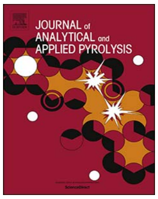
Journal of Analytical and Applied Pyrolysis 131 (2018) 1–8

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap



Sugarcane bagasse *ex-situ* catalytic fast pyrolysis for the production of Benzene, Toluene and Xylenes (BTX)

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ARTICLE INFO

Keywords:
Ex-situ catalytic fast pyrolysis
ZSM5
BTX
Sugarcane bagasse

ABSTRACT

The *ex-situ* catalytic pyrolysis of sugarcane bagasse with various HZSM-5 (23, 50, and 80) catalysts was studied in a tandem micro reactor-GC/MS at 400 °C, 450 °C, 500 °C and 550 °C with a catalyst to biomass (C/B) ratios ranging from 2 to 23. The yields of benzene, toluene and xylenes (BTX) were significantly affected by pyrolysis temperature and C/B ratio. The highest BTX yield of 22% was obtained for the HZSM-5 (23) catalyst at C/B ratio of 12.5 and a temperature of 475 °C. Finally, an experimental design was performed to determine the optimal process conditions for BTX yields.

1. Introduction

The world demand for benzene, toluene and xylenes (BTX) was around 115 million MT/a in 2014 [1]. BTX is widely used in the chemical industry [2–6] for the production of a large range of bulk chemicals and plastics derived thereof. Examples are styrene, phenol, nylon, aniline, anti-knock gasoline additives, various solvents, phtalic anhydride (o-xylene), isophtalic acids (m-xylene), terephtalic acid and dimethyl terephtalate (*p*-xylene) for PET fibers, resins films etc. [2,7]. Decreasing fossil resources and anticipated growth of the BTX market, paves the way for the production of “green” BTX from lignocellulosic biomass. A number of technologies have been proposed for this purpose. For example, the company GEVO reported that *p*-xylene potentially can be produced *via* enzymatic conversion and subsequent catalytic transformations of sugars [18]. Moreover, *p*-xylene can also be obtained from biomass sources like cellulose *via* thermochemical processes [19]. For instance, the BTA process involves biomass gasification towards synthesis gas that is subsequently converted to BTX *via* methanol [20]. BTX synthesis *via* in- and *ex-situ* catalytic fast pyrolysis is also considered an attractive option. It involves pyrolysis of the biomass source in the presence of aromatization catalysts to obtain BTX. *In-situ* catalytic pyrolysis uses a physical mixture of biomass and catalyst, while *ex-situ* catalytic pyrolysis involves the catalytic upgrading of the hot pyrolysis vapours downstream of the pyrolysis reactor. Table 1 presents examples of both *in-situ* and *ex-situ* catalytic pyrolysis of biomass for BTX synthesis. For instance, Karagoz et al. [21] studied HZSM-5 catalysed pyrolysis of various lignocellulosic biomass types using a micro-reactor-GC/MS. It was reported that the yield of BTX was a strong function of the feedstock composition. According to Zheng et al. [22], selectivity towards aromatics for catalytic fast pyrolysis of biomass was significantly affected by the ZSM-5 crystallite size with 50 nm for the highest selectivity but lowest yield and 200 μm for the highest yield. The BTX yields when using ZSM-5 with a crystallite size of 50 nm for cellulose and pine wood were 13.9% (mol%-carbon) for cellulose and 10.2% (mol%-carbon) for pine, while BTX yields of 13.3% for cellulose and 8.5% for pine were obtained when using ZSM-5 with a crystallite size of 200 nm. Zheng et al. [22] indicated that the order of BTX selectivity ranged from alkali lignin > hemicellulose > straw > pine > corncob > cellulose. Carlson et al. [23] found that the BTX selectivity is strongly affected by pyrolysis temperature and catalyst to glucose weight ratio. They reported that a maximum BTX yield of 16.5% (mol%-carbon) can be obtained at 600 °C and a ZSM-5 catalyst to glucose ratio of 19 (w/w).

Using different types of ZSM-5 catalysts in a semi-batch fixed-bed reactor, Foster et al. [25] showed that glucose, furan and maple wood are preferentially converted to BTX when using microporous ZSM-5s, while mesoporous zeolites shift the product distribution towards heavier alkylated monoaromatics. Further studies showed that the yield of hydrocarbons from ZSM-5 catalysed pyrolysis of carbohydrate-derived oxygenates such as 5-hydroxymethyl furfural, furfural, acetic acid,

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https://doi.org/10.1016/j.jaap.2018.02.019
Received 2 December 2017; Received in revised form 15 February 2018; Accepted 18 February 2018

Table 1
Overview of BTX production by catalytic fast pyrolysis.

Feed	Catalysts	Use	Method[a]	T (°C)	BTX yield	Ref
Beech wood, cellulose, microalgae	HZSM-5	*Ex-situ*	Tandem micro reactor	400–600	43.8%, 28.6%, 13.3%[b]	[21]
Pine, corncob, straw, cellulose, lignin, hemicellulose	ZSM-5	*In-situ*	Pyroprobe	600	10.2%,10.4%, 12%, 13.9%, 6.6%, 14.4%	[22]
Glucose	ZSM-5	*In-situ*	Pyroprobe	100–600	16.5%	[23]
Cassave rhizome	ZSM-5, Al-MCM-41,	*In-situ*	Pyroprobe	500	NA	[24]
Glucose, furan, maple wood	ZSM-5, HY, USY	*In-situ*	Pyroprobe	400–600	21.6%	[25]
Pine and Jatropha	ZSM-5, (Co, Mo, Ga, Pt, Pd and Ni)	*In-situ*	Pyroprobe	650	15%	[26]
Furfural	Lamellar and pillared ZSM-5, Mg/ZSM −5 and Zn/ZSM-5	*In-situ*	Fixed bed reactor	550	25.4%	[27]
Pyrolytic pinewood oil	Fe/ZSM-5	*In-situ*	Pyroprobe	650	28.9%	[28]
Corn stover	ZSM-5	*In-situ*	Pyroprobe	500	NA	[29]
Furan and pine	ZSM-5 and Ga/ZSM-5	*In-situ*	Fixed and fluidized bed	650	NA	[30]
Beech, cellulose and lignin	Mesoporous ZSM-5	*In-situ*	Pyroprobe	500	19.7%, 19.5%, 7.8%	[31]
Olive residue	Clinoptilolite, ZSM-5, HY	*In-situ*	Pyroprobe	350–500	NA	[32]
Hybrid poplar	HZSM-5	*In-situ* & *ex-situ*	Tandem micro reactor	400–700	19.7%	[33]
Beech wood	HZSM-5	*In-situ*	Circulating fluidized bed reactor	520	NA	[34]
Sugarcane bagasse	–	*In-situ*	Fluidized bed reactor	500 & 550	NA	[35]
Sugarcane bagasse; agricultural residues	Activated carbon	*In-situ* & *ex-situ*	Pyroprobe	250–450	12.5%	[36]
Sugarcane bagasse and pine	ZSM-5	*In-situ*	Fluidized bed reactor	500	NA	[37]
Sugarcane bagasse	–	*In-situ*	Semi-batch reactor	350–650	NA	[38]
Sugarcane bagasse and palm	–	*In-situ*	Fixed bed reactor	400–600	NA	[39]

[a] Typically micro to milligramme scale of operation.
[b] Maximum relative yield (area% of all detected peaks).

levoglucosan and glycolaldehyde was strongly affected by functionality and molecular size of the substrate (Wang et al. [33]). In addition, it was shown that the temperature did not significantly affect the product distribution for *ex-situ* pyrolysis of hybrid poplar with HZSM-5 between 400 and 700 °C. In addition, *in-situ* catalytic pyrolysis produced more aromatics than the *ex-situ* approach under comparable conditions. Paasikallio et al. [34] found that the ratio catalyst to biomass (C/B) for an *in-situ* pilot circulating fluidized bed reactor system strongly influenced the overall product quality and acknowledged the importance of optimization the C/B ratio for both the quantity and composition of the bio-oil product.

In general, integrated and systematic approaches are scarce, *e.g.* regarding type of biomass, catalyst characteristics, catalyst use (in-, or *ex-situ*), catalyst/biomass ratio, pyrolysis technology, pyrolysis operation conditions, etc. A potentially very attractive biomass source for BTX production is sugarcane bagasse. Bagasse is a by-product of sugar milling and potentially presents an important resource for the production of biofuels and biochemicals. Its high volatile matter (nearly 80% (w/w)) indicates a high potential for BTX production by fast pyrolysis. In addition, bagasse is the most abundant Iranian agro-industrial waste, of which more than 2 million metric tons per year is produced in Iran. However, the production of BTX from bagasse has not been investigated yet among the few studies on catalytic pyrolysis of bagasse in general. For instance, a maximum bio-oil yield of 53.4 wt% was obtained at 560 °C for the fast pyrolysis of 0.5–0.85 mm particles of sugar cane bagase in a fast pyrolysis, fixed-bed reactor [39]. Montoya et al. [35] investigated the production of bio-oil from Colombian sugarcane bagasse in a fluidised bed reactor. They indicated that operational parameters such as temperature, particle size, gas flow and feed rate promote the devolatilisation and yield of the bio-oil. Varma and Mondal [38] reported that bio-oil from the fast pyrolysis of sugarcane bagasse can potentially be valuable as a renewable fuel after upgrading and as chemical feedstock because of its valuable and complex mixture of chemical compounds including acids, alcohols, aldehydes, furfural, furan, phenols and aromatic compounds. Bagasse was selected as the best material for the production of high-value 4-vinylphenol *via* non-catalytic fast pyrolysis and for the production of 4-ethyl phenol *via* catalytic fast pyrolysis with activated carbon as catalyst [36]. Catalytic fast pyrolysis of bagasse with ZSM-5 yielded a significantly greater amount of valuable aromatic compounds, such as toluene, xylenes, and ethyl-benzene in comparison with the catalytic fast pyrolysis of pine wood in a pilot scale unit [37].

In this study, the effect of pyrolysis temperature, types of HZSM-5 catalysts (different Si/Al ratio), and catalyst to biomass ratio on the yield of BTX from low cost sugarcane bagasse *via ex-situ* catalytic pyrolysis was investigated using a tandem-microreactor system.

To the best of our knowledge, sugarcane bagasse has not been used as a source for BTX synthesis using catalytic pyrolysis. Process conditions were optimized *via* response surface methodology (RSM). This combination of an experimental screening study with variation of crucial pyrolysis parameters and RSM optimisation to elucidate the conditions for maximum BTX yield from sugarcane bagasse is novel and has not been reported before.

2. Material and methods

2.1. HZSM-5 catalysts

Three HZSM-5 catalysts with Si/Al ratios of 23, 50 and 80, were purchased from Zeolyst (Netherlands). The catalysts were calcined in a muffle furnace for 5 h, then crushed and sieved to 300–500 μm and finally used for the catalytic pyrolysis of the biomass samples.

2.2. Sugarcane bagasse

The sugarcane bagasse used in this study was taken from the southern part of Iran. To decrease the moisture content below 10% (w/w), the material first was pre-dried in the sun for two days after which it was further dried in an oven at 105 °C for 2 h. The material was subsequently comminuted to a size of less than 0.25 mm for analytical procedures. The composition of the sugarcane bagasse was determined *via* proximate (moisture, volatile matter, fixed carbon, and ash content) and ultimate analysis (carbon, hydrogen, nitrogen, and sulfur).

2.2.1. Characterization

To establish the elemental composition (CNHOS), an adjustment of

Table 2
Physical-chemical sugarcane bagasse composition before washing.

Component	Weight%	Standard method
Biochemical composition sugarcane bagasse (wt%, daf[a])		
Cellulose	50.5	Kurshchner-Huffer
Hemicellulose	24.5	Wise et al
Lignin	23.5	TAPPI T222 om-88
Extractives	1.5	TAPPI 204 om-88
Proximate Analysis (wt%, ar[a])		
Moisture	9	ASTM D 3173
Volatile	75	ASTM 3174
Fixed carbon	13.5	ASTM 3175
Ash	2.5	ASTM 3172
Ultimate Analysis (wt%, db[a])		
C	41.9	ASTM D 4239
H	5.5	ASTM D 4239
N	0.29	ASTM D 4239
S	0.01	ASTM D 4239
O	52.2	By difference
Heavy metals (ppm, db[a])		
Ca	11120	ASTM D 5373
Fe	1268	ASTM D 5373
Mg	1772	ASTM D 5373
Na	600	ASTM D 5373
P	344	ASTM D 5373
Al	1377	ASTM D 5373
K	2400	ASTM D 5373
Ti	29	ASTM D 5373
Zn	20	ASTM D 5373

[a] daf = dry ash free, ar = as received, db = dry base.

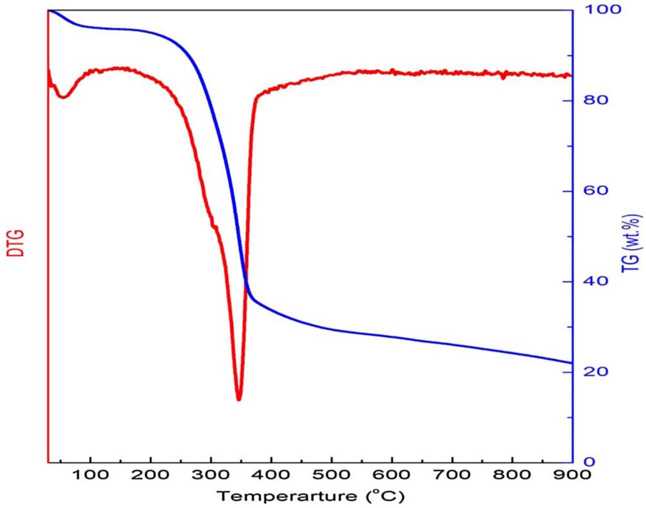

Fig. 1. Thermogravimetric analysis (TGA) and differential thermal analysis (DTG) of sugarcane bagasse under N_2 gas at a heating rate of 10 °C/min.

the ASTM D5373 standard was used by applying an EXETER CE 490 elemental analyzer [40]. The ultimate analysis was performed by adapting the ASTM protocols established for biomass. The chemical compositions of bagasse were characterized according to following standard methods: cellulose (Kurshchner-huffer [41]), holo-cellulose [42], and lignin (TAPPI T222 om-88), acetone or ethanol extractable (TAPPI T 204 om-88). Analysis results are presented in Table 2 in the results section.

2.2.2. Hot water pre-treatment

A hot water pre-treatment was performed to remove inorganic materials from the sugarcane bagasse. The biomass- water mixture was heated to a temperature of 90 °C during 0.5 h with a water to solid mass ratio of approximately 20. Following the hot water treatment, the sample was washed and oven dried at 105 °C for 5 h to decrease the moisture content below 10%. Subsequently, the sample was comminuted using a 1 mm hammer mill and sieved to a particle size between 0.25 mm and 1 mm. The washed samples were subsequently used for the thermogravimetric analysis and catalytic fast pyrolysis experiments.

2.2.3. Thermogravimetric analysis

A Perkin Elmer Pyris 1 thermogravimetric analyzer (Shelton, U.S.A) was used to conduct the TGA experiments. The carrier gas was N_2 at a flow rate of 10 ml min^{-1}. Bagasse samples were heated up from 32 to 105 °C at 25 °C min^{-1} after which they were kept isothermal at 105 °C for 5 min. Subsequently, the sample was heated up from 105 to 905 °C at 25 °C min^{-1}. After 15 min at 905 °C the sample it was cooled down from 905 to 200 °C at 25 °C min^{-1}.

Finally, the sample was heated up from 200 to 575 °C in 20 ml min^{-1} air at 100 °C min^{-1} and kept at 575 °C for 15 min.

2.3. Ex-situ catalytic fast pyrolysis experiments

Ex-situ catalytic fast pyrolysis was conducted in a tandem micro-pyrolyzer system (Rx-300 TR, Frontier Laboratories, Japan). A schematic representation of the setup of the system can be found elsewhere [33]. The system consists of two independently temperature programmable micro-reactors interfaced to a GC split injection port. Microgram quantities of the biomass are placed in a 80 μl deactivated stainless steel cup. The cup is dropped into the 1st reactor and the sample is pyrolyzed. The pyrolysis was carried out at setpoint temperatures from 450 °C to 600 °C. The gas-phase pyrolyzates directly flow through a fixed bed of catalyst, located in the 2nd downstream quartz-tube reactor and set at a fixed temperature of 450 °C. The 2-reactor set-up is connected *via* a dedicated interface to a GC–MS that separates and analyzes the volatile products from the pyrolysis (pyrolysis temperatures in the range 400–600 °C). The GC oven temperature was kept at 45 °C for 3 min, then ramped up to 280 °C with a heating rate of 10 °C min^{-1}, where it stayed for an additional 6 min. The front inlet temperature was kept at 300 °C to prevent condensation of the products. Helium was used as the carrier gas with a constant flow rate of 1 ml min^{-1} and a 1:50 split ratio. All measurements were performed at least in duplicate to verify the reproducibility of the data. For each GC–MS identified compound, the yield was determined through calibration with an external standard sample (without using the catalyst).

The final product distribution was reported as molar carbon yield, defined as the molar ratio of carbon in a specific product to the molar ratio of carbon in the feedstock according to the following formula:

$$\text{BTX yield} = \frac{Moles\ \ of\ \ carbon\ \ in\ \ BTX}{Moles\ \ of\ \ carbon\ \ in\ \ feedstock} \times 100 \tag{1}$$

Table 1 in the Supplementary information presents an overview of the main experimental conditions and obtained BTX results.

2.4. Optimization by response surface methodology

To identify and optimise the effects of process conditions on the yield of BTX, a central composite design (CCD) was applied. The pyrolysis temperature, C/B ratio, and acidity of the HZSM-5 catalyst (expressed as Si/Al ratios viz. 23, 50, 80) were the independent variables. The BTX yield was set as the dependent variable. A least square multiple regression methodology was performed to analyse the data using the Design expert 7 software package. The experimental design results were fitted using Eq. (2):

$$Y = \beta_{k0} + \sum_{i=1}^{4} \beta_{ki} x_i + \sum_{i=1}^{4} \beta_{kii} x_i^2 + \sum_{i<j=2}^{4} \beta_{kij} x_i x_j \tag{2}$$

Y is the predicted response (BTX yield); β_{k0}, β_{ki}, β_{kii} and β_{kij} represent regression coefficients; and x_i x_j are the coded independent factors

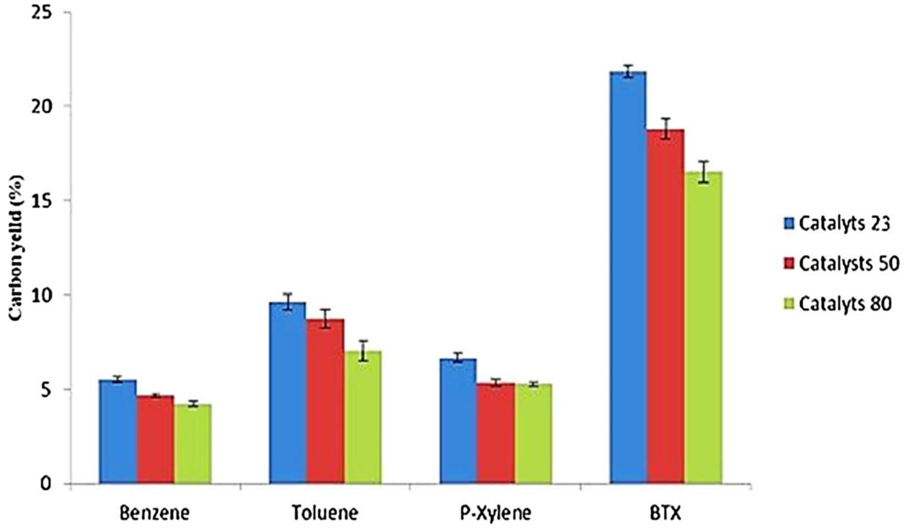

Fig. 2. Representative carbon yields and standard deviation (triplicate measurements) of BTX. from the pyrolysis of sugarcane bagasse with different catalysts (475 °C).

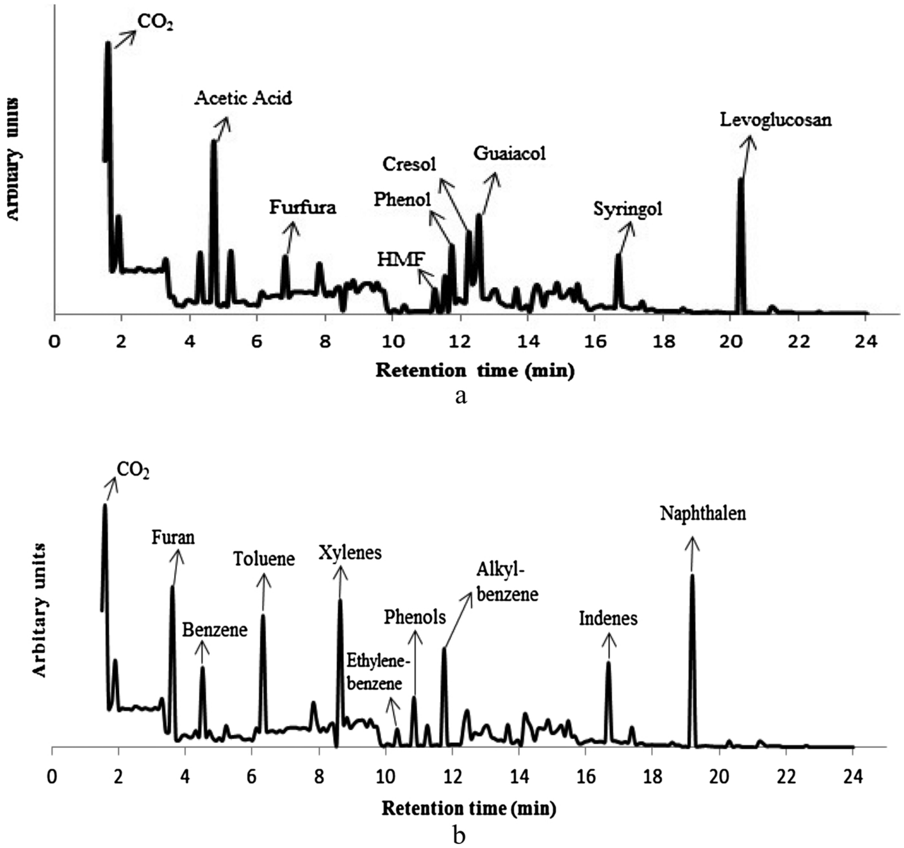

Fig. 3. a. Py-GC–MS result of sugarcane bagasse pyrolysis at 450 °C without catalyst. b. Py-GC–MS result of sugarcane bagasse pyrolysis at 450 °C with HZSM-5 (23).

(temperature, C/B ratio, and catalyst acidity) The best model was selected based on the coefficient of determination (R^2), the adjusted coefficient of determination (R^2-adj), the predicted coefficient of determination (R^2-pred), root mean square error of the predictions (RMSEP, see Eq. (3)), and the absolute average deviation (AAD). Preferably, R^2 must be near to 1 and the RMSEP and AAD (see Eq. (4)) between the estimated and observed data must be as low as possible [43].

$$\text{RMSEP} = \sqrt{\frac{\sum_{i=1}^{N} (ypre - yexp)2}{N}} \tag{3}$$

$$\text{ADD} = \left\{\sum_{\text{i}=1}^{\text{N}} (|\text{yexp} - \text{ypre}|/\text{yexp})/N\right\} \times 100 \tag{4}$$

Y_{pre}, Y_{exp}, and N are the predicted data, observed data, and number of treatment, respectively. After selecting the most accurate model, the analysis of variance (ANOVA) was used to determine the statistical significance of the regression coefficients by conducting ae Fisher‘s F-test at 95% confidence level. The interactive effects of the factors were observed using surface plots, derived from the chosen model [44]. Finally, the process was optimized. The aim of the optimization was to maximize the BTX yield with the same weight (w = 1) and the

Table 3
The carbon yield[a] of BTX from sugarcane bagasse *via ex-situ* catalytic pyrolysis using HZSM-5 (23) at different pyrolysis temperatures (12.5 mg catalyst per 1 mg sugarcane bagasse).

Pyrolysis temperature→ Compounds ↓	400 °C	450 °C	500 °C	550 °C
Benzene	3.1%	5.9%	3.7%	3.1%
Toluene	9.1%	10.5%	9.1%	6.6%
p-Xylene	3.9%	4.8%	3.5%	3.1%
BTX	16.1%	21.2%	16.3%	12.8%

[a] The molar ratio of carbon in a specific product to the carbon in the feedstock in%.

Table 4
The carbon yield[a] of BTX from sugarcane bagasse *via ex-situ* catalytic pyrolysis at 475 °C using HZSM-5 (23) catalysts at different catalyst/biomass (C/B) ratios.

C/B ratio (m/m/) → Compounds ↓	5	12.5	23
Benzene	3.2%	5.4%	2.9%
Toluene	6.3%	9.8%	6.5%
P-xylene	5.1%	6.8%	6.1%
BTX	14.6%	22%	15.5%

[a] The molar ratio of carbon in a specific product to the carbon in the feedstock.

Table 5
The carbon yield[a] of BTX from sugarcane bagasse *via ex situ* catalytic pyrolysis at 450 °C with different types of HZSM-5 catalysts, catalyst loading: 12.5 mg per 1 mg biomass).

HZSM-5 catalyst → Compounds ↓	23	50	80
Benzene	5.9%	4.8%	4.2%
Toluene	10.5%	8.3%	6.1%
p-Xylene	4.8%	4.7%	4.8%
BTX	21.2%	17.8%	15.1%

[a] The molar ratio of carbon in a specific product to the carbon in the feedstock.

credibility of the optimum conditions was diagnosed through the desirability values of the responses which range from 0 to 1. The closer values of desirability to 1 showed the more desirable and credible optimal conditions.

Details on the conducted RSM modelling such as model statistics and the ANOVA results can be found in Tables 2–4 and Figs. 1 and 2 in the Supplementary information.

3. Results and discussion

3.1. Sugarcane bagasse composition

The composition analysis results for the fresh sugarcane bagasse are given in Table 2 from which it is obvious that the sugarcane bagasse contains substantial amounts of extractives and inorganic matter, predominantly Ca, K and Mg, characteristic for (herbaceous) lignocellulosic biomass.

It is assumed that substantial amounts of (water-soluble) inorganic material are removed due to the washing procedure.

3.2. Thermogravimetric analysis (TGA)

The thermal degradation characteristics of sugarcane bagasse were measured *via* TGA. The TGA weight loss curve and its first derivative (differential TG curve (DTG)) are presented in Fig. 1. The first weight loss step commences at 100 °C due to moisture elimination, resulting in 8.5% mass loss. The second weight loss step occurs between 250 °C–350 °C due to a progressive decomposition of hemicellulose, lignin and cellulose. The DTG curve in Fig. 1 shows a shallow shoulder around 300 °C, that most likely originates from the degradation of the hemicellulose. Here the absence of a clear resolution indicates a strongly overlapping thermal degradation of hemicellulose and cellulose and possibly also lignin [45,46]. The degradation rate becomes relatively constant around 400 °C–600 °C. The residue of the pyrolysis process accounts for 20% of the initial dry mass and mainly consists of carbonaceous char and some ash (inorganic compounds). Fernandez Pereira et al. [47] reported that the thermal decomposition of unmodified bagasse starts near 110 °C, after which two peaks appear at 310 °C and 385 °C, respectively. The results of TGA indicated that most of the sugarcane bagasse is vaporized below 400 °C, indicating that the pyrolysis temperature should be above 400 °C.

3.3. Reproducibility pyrolysis approach

Triplicates of benzene, toluene, and *p*-xylene from GC–MS for experiment at 475 °C were obtained using the three zeolite catalysts. Carbon yields and their standard deviation are presented in Fig. 2.

Each sample was analyzed in triplicate so that the standard deviation of benzene, toluene, *p*-xylene from CFP with catalysts (Si/Al ratio 23) were determined. The standard deviation derived from the calibration and sample data was ≤5%. The analysis shows a good reproducibility for each product.

3.4. Effect of pyrolysis temperature on BTX yield

In this study, the sugarcane bagasse is pyrolysed in the first reactor, after which the hot pyrolysis vapours pass through the second (catalytic) reactor that is kept at 450 °C for all pyrolysis experiment. Fig. 3 presents a typical Py-GC–MS chromatogram illustrating the distribution of products derived from the pyrolysis of sugarcane bagasse at 450 °C without catalysts (Fig. 3a) and with HZSM-5 (23) catalyst (Fig. 3b). No pyrolytic products were detected by GC–MS at pyrolysis temperatures lower than 400 °C. When the set point temperature was higher than 400 °C, pyrolysis products were detectable. In general, for the non-catalytic pyrolysis the major compounds observed were levoglucosan, acetic acid and carbon dioxide. The compounds identified in the catalytic fast pyrolysis with HZSM-5 (23) were furan, benzene, toluene, xylenes, ethylene-benzene, indenes, and naphthalene completely totally different from those in the non-catalytic fast pyrolysis as is illustrated in Fig. 3b.

Table 3 shows the effect of temperature on the distribution of BTX from the catalytic pyrolysis of sugarcane bagasse with HZSM-5 (23) at 400, 450, 500, and 550 °C. The table indicates that the carbon yield of BTX increases from 16.1% to 21.2% by increasing the temperature from 400 °C to 450 °C, after which the BTX yield substantially decreases from 500 °C to 550 °C. It is indicated that the cracking of ethyl-benzene into benzene and ethylene are increased at higher temperature through alkylation reaction. At temperature of 550 °C, benzene and toluene production were reduced because of generation of low carbon hydrocarbons and reduction of selectivity of these compounds at alkylation reaction [48]. The BTX yield of 19.8% from glucose at pyrolysis temperature 500 °C was reported by Wang et al. [43]. Karagoz et al. [21] reported that the relative yields (peak area%) of benzene and toluene at 400 °C were 6.8% and 21.5%, respectively. These yields were clearly higher than those obtained at 600 °C (3.4% for benzene and 14.1% for toluene). They also observed that acetic acid in the 1st reactor was converted to benzene or toluene by HZSM-5 in the 2nd reactor in the tandem micro-reactor. In agreement with the results reported by Karagoz et al. [21], this study shows that the BTX distribution significantly depends on the pyrolysis temperature in the 1st reactor.

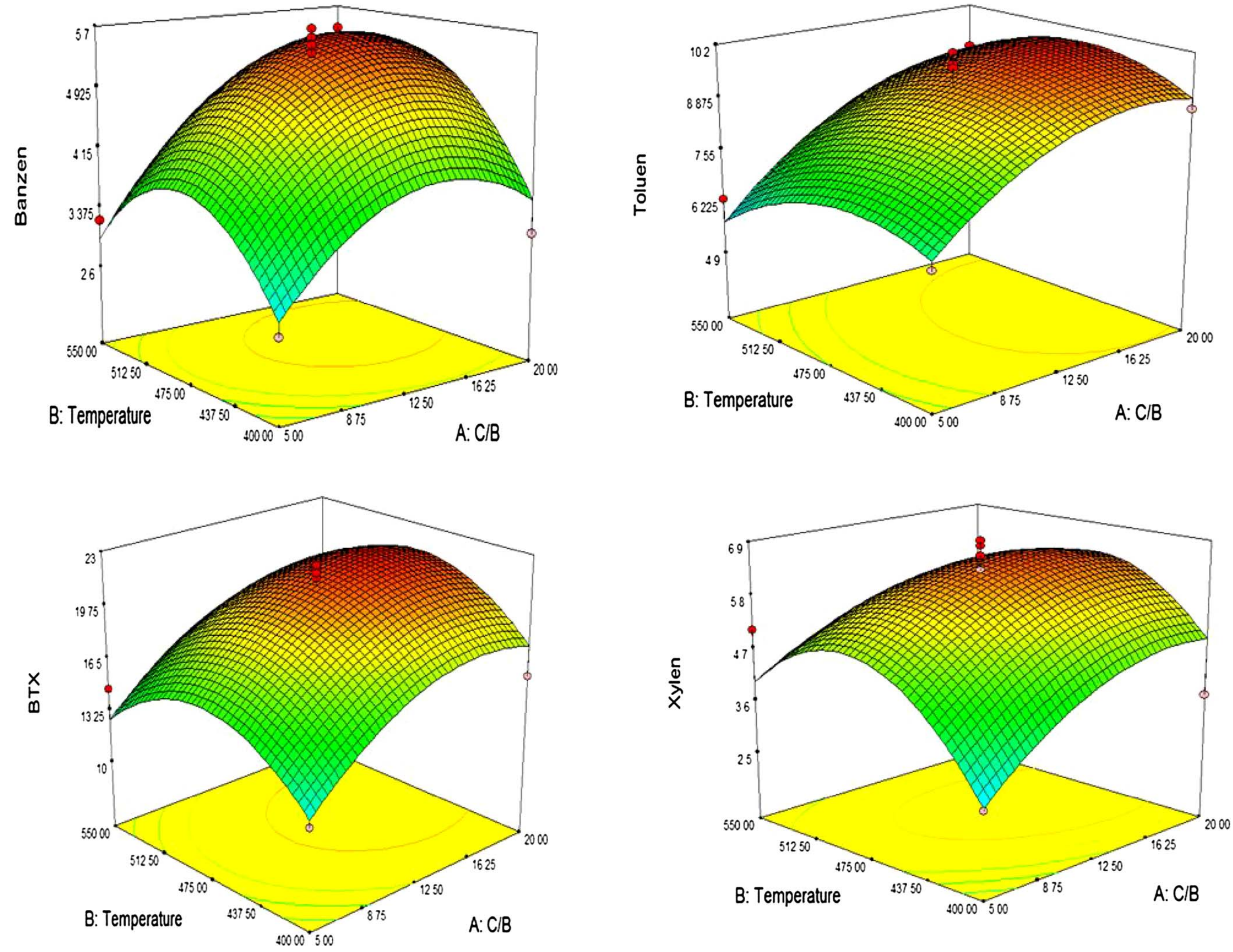

Fig. 4. Optimization of yield of BTX with HZSM-5 (23) catalyst at different process conditions.

3.5. Effect of catalyst/biomass (C/B) ratio on BTX yield

The effect of the C/B ratio on the BTX yield at a pyrolysis temperature of 475 °C is presented in Table 4 for catalyst HZSM-5 (23). The yield initially increases with increasing the C/B ratio from 2 to 12.5 after which it decreases at a C/B ratio of 23. The higher BTX yield can be attributed to an increase of cracking reactions of the primary pyrolysis products taking place on Brønsted acidic sites on the HZSM-5 zeolite catalyst.

The yield of gaseous products should be affected by the strength of the Brønsted acidic sites with increased yield of CO and C2 –C3 hydrocarbons. On the other hand, at a higher C/B ratio, the increased carbon yield of the char/coke fraction is mainly attributed to a higher amount of catalytic coke [34]. Therefore, the yields of compounds from biomass decrease when increasing the C/B ratio due to coke formation which deactivates the Brønsted acidic sites.

3.6. The effect of various HZSM-5 types on the BTX yield from sugarcane bagasse

The performance of three types of HZSM-5 with different $SiO_2\backslash Al_2O_3$ ratios; HZSM-5 (23), HZSM-5 (50), and HZSM-5 (80) was investigated for the *ex-situ* pyrolysis of sugar cane bagasse. Results are presented in Table 5 which indicates that the BTX carbon yield of around 21% with HZSM-5 (23) is higher than the yield for the other catalysts, while the yield of *p*-xylene is roughly identical for all the zeolite catalysts. In general, HZSM-5 types (23) and (50) show a significant increase in the yield of BTX in the tandem micro-reactor when compared to HZSM-5 (80). HZSM-5 (80) exhibited the lowest yield of BTX corresponding to the fact that an increase of SiO_2/Al_2O_3 ratio results in a decrease of acidic sites [49]. The macromolecular cracking products and hydrogen transfer reaction were increased by increasing of acidic sites. Thus, when HZSM-5 was 23, the yield of BTX was enhanced.

3.7. Optimization of process conditions and catalysts ratio for maximum BTX yields

Response surface methodology was also used to evaluate the optimal process parameters for maximum BTX yields from sugarcane bagasse. Comparing the linear interaction, full quadratic and cubic models, it can be concluded that full quadratic model of C/B ratio and catalyst was significant on BTX yield, while the temperature did not show a significant term. The interaction between reaction temperature, C/B ratio and catalysts did not affect the BTX yield significantly. For HZSM-5 (23) a temperature around 480 °C and a C/B ratio of 17 were found to be the optimum conditions. The carbon yields of benzene, toluene, and xylenes were 5.5%, 9.8%, and 6.5%, respectively (Fig. 4). These results were validated by a control experiment under the predicted optimum conditions. The second best catalyst is HZSM-5 (50) with an optimum temperature of 450 °C and an optimum C/B ratio of 12.5. The BTX yield from HZSM-5 (50) is higher than HZSM-5 (80) but less than HZSM-5 (23). The results show that the HZSM-5 (23) is more efficient catalyst rather than two other catalysts for production of BTX from sugarcane bagasse. The effects of the temperature and C/B ratio indicated that the yield of BTX passes through a maximum for both parameters (Fig. 4). The comparison of the BTX yields at 500 °C from this study with BTX yields at 500 °C from other types of biomass shows that the BTX yield of 12.8% for sugarcane bagasse with HZSM-5 catalysts is lower than the BTX yield for red oak (14.7%), hybrid polar (19.7%), and glucose (19.8%) at the same pyrolysis conditions, while the maximum BTX yield of 22% (at optimized conditions) for sugarcane bagasse is higher than the BTX yields in those studies [48,50,51]. The increased temperature of pyrolysis from 400 °C to 500 °C causes increased decomposition of the sugarcane bagasse towards (oxygenated) aromatics and furans. Upon contact with the catalyst the oxygenated aromatics get converted to BTX.

Increase of C/B ratio from 5 to 18 causes a longer gas-catalyst contact time, thereby increasing the reaction time. Further increase of catalyst to biomass ratio corresponds to an even longer reaction time (catalyst contact time) and will progressively promote coking [52–56].

Additionally, it was demonstrated that the BTX yield also passes through a maximum as function of the C/B ratio. A higher C/B ratio leads to progressive cracking and −as a consequence- enhanced production of light (oxygenated) hydrocarbons with corresponding removal of oxygen from the pyrolysis vapours as CO. This trend levels off and decreases at higher C/B ratios because of coke formation [34,57–59]. Finally, the results indicate that the HZSM-5 (23) zeolite catalyst is more efficient than HZSM-5 (50) and HZSM-5 (80). This is most likely due to enhanced C—C bond forming and acylation reactions. This results in better conversion and elimination of oxygen, especially in the aromatic (lignin-derived) compounds of the biomass at higher concentrations and acidity of Brønsted acid sites at lower Si/Al ratios [60–62].

4. Conclusions

This study on the catalytic fast pyrolysis of sugarcane bagasse with various HZSM-5 catalysts, shows that the zeolite acidity and the catalyst to biomass (C/B) ratio clearly affect the yield of BTX during *ex-situ* catalytic fast pyrolysis. The BTX carbon yield increases from 16.1% to 21.2% by increasing the temperature from 400 °C to 450 °C at a C/B ratio of 12.5 with HZSM-5 (23). BTX yields of 15.1% and 17.8% were obtained from respectively HZSM-5 (80) and HZSM-5 (50) at 450 °C and a C/B ratio of 12.5.

The modelled optimisation of process parameters with HZSM-5 catalysts indicates that with HZSM-5 (23) at a temperature around 480 °C and a C/B ratio of 17 an optimum BTX carbon yield of 22% is obtained. Under identical pyrolysis conditions, the BTX yield from sugarcane bagasse is generally higher when compared to the BTX yields from other lignocellulosic materials such as hybrid poplar and red oak [43–45]. In addition, the *ex-situ* catalytic pyrolysis of sugarcane bagasse shows a considerable change in the yield of BTX, depending on the type of HZSM-5 catalyst used. Results indicate that Brønsted acidity leads to increasing conversion of biomass to aromatic products at lower Si/Al ratios of the HZSM-5 catalysts used. This study has revealed that the *ex-situ* catalytic pyrolysis is an effective technique for the production of BTX and valuable chemicals from bagasse.

Acknowledgments

The authors greatly acknowledge the financial support from Bio-BTX/Syncom Company. Authors acknowledge Dr. André Heeres, Dr. Niels Schenk and Mrs. Inuk Muizebelt from Bio-BTX/Syncom for their technical support and Jan Henk Marsman and Leon Rohrbach (University of Groningen) for elemental analysis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jaap.2018.02.019.

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