 wt.%) and a very small yield in coke was again confirmed (between 0.1 and 3.3 wt.%). A clear tendency on decreasing coke formation can be observed: USY > Y > BEA $\approx$ ZSM-5. This tendency will also be discussed in the next section.

As shown in Table 2, an aqueous phase was observed when DX was present in the feed. It was colorless with no organic products detected by GC-MS. The phase's amount was slightly superior for tests using Pd/HUSY and Pd/HBEA catalysts. Remarkably, both Pd/HUSY and Pd/HBEA also produced lower oxygenates than Pd/HY and Pd/HZSM-5. Nonetheless, oxygenates were produced only in a small amount in all cases. These intermediate products resulted from the incomplete conversion of DX into hydrocarbons, and probably the smaller pores of Pd/ZSM-5 and the lower activity Pd/HY led to less complete conversion.

The main products of pristine n-hexane were isomers and followed by a small amount of light products. Usually the overall selectivities to isomerization of n-hexane in hydro-isomerization in the presence of metal-zeolite catalysts are very high [27-29]. Yet, both cracking by β-scission and hydrogenolysis are unfavorable under the reaction conditions [30]. In the presence of DX, light hydrocarbons (A_{5-}), increased. Remarkably, cycloalkanes with six or more carbons and alkanes with 7 or more carbons were produced. The amount of these compounds obtained were between 13.9 and 29 wt.% of the liquid product which indicatesas a first supposition, DX is responsible for their formation.

Most of A_7^+ compounds contains seven and eigtht carbons (Supplementary Table 2 and 3). Alternatively, CyA_{6+} compounds contained mainly hydrocarbons with six, seven and eight carbons, except for Pd/HY, which showed high hydrocarbons with nine carbons selectivity. Also, the highest amount alkanes and cycloalkanes (up to 10 and 11 carbon atoms, respectively) were observed in the presence of Pd/HY. This suggests that this catalyst might be more suitable to produce high carbon chain products, favored by the large pore zeolites and low acidity of Y zeolite [31].

Gas products produced in the flow reaction are methane, ethylene, ethane, propane, propylene, butanes and pentanes, CO, and CO_2, but they are not quantified, table S4. The CO/CO_2 ratio was higher than one for metal zeolite catalysts. Also, the CO + CO_2 / methane ratio following Pd/USY> Pd/Beta > Pd/HY > Pd/ZSM-5. Water yield follows the same order. These results suggest that deoxygenation is favored in large porous size (like Pd/USY) and external accessibility (like Pd/Beta). But a lower CO and CO_2 formation would indicate preliminarily less carbon loss.

In summary, through these results, we observed that DX is readily fully converted, indicating we can test milder conditions. However, the material weight balance was not satisfactory, probably due to the loss of light products (the material weight balances are 80% or less). The Pd/ZSM-5 catalyst was a promising catalyst due to the lower coke deposition and higher yield of A_{7+} hydrocarbons. Also, when biomass is converted into biocrude by acetalization reaction sugar-acetal derivative, up to 700 daltons are observed [22]. Hence, batch reaction conditions would be more suitable to convert these large molecules than a fixed bed reactor. Thus, we would test Pd/ZSM-5 in a batch reactor and vary more testing conditions to obtain a better insight into the DX transformation.

3.2 Zeolite suppoted catalyst: characterizations suggested interpretations

For better interpretations of the tests results, the four Pd zeolite catalysts were characterized in more detail. XRD patterns of all catalysts are presented in Supplementary Figure 1. In all cases, the X-ray diffraction patterns corresponded to what was expected for each zeolite framework [32]. No PdO or Pd^0 crystallite peaks were observed. The physicochemical properties of Pd/Zeolite catalysts and their respective supports are described in Table 3 (nitrogen adsorption-desorption isotherms are shown in Supplementary Figure 2). N_2 physisorption and textural properties data showed no significant changes by the impregnation of palladium on the zeolites. EDX results showed that the metal content (wt.%) is similar to the nominal value (0.5 wt.%)

for all Pd/Zeolite catalysts. The distribution of acid sites of catalysts and their respective supports were determined by NH_3-TPD. The obtained profiles are shown in Supplementary Figure 3.

Table 3. Physicochemical properties of all Pd/Zeolite catalysts and their respective support, acidity obtained by NH_3-TPD and XPS results (see Supplementary Figure 4 and Supplementary Table 1).

Catalyst	Si/Al	Si/Al FRX	N_2 physisorption				NH_3-TPD		XPS		
			S_{BET} ($m^2.g^{-1}$)	S_{ext} ($m^2.g^{-1}$)	V_p ($cm^3.g^{-1}$)	V_{micro} ($cm^3.g^{-1}$)	Weak mmol.g_{cat}^{-1}	Strong mmol.g_{cat}^{-1}	Pd_{XPS}	Pd_{FRX}	Pd_{xps}/Pd_{FRX}
HUSY	6	-	651	64	0.37	0.27	0.90	1.21	-	-	-
Pd/HUSY	6	4.9	633	66	0.39	0.26	0.98	1.09	0.3	0.4	0.75
HY	5	-	692	74	0.30	0.24	1.29	1.32	-	-	-
Pd/HY	5	4.3	684	82	0.30	0.24	1.09	1.14	0.1	0.41	0.24
HBEA	14	-	653	221	0.75	0.20	0.82	0.80	-	-	-
Pd/HBEA	14	16.2	645	235	0.87	0.17	0.85	0.66	0.4	0.45	0.89
HZSM-5	23	-	394	118	0.21	0.12	0.58	0.59	-	-	-
m-ZSM-5	14	-	484	237	0.50	0.10	n.d.	n.d.	-	-	-
Pd/HZSM-5	23	18.8	378	137	0.21	0.10	0.70	0.38	0.3	0.52	0.58
Pd/m-HZSM-5	14	-	488	241	0.53	0.10	n.d.	n.d.	-	-	-

First, we observed that while the total acidity decreased in the order Pd/Y ≈ Pd/USY > Pd/HBEA > Pd/ZSM-5, and the n-hexane cracking followed the order: USY > ZSM-5 ~ BEA > Y. Since n-hexane cracking demands strong acid strength sites, this may explain Y zeolite smaller activity and ZSM-5 zeolite higher conversion when compared to the BEA zeolite.

Next, even though DX was totally converted in all cases, in fact Pd/HUSY and Pd/HBEA carried out more transformation of the intermediates, producing lower amount of oxygenates and higher aqueous phase. Here, in addition to the high acidity, we would note that BEA zeolite has the highest external area. This may facilitate the transformation of the larger DX molecule. As shown in the table, the external area decreased in the order BEA > ZSM-5 > Y ≈ USY. The alkaline treatment to produce the m-HZSM-5 increases the external area due to the creation of mesopores. Additionally, the internal area was slightly lower in m-ZSM-5 compared to the start zeolite. This slight reduction indicates that the alkaline treatment slightly damaged the zeolite framework.

The tendency on coke formation observed USY > Y > BEA ≈ZSM-5 can be readily rationalized. The low yield of coke for ZSM-5 (0.6 wt.%) is most likely due to the smaller pore size of the MFI framework, which limits bimolecular reaction [25, 26, [32, 33]. On BEA zeolite, the high external area enables a faster diffusion of the coke precursors from the zeolite grain leading to a smaller coke formation [34]. By contrast, the larger pore volume (Table 3) and higher acid site density of USY and Y zeolites increased the coke yield. In particular, on USY, the extra-framework aluminum may promote coke formation [35].

Pd determination by XPS and FRX is presented in Table 3 along with Pd ratio obtained by XPS and FRX. This ratio follows the order Pd/BETA > Pd/USY > Pd/ZSM-5 >> Pd/HY. This order represents the relative accessibility of the metal sites and could be interpreted in terms of zeolite properties. For example, higher external area and higher SAR limit ionic exchange, both properties favor metal on the external surface of the catalyst. These are in line with the properties of BEA and USY. By contrast, Y zeolite with high internal exchange sites, favor Pd in the interior of the zeolite grain. If we speculate external Pd sites favor hydrogenolysis, then, Pd/HY catalyst would provide the least hydrogenolysis of long-chain products as observed. Note that in this case, we speculated that the metal effect is acting on the DX derivatives and not on the initial step of the transformation of the DX molecule.

3.3 Pd/ZSM-5 testing in batch conditions: Effect of catalyst to DX ratio

The DX and n-hexane conversions, yields of coke, gas, and liquid fractions of tests with varying DX/catalyst ratios are presented in Table 4 (detailed information can be found in Supplementary Table 6). In the batch process, the weight balance closed above 92%. Pure n-hexane was almost fully converted, but in the presence of DX, n-hexane conversion remarkably decreased. For example, in the test T30/5, only 2.5% of n-hexane was converted. Increasing the amount of catalyst (decreasing the DX/Catalyst ratio), the n-hexane conversion increased. In all cases, DX was fully converted. The higher reactivity of DX compared to n-hexane suggests that by changing the reaction conditions, the conversion of the co-reactant can be minimized.

Table 4: Hydroconversion in batch condition ((n) g of DX + 90 g of n-hexane using (m) g of Pd/HZSM-5, Tn/m). N-hexane and DX convesioin. Coke and liquid yield (wt.%). Products selectivity the liquid phase (wt.% based on carbon intensity), A_{5-} are hydrocarbons with 5 carbons or less, branched A_6 are branched hydrocarbons containing six carbons, CyA_{6+} are naphthenics containing cyclopentane and cyclohexane with 6 or more carbons, A_{7+} are hydrocarbons with 7 carbons or more.

	n-hex	T30/5	T20/5	T15/5	T15/10	T15/15
Conversion (%)						
DX	-	100	100	100	100	100
n-hexane	98	2.5	2.3	3.0	4.4	10.2
Yield (wt.%)						
Coke	0.1	3.0	1.71	0.78	0.83	0.71
Liquid (Organic liquid phase)	29.9	90.8	91.6	92.0	89.3	90.2
Aqueous phase	-	0.8	0.6	0.2	-	-
Gas	67.2	1.9	2.4	2.0	2.0	2.5
Total	97.2	96.5	96.2	94.9	92.1	93.4
Selectivity (by carbon intensity in wt.%)						
A_{5-}	88.9	4.5	7.0	10.4	17.8	16.8
branched A_6	7.9	1.4	1.1	1.7	11.0	28.4
A_{7+}	<0.1	1.2	0.4	2.3	3.0	3.1
CyA_{6+}	-	1.3	0.5	3.5	7.7	11.1
Mono-Aromatics	-	0.2	0.2	1.0	4.9	2.1
Polyaromatics	-	-	-	-	1.0	0.9
Oxygenates	-	56.0	51.4	31.6	1.2	-
Non-identified	-	4.3	3.6	9.4	1.6	0.7

The coke yield is an important consideration in this hydroconversion process. Naturally, pristine n-hexane produces a very small coke yield. When converting the DX and n-hexane mixtures, a high DX/catalyst ratio gave rather high coke. For example, the test T30/5 produced 3 wt.% of coke. However, keeping the amount of DX constant at 15 grams, and increasing the catalyst did not affect the coke yield (T15/5-T15/15). Indeed, a remarkable low coke yield could be obtained. For instance, 0.7 wt.% yield of coke from a feed with 15 wt.% DX means approximately 5 wt.% of DX is converted into coke.

The liquid fraction analysis in Table 4 shows that the mixtures of DX and n-hexane produced mainly liquid organic phase. With a high DX/catalyst ratio, oxygenates were the main products. Yet, increasing the amount of the catalyst remarkably decreased oxygenates, and they were absent in the test T15/15. Probably, oxygenates were intermediates, and more catalyst present transformed them into hydrocarbon.

The aqueous phase was observed in the experiments with a high DX/catalyst ratio. Lower or even absence of the water phase was observed by increasing the amount of catalyst per DX. We suggest that the water produced was trapped in the zeolite catalyst. Worth mentioning is that the presence of water may have several effects. It may affect the performance of the catalysts and inhibit the reaction of the intermediate compounds. Further, the presence of acid sites and water may revert an acetal of sugar into the corresponding ketone and sugar. Thus, we evaluated the conversion of a mixture of xylose and acetone in the following section.

In short, even though DX is 100% converted in all tests, using a small catalyst amount in relation to DX resulted in a high amount of oxygenates, probably being intermediates to hydrocarbons. We attained total conversion to hydrocarbon by increasing the catalyst to the DX ratio up to 1. It is important to mention that this was attained at a lower temperature by the batch reactor (250 °C) than the flow reactor (350 °C). Also high liquid yield of 90 wt.% was obtained. Further, we had a good weight balance using the batch reactor.

Pristine n-hexane produced mainly hydrocarbons containing five and fewer carbons. Isomers with six carbons represent 8 wt.%. In Table 4, comparing pristine n-hexane to tests T30/5, T20/5, and T15/5, we observed that the branched isomers containing six carbons drop 5 fold in intensity, considering n-hexane gave less than 30 wt.% liquid yield. In contrast, the other test gave ~ 90 wt.% liquid yield, in fact, the yield of isomer dropped even more drastically. Yet, increasing the catalyst amount branched isomers, A_6, increased and the test T15/15 showed a higher A_6 selectivity than pure n-hexane. As n-hexane was poorly converted, we were led to conclude that DX is converted to these compounds. Indeed, A_6 could be considered as one of the major product of the conversion of DX.

Pristine n-hexane did not produce cycloalkanes and hydrocarbons containing seven or more carbons are less than 0.1 wt%. In contrast, both cycloalkanes (CyA_{6+}) and alkanes (A_{7+}) were observed in the presence of DX and their amount increased with catalyst amount. Particularly, on T15/10 and T15/15, CyA_{6+} was superior to A_{7+}. This result was also observed in the fixed bed tests. The former showed most hydrocarbons containing 8 carbons, such as ethyl-cyclohexane, but compounds up to 11 carbons could be observed (see Supplementary Table 5 and Supplementary Figure 5). Regarding A_{7+}, compounds up to 10 carbons were observed and alkanes with 7 carbons such as heptane and 2-methylhexane were the main products. In general, the type of these products was similar to those observed in fixed-bed conditions. Aromatics were not observed in pristine n-hexane and observed in a lower amount for both T15/10 and T15/15 tests. They are mainly mono-aromatic compounds with 7 to 10 carbons, such as 1,3-dimethylbenzene and 1,2,4-trimethylbenzene. Also, in lower amounts, polyaromatics like indenes and naphthalenes were observed. These compounds were absent in a higher DX/ catalyst ratio or in the fixed bed tests.

From the above results, it is worth indicating that this possibility of producing several classes of hydrocarbons (branched and linear alkanes, cycloalkanes, aromatics) implies that green fuels like gasoline, jet-fuel, for example, could be produced from DX.

The fraction of A_{5-} in the liquid organic phase also contains dissolved light hydrocarbons such as propane and butane. We combined these dissolved species with the collected gas products and presented them in Table 5 (also in Supplementary Table 4). Pristine n-hexane produces mainly propane, in general the light produts are related to the hydrogenolysis of n-hexane [36, 37]. The amount of A_{5-} products remarkably increased compared to a fixed-bed reactor, as higher residence time was used in bath reactor, thus favor sequentiall reactions of the isomers of n-hexane. Decreasing the DX/catalyst ratio butanes and pentanes are main products, as n-hexane conversion remarkably decreased, DX had an important contribution to these products. Also, the conversion of DX into methane, ethane, and propane cannot be ruled out.

Table 5: Hydroconversion in batch condition (90 g of n-hexane with (n) g of DX using (m) g of Pd/HZSM-5, Tn/m). Selectivity (wt.%) of CO, CO_2 and hydrocarbons with 5 carbons or less and CO_2/CO ratio.

	n-hexane	T30/5	T20/5	T15/5	T15/10	T15/15
Methane	4.0	0.8	1.0	1.3	0.1	0.9
Ethane	6.5	0.6	0.8	1.1	0.9	1.2
Propanes	41.1	1.0	1.7	2.1	3.1	1.9
Butanes	20.2	0.9	2.5	2.9	6.7	6.0
Pentanes	17.2	1.1	0.9	3.1	7.0	6.9
CO	-	1.2	1.3	0.7	0.6	0.3
CO_2	-	2.8	4.5	3.7	2.9	4.9
CO_2/CO	-	2.4	3.5	5.3	4.7	16.8

Three important observations could be made from the analysis of CO and CO_2 in this light fraction. First, CO+CO_2 represent an important fraction of the light gases. Second, CO_2 was always superior to CO, and the CO_2/CO ratio considerably increased with increasing catalyst amount, up to 16.8 for T15/15. Hence, the catalyst promoted more formation of CO_2 and removed oxygen from the feed with less carbon loss. Third, considering the last case (T15/15), CO_2 + CO was 1.25 g, i.e. 8.3 wt% of DX. From an oxygen balance, we deduced that water was the main product of deoxygenation. The amount of water produced will be further discussed in the subsequent tests.

To enhance hydrocarbon production with special emphasis on the heavier hydrocarbons (A_{7+} and CyA_{6+}) fractions, we explored the effect of increasing mesopores of the catalyst on the DX conversion. The ZSM-5 zeolite with mesopores generated from the original ZSM-5 used by alkaline treatment was used as support. The resulted catalyst was named Pd/m-HZSM-5, with characteristics already presented in Table 3. The comparison of the test results with the original Pd/ZSM-5 catalyst was shown in Table 6.

Table 6: Hydroconversion in batch condition (15 g of DX + 90 g of n-hexane using 15 g of Pd/HZSM-5 or Pd/m-HZSM-5). DX and n-hexane conversion. Selectivity (wt.%), products yield (wt.%), and amount of products (g). A_{5-} are hydrocarbons with 5 carbons or less, branched A_6 are branched hydrocarbons containing six carbons, CyA_{6+} are cycloalkanes containing cyclopentane and cyclohexane with 6 or more carbons, A_{7+} are hydrocarbons with 7 carbons or more.

	Pd/HZSM-5	Pd/m-HZSM-5	Pd/HZSM-5	Pd/m-HZSM-5
DX conv. (%)	100	100	-	-
n-hex. conv. (%)	10.2	3.3	-	-
	Selectivity (wt.%)		Product (g)	
Coke	2.9	3.5	0.71	0.63
Liquid	n.a	n.a.	90.2	93.1
Gas	10.3	7.8	2.5	1.4
Water *	17.8	26.2	4.3	4.7
Total mass	-	-	97.7	99.8
Feed converted	-	-	24.18	17.97
	Selectivity (wt.%)		Product (g)	
CO	0.3	0.1	0.07	0.02
CO_2	4.9	3.7	1.18	0.66
Methane	0.9	0.4	0.22	0.07
Ethane	1.2	2.2	0.29	0.39
Propanes	1.9	2.3	0.45	0.41
Butanes	6.0	12.6	1.45	2.26
Pentanes	6.9	6.6	1.66	1.18
branched A_6	28.4	11.8	6.88	2.11
A_{7+}	3.1	5.2	0.76	0.93
CyA_{6+}	11.1	15.6	2.69	2.79
Aromatics	2.1	4.8	0.51	0.87
Polyaromatics	0.9	0.7	0.22	0.13
Non-identified**	0.7	2.3	0.18	0.41
CO_2/CO	16.8	30.2	-	-
A_{5-}	16.8	24.1	4.07	4.31

* water formation was estimated to close the oxygen balance.
** estimated by carbon intensity

It is observed that n-hexane conversion decreased in the presence of Pd/m-HZSM-5 compared to Pd/HZSM-5. The gas yield decreased and the liquid yield increased. The coke yield also showed a slight decrease. These observations were consistent with the facilitated DX accessibility into the large porous volume, and favored competition with n-hexane for active sites. Thus, lowering n-hexane conversion. Mesopores may also favor the release of intermediate products, hence decreasing gas and coke yields and increasing liquid products.

Pd/m-HZSM-5 favored more deoxygenation by forming water instead of CO_2 and CO. CO being the least amount. It is also important to point out that the amount of oxygen estimated as water, from the oxygen balance between the feed DX, and the oxygen containing products, such as water, CO_2, and CO, nearly closed the material balance for both tests as presented in Table 6.

Mesopore supported catalyst gave higher yields of A_{7+} and CyA_{6+}. The selectivity of alkanes and cycloalkanes products for both tests are presented per carbon number for Pd/HZSM-5 and Pd/m-HZSM-5 in Figure 1. In the Pd/HZSM-5 a maximum was observed for compounds with eight carbons, while for Pd/m-HZSM-5, a maximum was observed for nine carbons. The mesopores presence also slightly increased the mono-aromatics and slightly decreased the polyaromatics. These results were again consistent with the increased pore size of the support, giving higher molecular weight hydrocarbon products on one hand yet avoiding polycondensation of intermediate aromatic products. Besides, as the silica to alumina ratio was lower for this support, more site density could favor hydrogen transfer reaction, thus increasing the aromatic compounds.

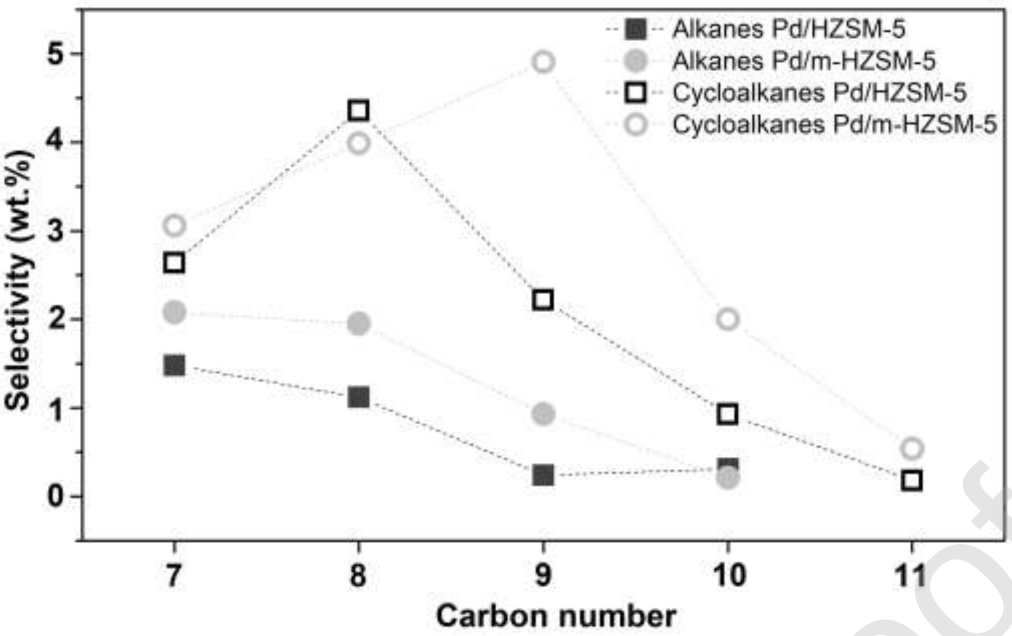


Figure 1: Alkanes and cycloalkanes selectivity (wt.%) obtained from the hydroprocessing of 15g DX in 90 g n-hexane using 15 g of Pd/ZSM-5 and Pd/mZSM-5.

Making use of the complete analysis of Table 6, we can further estimate the distribution of DX into products for both Pd/HZSM-5 and Pd/m-HZSM-5 catalysts to emphasize the effect of increased mesoporosity of the support. This is presented in Figure 2, which also shows Lewis structure of hydrocarbons per group. This was derived considering the only contributions of n-hexane were to the hydrocarbons containing six or less carbons (isomers A_6 + A_{5-}). These were discounted using the value observed in the test of pristine n-hexane multiplied by the n-hexane conversion in the mixture, assuming that n-hexane behaves equally when pure or in mixtures with DX. Non-identified products were not taken into consideration. Water was estimated to close the oxygen balance, i.e., discounting oxygen in CO_2 and CO from the oxygen in DX. Firstly, the amount of oxygen estimated as water to close the oxygen balance almost closed the material balance for both tests as presented in Table 6.

From Figure 2, we could observe two important features that are complementary. First, the presence of mesopores favored, even more, the main product of deoxygenation, water, rather than CO_2 or CO. Hence, it is more efficient in deoxygenation in terms of preserving carbon in the hydrocarbon product. Consistent with this, we observed all the hydrocarbon products increased. Indeed, the amount of green carbon of DX converted into hydrocarbons could be estimated: using Pd/HZSM-5, 70% of carbon from DX was converted into hydrocarbons, this value increased to 86% using Pd/m-HZSM-5.

The changes of the product profiles of A_{7+} have already been discussed and were consistent with the presence of mesopores. However, we did not have enough results to interpret the changes in the product profiles of branched A_6 and A_{5-} at present. We observe a shift from A_6 to A_{5-}. This could be a combination of factors. From the heavier hydrocarbons formed, there could be more cracking by acid sites (lower SAR of m-HZSM-5) and more hydrogenolysis due to more accessible metallic sites (due to mesopores). Further, there was a more direct contribution from the transformation of DX or the intermediate oxygenates. Indeed, the conversion of carbons from xylofuranose of DX into both A_{5-} and A_{7+} compounds in hydrotreatment conditions was demonstrated by using labeled molecules [12].

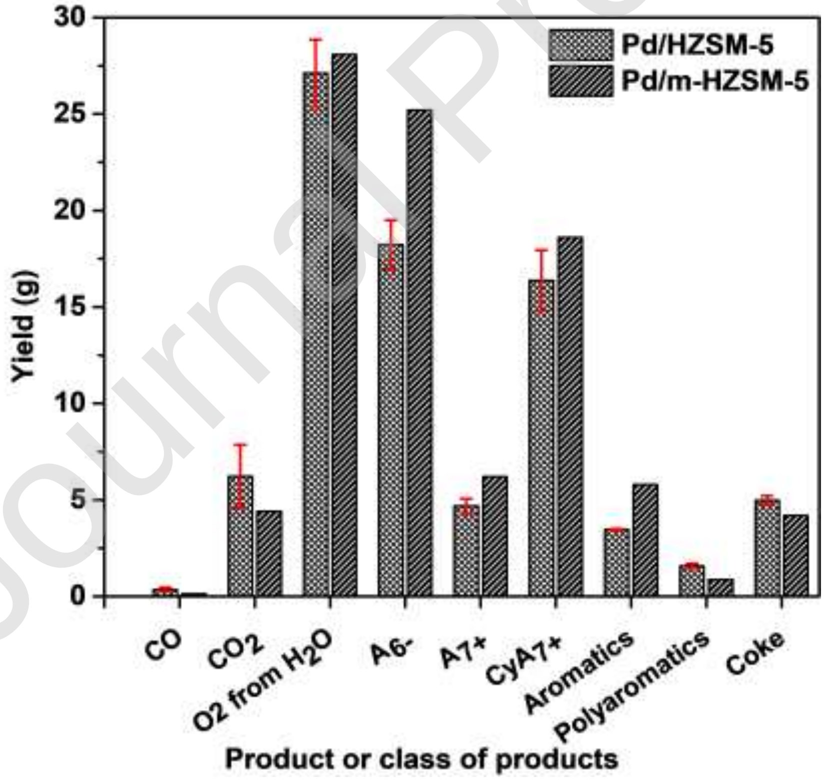


Figure 2: Products yield (wt.%) on a DX basis obtained from the hydroprocessing of 15 g of DX in 90 g n-hexane using 15 g of Pd/HZSM-5 and Pd/HZSM-5 MESO. Error bars were determined by three repetitions using only the Pd/HZSM-5 catalyst.

3.4 A comparison with conversion of cellulose and sugars without protection.

We can only give a general discussion because comparing this work with relevant works is difficult due to the great variety in the experimental conditions used and in the type of target products. The conversion of sugar and second-generation biomass into furfural and HMF (5-hydroxylmethylfurfural) was widely investigated [38]. Furfural, HMF, and other derivatives are explored as a platform for chemicals and fuels [39-42]. Less amount of work was devoted to obtain green-hydrocarbon, particularly with a longer carbon chain. Here, we will restrict our discussion on the type of hydrocarbon products.

Simple, one-step processes used cellulose, hexoses, and pentoses as platforms for producing hydrocarbons in hydro-de-oxygenation conditions (temperature in the range 250-350 ^{o}C and low to high H_2 pressure). In the presence of Pt/USY catalyst, glucose and fructose were converted with high selectivity into hydrocarbons containing four carbons and xylose into hydrocarbons with three carbons. The reaction pathway was proposed to occur through furfural derivatives and acids [43]. In another approach, Dumesic and co-workers developed aqueous-phase catalytic processes to convert sugars [44]. The overall strategy consists of mainly three-step process: 1- Hydrolysis to mono-saccharides; 2- hydroconversion of mono-shacharades into to a hydrophobic organic liquid containing alcohols, ketones, carboxylic acids, and alkanes containing four, five, or six carbon atoms, as well as heterocyclic tetrahydrofuran and tetrahydropyran compounds; 3 – further, sequential processes (cracking, aldol condensation ketonization, for example) convert the organic liquid into several types of fuel, [45], which includes compounds in gasoline, or longer-chain useful as diesel [46]. Recently, in a biphasic reactor, green naphtha containing mainly hydrocarbons with five and six carbons, including cyclo and branched alkanes [47], was obtained by a combination of sequential processes (including hydrolysis, hydrogenation, acylation, alkylation among other reactions). Then, compatible with further downstream petro-refinery operations.

These deoxygenation processes involve dehydration, hydrogenation, hydrogenolysis (C-O and C-C bonds) and their combinations. Thus, limiting the hydrocarbon carbon chain equal to or less than the precursor sugar. Longer carbon-chain and cyclic-alkanes are obtained using sequential reactions, mostly related to acyl intermediates [48]. In general, multiple and sequential processes may reduce the yield of a key product. This is particularly important for a carbohydrates's deoxygenation reaction (which contains lower carbons like hexoses and pentoses) into long carbon-chain hydrocarbons (useful as regular fuels like gasoline, jet fuel, and diesel).

Finally, worth mentioning an alternative approach, alkanes containing 2-9 carbons were the main products, yet, C_{10}-C_{20} compounds were also obtained. Various biomass-materials, including different wood flours and cellulose were transformed in the presence of Pt/HZSM-5 [49]. The biomass was pre-treated in alcohol at high temperatures for hours. The pretreated material was suspended in water and subject to hydrocracking at 673 K. The yields of C_2-C_9 hydrocarbons were very high, and much higher than the reference, untreated case. According to the authors, the reaction pathway includes lowering the molecular weight of cellulose materials, producing oxygenates intermediates which are further converted to alkane by successive hydrocracking and condensation.

At first glance, the pretreatment and the product profile prompted a better comparison with the present ketalization and hydrotreament. However, the material obtained after solvolysis by alcohol was not described in the report. Moreover, the hydrotreatment was made in the presence of a much larger amount of water than our present case where water is only one of the products. This will promote hydrolysis as the initiation step different from our transformation. Further, the amount of coke produced by this approach was not discussed.

3.5 Insights on pathway of DX conversion into hydrocarbons in hydro-conversion condition

The liquid products of test T15/15 (in the presence of HZSM-5) were monitored from 1-11 h on time on stream (TOS), as presented in Figure 3. Oxygenates decreased during TOS. The intensity of these products was obtained by carbon intensity (measures in the GC-FID). Though not in weight %, they represent the contribution of each type of product to the carbons in the mixture.

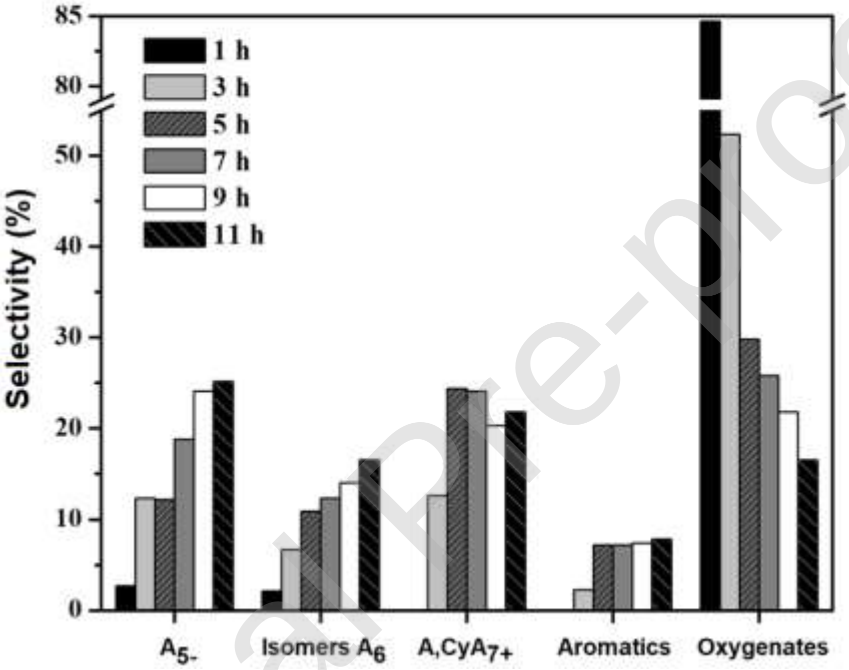


Figure 3: Product distribution in the liquid phase by carbon intensity (wt.% of carbon of a product / total wt.% of carbon in the products) obtained from the hydroconversion of 15 g of DX in 90 g of n-hexane using 15 g of Pd/HZSM-5. A_{5-} (alkanes with 5 or less carbons), A_6 Branched hydrocarbons with 6 carbons, A_{7+} (Alkane with 7 carbons or more), C_yA_{6+} (Cycloalkane with 6 carbons or more).

As observed from the previous sections of the catalyst to DX ratio study, oxygenates were intermediates that decreased with the reaction's progress. The identification and quantification of the oxygenated products are under investigation and presented in our next publications.

As the oxygenates decreased, all hydrocarbons increased but in a different manner. One of our main interests, cycloalkanes and alkanes (containing seven of more carbons) increasing from 1 to 3 h of time of reaction, then remaining constant. The aromatics behave similarly. Branched isomers containing six carbons and A_{5-} (propane, butanes, and pentanes) increased with time of reaction.

It is well known that a sugar acetal can be reverted into sugar and acetone in the presence of water and acid catalyst [50, 51]. We evaluated the importance of this contribution to the oxygenate pool. A preliminar test converted a mixture of xylose, acetone and n-hexane in the presence of Pd/ZSM-5, as presented in Figure 4. More detailed data are presented in Supplementary Table 7. A radically different product distribution was observed when compared to the DX conversion in the test T15/15. For example, coke yield increased 5-fold, and oxygenates are observed. More strikingly, cyclo-alkanes decreased 4-fold. These differences showed that the reverse reaction of DX (for example, into xylose and two acetones) contributed mainly to light hydrocarbons, aromatics, and coke, but did not lead to a broad range of hydrocarbons as observed to DX. Thus, compared to unprotected sugar, the presence of an isopropylidene group in DX decreased undesirable reactions like coke formaton and improved the flexibility in obtaining different hydrocarbons types and long carbon-chain.

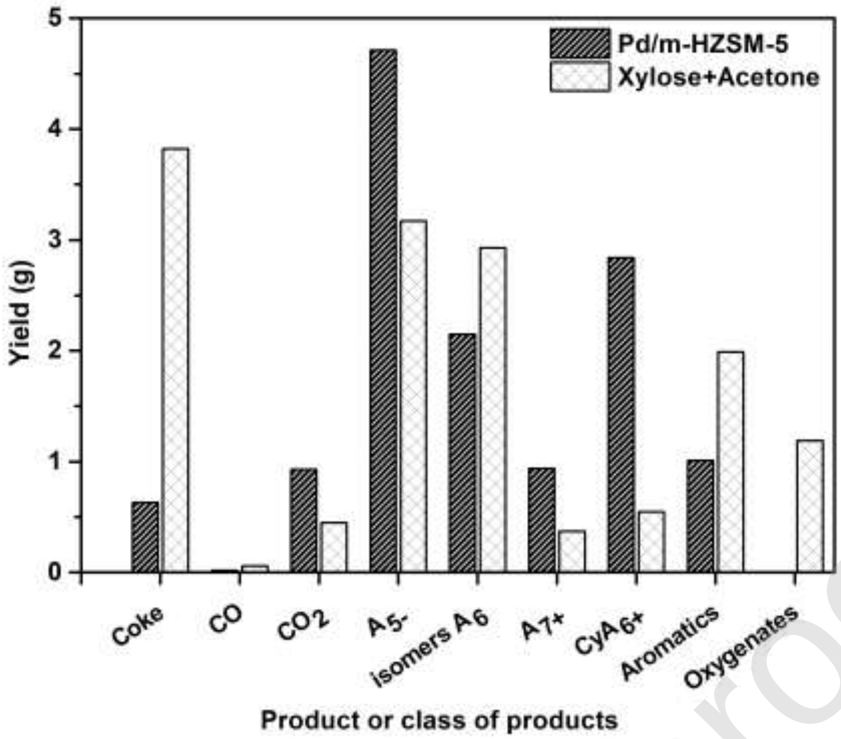
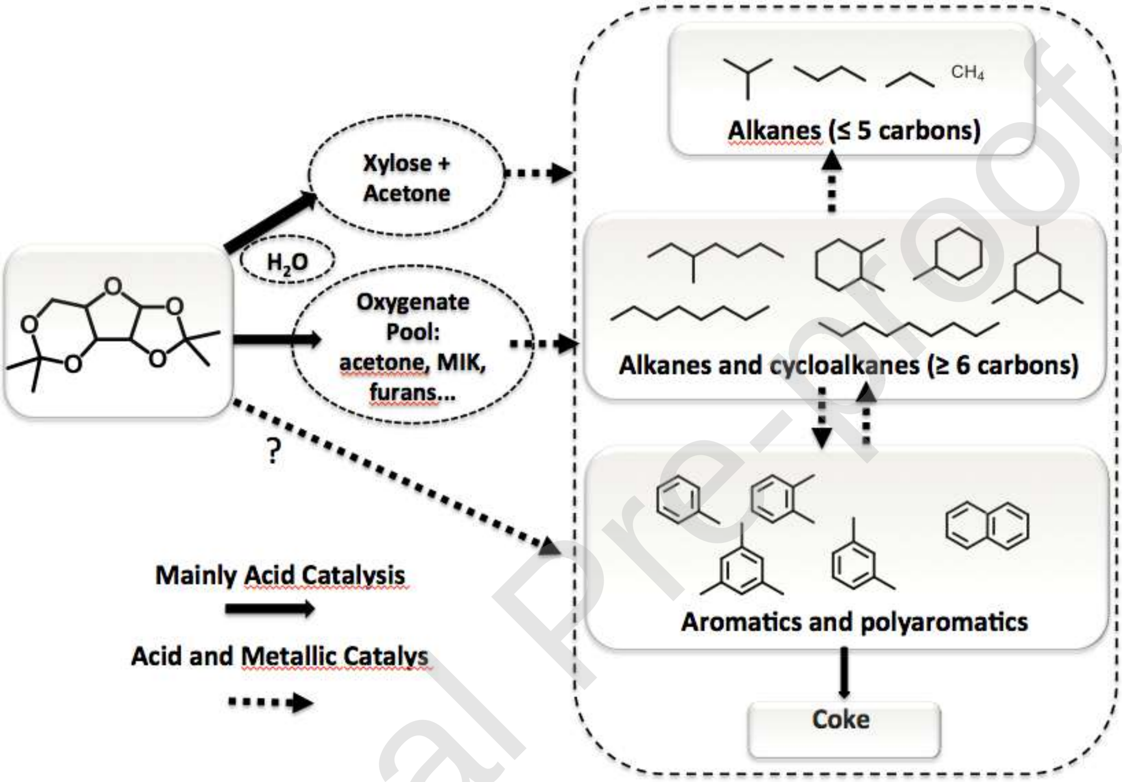


Figure 4: Products yield (g) produced by converting 15 g of DX + 90 g of n-hexane and 10 g of xylose + 5 g of acetone + 90 g of n-hexane (It was used 15 g of Pd/ZSM-5 and 24 hours of reaction). Note, the yield of oxygenates fraction was underestimated as it was derived from carbon intensity without correction of the weight of oxygen in these components.

An attempt to sumarise the possible routes of transformation of DX into hydrocarbons are presented in Scheme 1. DX can be converted into oxygenated compounds (a pool of oxygenates) and sequentially into alkanes, cycloalkanes and aromatics. Speculatively this first step obtaining oxygenate derivatives is mainly promoted by acid sites. These products can undergo further reactions. Now metal sites are operative in addition. First it plays a role in preventing coke deposition. Other examples are: aromatics can be converted to cycloalkanes and vice-versa by hydrogenation and dehydrogenation respectively, cycloalkanes and alkanes can be converted to lighter hydrocarbons by hydrogenolysis, cracking and hydrogen transfer reactions via acid catalysis also occur.

During the generation of oxygenates, water is also produced. Once this is present, the reverse reaction of ketalization could take place, giving Xylose and acetone. Their subsequent transformation to hydrocarbons could take place, but probably this is not the main reaction pathway.

Yet, it is not clear if DX itself can be converted directly to some types of hydrocarbons bypassing the oxygenates pool. Hence, a possible link is also drawn in Scheme 1.



Scheme 1: General reaction pathway of DX conversion on Pd/HZSM-5 catalyst.

As demonstrated DX, itself or via an oxygenated pool, produced a broad range of hydrocarbons containing up to 11 carbons. Potentially, the yield in target products may be improved in further works. As attempts to suppress further transformation of heavier hydrocarbons to lighter products, we have explored the modification of Pd to decrease hydrogenolysis [52] and reduce acid sites by increasing the SAR of the zeolites. These catalysts optimizations are subjects of our coming publications.

3 Conclusion

A representative carbohydrate-derived ketal compound from bio-crude 1,2:3,5-di-O-isopropylidene-α-D-xylofuranose, DX was converted in the presence of n-hexane under hydroprocessing conditions on several Pd/acid catalysts. Pd/HZSM-5 was less prompt to coke deposition and produced a high amount of hydrocarbons containing seven or more carbons. Thus it was selected study in various reaction conditions.

It was demonstrated that DX can be converted in both flow and batch conditions in termos of reaction conditions. The DX/catalyst ratio and the textural properties of the catalysts are important for DX hydroconversion.

Regarding the transformation process with Pd/HZSM-5 in the conditions studied, DX underwent deoxygenation in hydroconversion mainly as water (> 70 wt.% of oxygen) followed by CO_2 (around 20% wt.% of oxygen) and CO is less observed. A very small coke yield was observed. Oxygenates were important intermediates that can be fully converted to hydrocarbons by adjusting the DX/catalyst ratio

In terms of hydrocarbon products, the liquid product could be obtained in a very high yield. The product distribution responded to the change of catalyst properties. Notably, when mesoporous HZSM-5 was used as support, a higher amount of C_{7+} hydrocarbons with longer chains were produced compared to the normal ZSM-5 support. In this case, 86% of carbon from DX was converted into hydrocarbons.

These results reinforce the overall strategy: first transforming biomass by acetalization reaction into a biocrude composed mainly by acetal-derivative, then further converting the acetal derivative (pure or mixture in the form of the biocrude) into hydrocarbons. The broad range of hydrocarbons (branched and linear alkanes, cycloalkanes, aromatics and light hydrocarbons) supports that green-fuel (for example gasoline, diesel and jet-fuel) can be produced from biomass.

Declaration of interests

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.

credit author

Sérgio Castro Pereira and Matheus Souza carried out all experiments of HDO, Laura M. Esteves characterized catalysts by BET, XPS, DRX, FRX, Nuno Batalha helps in the interpretation and both Yiu Lau Lam and Marcelo Maciel Pereira conduct the research

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