Supplementary Materials for

# From biomass to fuels: a carbon-efficient route combining ketalization and fluid catalytic cracking

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### **1-Marerials and Methods:**

- All reagents and solvents were purchased from commercial suppliers and used without further purification if not otherwise mentioned. The sulfuric acid used in the bio petroleum synthesis was of P.A. grade (VETEC) and acetone (VETEC) was 99% pure
- The sugarcane bagasse obtained was washed with distilled water and dried at room temperature. The dried fibers were milled in a knife mil and separated into a specific particle size (0.125 and 0.85 mm). The sugarcane bagasse was washed with hot distilled water at 50 °C to remove extractives and lastly dried in a drying oven at 35 °C until constant weight (this was done to guaranty that we are converting exclusively bio-polymers, in a practical situation the sugar cane bagasse can be used without previously treatment).
- <sup>1</sup>H NMR (400.132 MHz), <sup>13</sup>C NMR (100.623MHz) were recorded on a BRUKER AVANCE III HD400 MHz spectrometer at 298 K unless otherwise stated. Chemical shifts are given in ppm ( $\delta$ ) and are referenced to the internal solvent signal or to TMS used as an internal standard.
- The Gas chromatographic analysis system was done in an Agilent Technologies 7890A CG coupled to a 5975C MS in electron impact mode, an Agilent HP-5MS column and an FID detector. The oven temperature was maintained at 40 °C for 2 min. followed by heating at a rate of 10 °C/min to 320 °C with a 5 min isotherm. The volume of injected liquid was 0.2 µL, using injection system in split mode and rate 100:1.
- Gas analysis was done with gas chromatograph (Agilent Technologies Micro-GC 490) with a Thermal Condutivity Detector (TCD detector)
- Coke analysis was done with Netzsch TG-IRIS in air, and corresponded to the weight lost at temperatures higher than 250°C up to 700°C, under heat rate of 10°C
- The physical-chemical characterization of bio petroleum such as density, viscosity, specific heat capacity and elemental analysis of CHN were measured and the detailed description of its components could be found in our previous publication (1).
- The CHN analysis was performed by the elemental analyzer (Perkin Elmer 2400 series II) located in the Instrumentation Analytical Center of the University of São Paulo. The tests were performed in duplicate using and the samples were subjected to combustion in an atmosphere of pure oxygen, and the gases resulting from this combustion were quantified in a TCD (thermal conductivity detector) detector.

#### 2-Bio petroleum Synthesis:

The bio petroleum was produced using a lab-built semi-continuous flow reactor as described in Figure S1. The sugarcane bagasse was converted into BP in a flow process, at  $120^{\circ}$ C, with 0.4 wt.% sulfuric acid (P.A., VETEC) in acetone (99%, VETEC). The chilled mixture of acetone:H<sub>2</sub>SO<sub>4</sub> was pumped using a Schimadzu LC-8A pump to a heated stainless steel reactor (255 mm long and 34 mm diameter) filled with 20g of pretreated sugarcane bagasse and acetone. The effluent from the reactor was cooled in an ice bath coil and collected in a glass fask. The system was maintained at a pressure of 15 bar using a Swagelok SS-4CA-150 valve (to guarantee the solvent in a liquid phase). After the reaction was complete (120 min.), the reactor was cooled to room temperature with a continuous flow of acetone to remove any residual oil present in the reactor system. The collected liquid was neutralized with solid sodium bicarbonate (NaHCO<sub>3</sub>) to pH 7, and acetone was removed under reduced pressure with a rotary evaporator to yield a brown oil (bio petroleo). The bio petroleo was weighed and stored in a refrigerator. Non-reacted

acetone was reused to BP production (without compromise BM conversion and BP yield).

#### 3-Experimental Procedure Detail of Catalytic cracking

The fluid catalytic cracking unit used to convert the bio-petroleum (BP) is presented in Figure S2. In this study, the BP was co-processed with vacuum gasoil (VGO) using a wide range of BP concentrations (from 9.9-74.9 wt.%). The tests were carried out by using 15g of a commercial FCC catalyst, the amount of BP and VGO in mL were selected (due to their densities, 1.1 and 0.87 respectively) to catalyst/feed=6and total feed varies from 2.87 to 2.42 to VGO and BP75 test respectively, as presented in tabS3. In the second part of catalytic cracking the amount of feed in g and mL are indicated in the respective tables.

The reactor (internal length = 740mm and internal diameter = 16.5mm) was operated in between 460 (bottom, the beginning of reactor zone) and  $535^{\circ}$ C (top, end of catalyst bed in fluidized condition) of considering the height of the fluidized catalytic bed, and N2 flow of 140 mL min<sup>-1</sup> to ensure fluidization of the catalyst. The commercial catalyst containing as the main component RE-USY (ultra-stable Y zeolite exchanged with rare earth elements), supplied by Petrobras, we select a particle diameter between 120-200 mesh equivalent to a particle size diameter of 0.125-0.08 mm. Before the reaction, the catalyst was activated in a nitrogen atmosphere during 60 min at 600°C.

To carry out the tests, BP and VGO were injected into the reactor using a syringe pumps 1 and 2 (Figure S2 (B)) over a period of 30s at a pre-established flow (30 mL  $s^{-1}$ ) of N<sub>2</sub> as carrier gas, regulated by a flowmeter **3**. Due to the viscosity of the BP, the injection line and the syringes were heated to 60°C to facilitate the flow of feed to the reactor. The reactor, heated by furnace 5, can be divided into two parts: the first, the section with the smallest diameter of reactor 4, corresponds to the reaction zone, the region in which the catalyst is fluidized, and the second is expansion region 6, which directs the products out of the reactor and prevent catalyst carryover. Upon leaving the reactor, the products are conducted through a condenser 7, submerged in a cooling bath **9** at approximately -16°C, where the heavier fractions are liquefied. After passing through the condenser, the lighter fractions of the products, which were not condensed, are directed to a gas measuring device 12, which consists of an Erlenmeyer flask containing saturated saline solution and works by mass displacement. As the gases produced reach the Erlenmeyer, they exert pressure on the solution, which is displaced outside and collected in a beaker. The gas mass was then determined by the difference in mass of displaced solution before and after the reaction. It is worth mentioning that, before each reaction, the nitrogen flow is measured and calibrated, using the gas meter **10** connected to vent **11**, calibrated for the same time as the reaction, in order to know the mass of solution displaced by nitrogen flow in the absence of reaction. The reaction time, that is, the period between the beginning of the charge injection and the moment when the gas measurement is interrupted is 30 min. At the end of this period, the mass of the liquid fraction of the generated products was determined directly by weight difference of the condenser before and after the reaction. The reaction products were distributed into liquid, gas, and coke fractions.

The liquid product is composed of aqueous and organic fractions, readily separated by density. The denser aqueous fraction was removed using a Pasteur pipette to a sample vial, and its mass was determined by weighing (we consider the aqueous phase as water produced from BP). The mass of the organic phase was determined by the difference of the mass of the total liquid the mass of the aqueous phase. The liquid organic fraction from the cracking reactions were analyzed off-line by GCMS/FID and <sup>13</sup>CNMR. The determination of liquid products was obtained based on MS (main important compounds were verified by co-infection

based on retention time) and the quantification was carried out in a GC-FID. All samples were injected without dilution. The distribution of liquid products was assigned into fractions: Gasoline (C5-C12 compounds), LCO (Light Cycle Oil, C13-C16 compounds) and bottom (up to C16 compounds). Moreover, the gasoline fractions were separated to different classes (paraffins, isoparaffins, olefins, naphtenes, aromatics and oxygenated compounds) and the LCO fractions were separated per carbon chain (C13-C14 and C15-C16) and per class of compounds (mono and polyaromatics, oxygenates and others) in order to facilitated data treatment and understanding of work, as well. The masses of liquid fractions were obtained by multiplying the FID area (%) of the fraction by the mass of liquid obtained in the reaction. The liquid fraction yield was obtained by dividing each mass by the total mass injected.

The volume of gas produced during the reaction was determined by displacement of water in an Erlenmeyer flask. The difference between the masses volume of water displaced before and after the reaction determined the volume of gas produced in the reaction. Using the value of gas volume and the ideal gas equation was calculated the partial pressures of gaseous products and their respective masses. Gas products (H<sub>2</sub>, CO, CO<sub>2</sub>, methane, and hydrocarbon up to C4) were analyzed using the average of three aliquots of gas (confined inside the Erlenmeyer flask) collected by a gas syringe 13 and injected into a micro-gas chromatograph with a TCD detector. Residual C5 hydrocarbons were observed and included in gasoline fraction. The gas inside the Erlenmeyer flask was assumed to be under ideal gas conditions. Separation of gas products was performed by three different channels and detection was performed by a thermal conductivity detector. Channels specification as well as operation temperatures and gas pressures setups are described as follows: Channel 1 = Molsieve 5Å (10m) maintained at 80°C under 150kPa of Ar; Channel 2 = PoraPlot (10m) maintained at 100°C under 150kPa of He; Channel 3 =  $AI_2O_3/KCI$  (10m) maintained at 100°C under 90kPa of He. Injector was maintained at 110°C. Retention times (RT) and molar response factors (MRF) were obtained using standard compounds at 10% mol mol-1 in He and used on gas products analysis. Gaseous product moles were calculated multiplying the gas Area by MRF. Molar fraction (% molar) of gaseous product on gas collected was calculated by division of mol of product by mol total. Finally, the mass of the gas product was obtained by the Equation S1 and yield (%) was obtained from Equation S2.

Equation S1: Mass of gas (g) = (total gas volume × MM × %molar)/ NTP gas volume

Equation S2: Gas yield (%) = %molar × ((mass of gas/injected mass) ×100).

The amount of coke in wt.% in the catalyst was determined through thermogravimetric analysis. Coke yield was measure by multiplied the wt. % of coke in the catalyst by the catalyst mass (used in the test) and divided by total feed introduced into the reactor (yield coke = (coke in wt% x mass catalyst) / (mass injected)).

At the end of each test, the material balance of the reaction was carried out comparing the total injected feed and the sum of the total mass of products obtained for liquid, solid and gas fractions. The yield of the products and fractions obtained, calculated in terms of mass, was obtained through the ratio between the mass of the product in question and the total mass of injected feed (VGO + bio-petroleum) and normalized, for comparison purposes between the tests, depending on the material balance of each experiment.

The results of models 1 and 2 are a result that touches on two important subjects of the BP transformation: the VGO-BP interaction, not only between these two reagents but also the intermediates derived from them, and the water formation, considering its importance to avoid carbon loss. Recently, we explored the effect of the type of hydrocarbons on the DX conversion, a model compound of BP(2). The competition for acid sites was demonstrated. DX primarily reacts and decreases the hydrocarbon conversion. This effect is affected by the type of hydrocarbon; DX conversion is reduced due to higher reactive and higher heat of adsorption of hydrocarbons. Hydrocarbons with increasing hydrogen transfer capacity (like methyl-cyclo-hexane compared to n-hexane) increased GACE. Also, bimolecular reactions between hydrocarbons and oxygenates reduced the protolysis of both  $\sigma$ C-C and  $\sigma$ C-H bonds, decreasing the formation of H<sub>2</sub> and light hydrocarbons. This donation can enrich H in the product, increasing the H/C ratio and facilitating the formation of OH groups that eventually is dehydrated. The possibility that hydrocarbons act as a reductive agent was already proposed for VGO and bio-oil cracking (3).

#### Text S2

We estimate the BP distribution in model 1, assuming no interaction between BP and VGO. The BP contribution to products was estimated by subtracting product yields obtained in the mixture from the VGO contribution. The contribution of VGO to products was estimated multiplying the amount of a product (in a feed) by the VGO amount that is converted (in a feed) and divided by the VGO amount converted in pure VGO). Then we subtract products in the mixture from the VGO contribution and determine the BP contribution to dry gas, gasoline, coke, LCO, and Bottom.

We estimate the BP distribution in model 2, assuming VGO contributes exclusively to LCO and Bottom. The VGO converted into products was determined by subtracting the VGO amount from LCO and bottom. The contribution of VGO to a product was estimated by multiplying the amount of a product (in a feed) by the VGO amount that is converted (in a feed according to model 2) and divided by the VGO amount converted in pure VGO. Then we subtract products in the mixture (BP+ VGO) to the VGO contribution and determine the BP contribution to dry gas, gasoline and coke.



Figure S1. Schematic of the flow process to convert BM in BP.



Figure S2. Schematic of the fluidized catalytic cracking Unit used in the BP/VGO experiments

<u>4-13C</u>{<sup>1</sup>H} NMR Spectroscopic data



Figure S3:  ${}^{13}C{}^{1}H$  NMR spectra of bio petroleum (BP) inacetone-d<sub>6</sub>



Figure S4: <sup>13</sup>C{<sup>1</sup>H}NMR spectra of cBP10 in Acetone-d<sub>6</sub>.



Figure S5:  ${}^{13}C{}^{1}H$  NMR spectra of cBP34 in Acetone-d<sub>6</sub>



Figure S6:  ${}^{13}C{}^{1}H$  NMR spectra of cBP55 in Acetone-d<sub>6</sub>



Figure S7:  ${}^{13}C{}^{1}H$  NMR spectra of cBP75 in Acetone-d<sub>6</sub>



Figure S8 -<sup>13</sup>C{<sup>1</sup>H} NMR spectra of cVGO in Acetone-d<sub>6</sub>



Figure S9 -<sup>13</sup>C{<sup>1</sup>H} NMR spectra of VGO in Acetone-d<sub>6</sub>

### **5-Graphics and tables**



Figure S9: yield of water in BP-VGO cracking.

Table S1: VGOproperties	
properties	VGO
Gravity g/cm <sup>-3</sup>	0.87
°API	17.3
Carbon conradsonwt %	0.47
Nitrogen mg kg <sup>-1</sup>	1241
Sulfur content wt %	0.6
Aniline Point °C (ASTM611)	77

## Table S2: Catalyst properties, main active phase is a USY zeolite

	SiO <sub>2</sub> wt.%	Al <sub>2</sub> O <sub>3</sub> wt.%	Na <sub>2</sub> O wt.%	RE∗ wt.%	Ni ppm	V ppm	Vol micro porous ml g <sup>-1</sup>	Area meso porous m <sup>2</sup> g <sup>-1</sup>	BET m²g⁻¹
CatA	39.4	55.2	0.39	3.26	1921	967	0.078	72	264

\* RE= total amount of rare earth elements (mainly La and Ce)

Table S3: BP-VGO cracking in FCC, LCO composition.

Feed wt.%	VGO	100.0	90.1	66.4	44.8	25.1
	BP	0.0	9.9	33.6	55.2	74.9
Feed mL	%VGO mL	2.87	2.59	1.91	1.29	0.72
	% BP mL	0.00	0.23	0.76	1.25	1.70
Yield wt.%	Per carbon-cha	in				
	C13-C14	22.2	17.2	13.6	11.6	10.6
	C15-C16	2.6	0.6	1.6	1.0	1.6
Yield	Per class of con	npound				
	Mono-aromatic	1.2	0.6	0.6	0.4	0.3
	Poly-aromatic	22.5	17.0	13.5	11.7	10.8
	Oxygenates	0.00	0.1	0.3	0.4	0.6
	Others	1.0	0.1	0.3	0.2	0.5
Selectivity	Mono-aromatic	5%	3%	4%	3%	2%
	Poly-aromatic	91%	96%	92%	92%	89%
	Oxygenates	0%	1%	2%	3%	5%
	Others	4%	1%	2%	2%	4%
Table S4: E Test	3P-VGO cracking	g in FCC, cVGO	gasoline cBP10	compos cBP34	ition (yie cBP55	ld wt.%). cBP75
Feedwt.%	VGO	100.0	90.1	66.4	44.8	25.1
	BP	0.0	9.9	33.6	55.2	74.9
Yield,	BP Paraffin	0.0 0.7	9.9 0.5	33.6 0.6	55.2 0.2	74.9 0.3
Yield, wt.%	BP Paraffin Iso-paraffin	0.0 0.7 5.4	9.9 0.5 2.2	33.6 0.6 2.3	55.2 0.2 0.9	74.9 0.3 1.0
Yield, wt.%	BP Paraffin Iso-paraffin Olefin	0.0 0.7 5.4 13.0	9.9 0.5 2.2 6.2	33.6 0.6 2.3 5.8	55.2 0.2 0.9 4.2	74.9 0.3 1.0 5.8
Yield, wt.%	BP Paraffin Iso-paraffin Olefin naphtenic	0.0 0.7 5.4 13.0 3.8	9.9 0.5 2.2 6.2 1.8	33.6 0.6 2.3 5.8 1.8	55.2 0.2 0.9 4.2 0.5	74.9 0.3 1.0 5.8 0.5
Yield, wt.%	BP Paraffin Iso-paraffin Olefin naphtenic monoaromatic	0.0 0.7 5.4 13.0 3.8 23.1	9.9 0.5 2.2 6.2 1.8 30.7	33.6 0.6 2.3 5.8 1.8 24.1	55.2 0.2 0.9 4.2 0.5 22.7	74.9 0.3 1.0 5.8 0.5 17.9
Yield, wt.%	BP Paraffin Iso-paraffin Olefin naphtenic monoaromatic diaromatic	0.0 0.7 5.4 13.0 3.8 23.1 12.8	9.9 0.5 2.2 6.2 1.8 30.7 9.6	<ul> <li>33.6</li> <li>0.6</li> <li>2.3</li> <li>5.8</li> <li>1.8</li> <li>24.1</li> <li>7.9</li> </ul>	55.2 0.2 0.9 4.2 0.5 22.7 7.1	74.9 0.3 1.0 5.8 0.5 17.9 6.7
Yield, wt.%	BP Paraffin Iso-paraffin Olefin naphtenic monoaromatic diaromatic oxygenate	0.0 0.7 5.4 13.0 3.8 23.1 12.8 0.0	9.9 0.5 2.2 6.2 1.8 30.7 9.6 0.4	33.6 0.6 2.3 5.8 1.8 24.1 7.9 0.7	55.2 0.2 0.9 4.2 0.5 22.7 7.1 2.0	74.9 0.3 1.0 5.8 0.5 17.9 6.7 3.9
Yield, wt.% selectivity	BP Paraffin Iso-paraffin Olefin naphtenic monoaromatic diaromatic oxygenate Paraffin	0.0 0.7 5.4 13.0 3.8 23.1 12.8 0.0 1.2	9.9 0.5 2.2 6.2 1.8 30.7 9.6 0.4 1.0	33.6 0.6 2.3 5.8 1.8 24.1 7.9 0.7 1.3	55.2 0.2 0.9 4.2 0.5 22.7 7.1 2.0 0.6	74.9 0.3 1.0 5.8 0.5 17.9 6.7 3.9 0.8
Yield, wt.% selectivity	BP Paraffin Iso-paraffin Olefin naphtenic monoaromatic diaromatic oxygenate Paraffin Iso-paraffin Olefin	0.0 0.7 5.4 13.0 3.8 23.1 12.8 0.0 1.2 9.2 22.1	9.9 0.5 2.2 6.2 1.8 30.7 9.6 0.4 1.0 4.2 12.2	33.6 0.6 2.3 5.8 1.8 24.1 7.9 0.7 1.3 5.4 13.4	55.2 0.2 0.9 4.2 0.5 22.7 7.1 2.0 0.6 2.4 11.1	74.9 0.3 1.0 5.8 0.5 17.9 6.7 3.9 0.8 2.8 15.9
Yield, wt.%	BP Paraffin Iso-paraffin Olefin naphtenic monoaromatic diaromatic oxygenate Paraffin Iso-paraffin Olefin naphtenic	0.0 0.7 5.4 13.0 3.8 23.1 12.8 0.0 1.2 9.2 22.1 6.4	9.9 0.5 2.2 6.2 1.8 30.7 9.6 0.4 1.0 4.2 12.2 3.4	<ul> <li>33.6</li> <li>0.6</li> <li>2.3</li> <li>5.8</li> <li>1.8</li> <li>24.1</li> <li>7.9</li> <li>0.7</li> <li>1.3</li> <li>5.4</li> <li>13.4</li> <li>4.2</li> </ul>	55.2 0.2 0.9 4.2 0.5 22.7 7.1 2.0 0.6 2.4 11.1 1.3	74.9 0.3 1.0 5.8 0.5 17.9 6.7 3.9 0.8 2.8 15.9 1.4
Yield, wt.%	BP Paraffin Iso-paraffin Olefin naphtenic monoaromatic diaromatic oxygenate Paraffin Iso-paraffin Olefin naphtenic monoaromatic	0.0 0.7 5.4 13.0 3.8 23.1 12.8 0.0 1.2 9.2 22.1 6.4 39.3	9.9 0.5 2.2 6.2 1.8 30.7 9.6 0.4 1.0 4.2 12.2 3.4 59,6	33.6 0.6 2.3 5.8 1.8 24.1 7.9 0.7 1.3 5.4 13.4 4.2 55.9	55.2 0.2 0.9 4.2 0.5 22.7 7.1 2.0 0.6 2.4 11.1 1.3 60.4	74.9 0.3 1.0 5.8 0.5 17.9 6.7 3.9 0.8 2.8 15.9 1.4 49.6
Yield, wt.%	BP Paraffin Iso-paraffin Olefin naphtenic monoaromatic diaromatic oxygenate Paraffin Iso-paraffin Olefin naphtenic monoaromatic	0.0 0.7 5.4 13.0 3.8 23.1 12.8 0.0 1.2 9.2 22.1 6.4 39.3 21.8	9.9 0.5 2.2 6.2 1.8 30.7 9.6 0.4 1.0 4.2 12.2 3.4 59,6 18.7	33.6 0.6 2.3 5.8 1.8 24.1 7.9 0.7 1.3 5.4 13.4 4.2 55.9 18.2	55.2 0.2 0.9 4.2 0.5 22.7 7.1 2.0 0.6 2.4 11.1 1.3 60.4 18.9	74.9 0.3 1.0 5.8 0.5 17.9 6.7 3.9 0.8 2.8 15.9 1.4 49.6 18.6

 Table S5: BP-VGO cracking in FCC, main oxygenates.

tests oxigenates BP10 BP34 BP55 BP75

Yieldwt.%	Ketone	0.2	0.28	0.88	2.08
	furane	0.14	0.31	0.58	1.10
	phenol	0.06	0.1	0.55	0.53
	furfural	0.00	0.00	0.22	0.21
	alchool	0.00	0.00	0.00	0.01
	aldehyde	0.00	0.00	0.00	0.02

## Table S6: BP-VGO cracking in FCC, type of oxygenates in gasoline.

tests	BP75	BP55	BP34	BP10
Furan	у	у	n	n
Furan, 2-methyl-	у	у	у	n
Furan, 2-ethyl-	У	У	У	У
Furan, 2,5-dimethyl-	Y	У	У	n
Furan, 2,3,5-trimethyl-	У	n	n	n
Furan, 2-ethyl-5-methyl	у	n	n	n
Benzofuran	У	у	n	n
3-Furaldehyde	у	n	n	n
Furfural	у	у	n	n
Phenol	У	n	n	n
Phenol, 2-methyl-	У	У	n	n
Phenol, 2,6-dimethyl-	У	У	n	n
Phenol, 2,4-dimethyl-	У	У	У	У
Phenol, 2,5-dimethyl-	У	У	n	У
Acetone	У	у	У	у
2-Butanone	у	у	У	у
3-Pentanone	У	n	n	n
Propanal, 2-methyl 38%	У	n	n	n
Hexanal, 2-ethyl 37%	У	n	n	n
3-Penten-2-one, 4-methyl-	У	n	n	n
Cyclopentanone	У	n	n	n
3-Hexen-2-one, 3,4-dimethyl-,	У	n	n	n
2-Ethyl-3-methylcyclopent-2-en-1-	У	n	n	n
one				
Cyclohexanemethanol, 4-	У	n	n	n
metnyiene				

BP10		cVGO	cBP75	cBP55	cBP34	cBP10
Feedwt.%	VGO	100	90.1	66.4	44.8	25.1
	BP	0	9.9	33.6	55.2	74.9
Yieldwt.%	Drygas					
	H2	0.64	0.18	0.26	0.24	0.65
	Methane	2.94	5.33	8.19	7.46	7.62
	Ethene	0.50	0.44	0.65	0.59	0.73
	Ethane	0.47	0.46	0.68	0.61	0.73
	CO	0.02	4.92	4.32	3.96	0.93
	CO2	0.05	5.19	4.15	3.77	1.15
Yieldwt.	GLP					
	Propane	0.21	0.20	0.33	0.30	0.49
	Propene	1.00	1.20	1.87	1.72	1.91
	Iso-Butane	0.46	0.63	1.14	1.05	0.95
	n-Butane	0.10	0.06	0.13	0.12	0.20
	C4 Oleffins	0.97	3.26	3.73	3.42	1.78
	Iso-Pentane	0.27	0.08	0.00	0.00	0.00
	1.3-	0.04	0.00	0.14	0.12	0.36
	Butadiene					
	C5- (liquid)	0.28	0.06	0.03	0.01	0.01
Table S8: E	P-VGO crackin	ig in FC	C, oxyge	n distribu	ution in p	products.
Test			BP1	0 BP34	BP55	BP75
Feedwt.%	VGO		90.1	66.4	44.8	25.1
	BP		9.9	33.6	55.2	74.9
Yieldwt.%	H <sub>2</sub> O		2.81	7.14	11.66	15.12
	CO		0.93	3.97	4.32	4.92
	$CO_2$		1.15	3.77	4.15	5.19
Oxygenwt.%	% in H <sub>2</sub> O/ in CC	) + CO <sub>2</sub>	1.83	1.27	1.89	2.04
	H2O +CO+ (	$O_2$	3.87	11.35	15.85	20.03
	in gasoline (t	by GC)*	0.11	0.19	0.67	1.11
	in BP	-	3.56	12.10	19.87	26.96
	Oxygen bala	nce (GC)	)** 0.42	-0.55	-3.35	-5.82

Table S7: BP-VGO cracking in FCC, liquefied petroleum gas, LPG and Dry gas composition

\* using five carbon to one oxygen as an average stequiometry\*\* GCMS/FID underestimated oxygenates, particularly in high BP wt.%, up to 35% most oxygen was released as water and COx, thus its material balance are considered satisfactory. \*\*\*residual coke at 900°C in this sample was observed visually by CHN, this effectmayslight increase artificially oxygen wt. % in the sample. Sample cBP55 showed satisfactory oxygen material balance.

n.d

Oxygen balance (CHN) **n.d** 

0.98 2.17\*\*\*

#### Table S9 CHNO composition

In wt.%	С	Н	Ν	0
BP	57.1	6.5	0.5	35.9
BP	56.9	6.3	0.6	36.2
averageBPp/p%	57.0	6.4	0.6	36.0
cVGO	87.9	10.2	0.2	1.7
cBP55	85.7	9.1	0.1	5.0
cBP75	81.6	9.0	0.2	9.1

## Table S10: BP and VGO conversion in less severity (using 10g, a less active catalyst CatB, and lower Catalyst/feed ratio).

Test			6	7
Feed wt.	VGO p/p		100	75
	BP p/p		0	25
g	VGO		3	3
	BP		0	1
mL	VGO		3.45	3.45
	BP		0.00	0.91
Catalyst/feed			3.3	2.5
Yield wt.	Aqueous phase		n.d	n.d.
	Coke		7.33	5.33
	Dry gas		4.73	5.8
	CO <sub>x</sub>		0.08	0.95
	LPG		2.99	4.17
Yield wt.	Gasoline		41.9	38.8
Selectivity in gasoline	Paraffin		1.1	1.3
	lso-paraffir	۱	0.5	3.4
	Olefin		34.1	29.3
	Naphtenic		2.0	3.8
	Aromatic		62.3	50.9
	Oxygenate	9	0.0	11.3
Yield wt.	LCO Bottom	+	42.9	44.9
Conversion	Overall		57.1	55.1

Feeed wt.	VGO BP	75 25
Catalyst/feed		2.5
Yield wt.	Kenotes Furan Aldehyde Alcohol Furfural Acetic acid Others DX*	6.98 0.59 0.14 1.12 1.47 0.1 0.91 0.55

\*1,2:3,5-di-O-isopropylidene- $\alpha$ -D-xylofuranose

Table	S	12:	Types	of main	oxygenates	in test	7.
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Ketones	Acetone
	4-Penten-2-one. 4-methyl-
	3-Penten-2-one. 4-methyl
	3-Buten-2-one. 4-(2-furanyl)-
Furan	Furan. 2-methyl-
	Furan. 2.5-dimethyl-
	Furan. 2-(2-propenyl)-
	Furfural
Alcohol	cis.cis-4.6-Octadienol
	2-Nonyn-1-ol
	cis-p-mentha-1(7).8-dien-2-ol
Aldehyde	Propanal. 2-methyl-
	7-Hexadecenal
Acid	Acetic acid

### Table S13: BP-VGO cracking in FCC converted catalyst/feed ratio=7.73.

Feedwt.%		%VGO p/p	45
		%BP p/p	55
(g)		VGO	0.87
		BP	1.07
mL		VGO	1.00
		BP	0.97
Catalyst/feed			7.73
Yieldwt.%		Aqueousphase	10.38
		coke	18.84
		Drygas	10.55
		COx	8.78
		LPG	7.15
Yieldwt.%		Gasoline	33.06
Selectivity	in	Others	16.2
gasoline %			
		Aromatics	80.2
		oxygenates	3.6
Yieldwt.%		LCO + Bottom	11.17
Conversion %		Overall	88.93

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