

PAPER IV

**Wood-derived olefins by steam cracking
of hydrodeoxygenated tall oils**

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Wood-derived olefins by steam cracking of hydrodeoxygenated tall oils

Steven P. Pyl^a, Thomas Dijkmans^a, Jinto M. Antonykutty^b, Marie-Françoise Reyniers^a, Ali Harlin^b, Kevin M. Van Geem^{a,*}, Guy B. Marin^a

^aLaboratory for Chemical Technology, Ghent University, Ghent, Belgium

^bVTT Technical Research Center of Finland, Espoo, Finland

HIGHLIGHTS

- ▶ Tall oil fatty acid and distilled tall oil hydrodeoxygenation produces paraffinic liquids.
- ▶ Steam cracking of hydrodeoxygenated tall oils at pilot plant scale.
- ▶ High light olefin yields when cracking hydrodeoxygenated tall oil fatty acids.
- ▶ Pilot plant cokes test indicates that reasonable run lengths can be expected.

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ABSTRACT

Tall oil fractions obtained from Norwegian spruce pulping were hydrodeoxygenated (HDO) at pilot scale using a commercial NiMo hydrotreating catalyst. Comprehensive two dimensional gas chromatography (GC × GC) showed that HDO of both tall oil fatty acids (TOFA) and distilled tall oil (DTO) produced highly paraffinic hydrocarbon liquids. The hydrotreated fractions also contained fatty acid methyl esters and norabietane and norabietatriene isomers. Steam cracking of HDO–TOFA in a pilot plant revealed that high light olefin yields can be obtained, with 35.4 wt.% of ethene and 18.2 wt.% of propene at a coil outlet pressure (COP) of 1.7 bara, a dilution of 0.45 kg_{steam}/kg_{HDO–TOFA} and a coil outlet temperature (COT) of 820 °C. A pilot plant coking experiment indicated that cracking of HDO–TOFA at a COT of 850 °C results in limited fouling in the reactor. Co-cracking of HDO tall oil fractions with a typical fossil-based naphtha showed improved selectivity to desired light olefins, further demonstrating the potential of large scale olefin production from hydrotreated tall oil fractions in conventional crackers.

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1. Introduction

Ethene, propene, 1,3-butadiene, benzene, toluene and xylenes are produced and consumed in enormous amounts every year, as these base chemicals are the building blocks for most polymers and the starting materials for many additives, solvents, and other high-value chemicals. Currently, steam cracking of fossil feedstocks is mainly responsible for their production. For example 140 × 10⁶ tons of ethene were produced in 2010 with an estimated growth rate of 5.3% (Zimmermann and Walzl, 2009). Therefore, producing these chemicals from renewable resources represents an enormous opportunity, and would contribute to the transition from a petrochemical to a green chemical industry.

Recent research has focused on several alternative technologies for production of olefins such as bio-ethanol dehydration (Kagymanova et al., 2011), methanol-to-olefins (MTO) (Chen

et al., 2005), catalytic fast pyrolysis of lignocellulosic biomass (Carlson et al., 2011; Lavoie et al., 2011), bio-oil upgrading (Gong et al., 2011), etc. However, despite these research efforts and despite continuously increasing oil prices, petroleum conversion and petrochemical production processes are still highly profitable and crude oil remains the most important resource used by the chemical industry. The main reasons are the magnitude of past investments and the operating scale of current units. The use of biomass-derived feedstocks in existing conversion and production units is therefore a very interesting option, since it would allow production of renewable fuels and chemicals without the need to build new production facilities (Huber and Corma, 2007). For example, fluid catalytic cracking (FCC) of vegetable oils, or their mixtures with vacuum gas oil, using conventional FCC technology has already been studied (Bielansky et al., 2011; Dupain et al., 2007; Melero et al., 2010). However, although process conditions can be optimized to maximize propene yields, FCC is mainly used to produce liquid fuels. Alternatively, several types of low cost biomass resources are, after effective upgrading, suitable renewable

* Corresponding author.

E-mail address: kevin.vangeem@ugent.be (K.M. Van Geem).

Notation

COP	coil outlet pressure [bar]	P/E-ratio	ratio of propene yield over ethene yield [kg/kg]
COT	coil outlet temperature [°C]	PAH	polyaromatic hydrocarbons
DHA	detailed hydrocarbon analyzer	PGA	permanent gas analyzer
DTO	distilled tall oil	RGA	refinery gas analyzer
FAME	fatty acid methyl esters	TOFA	tall oil fatty acids
FFA	free fatty acids	ToF-MS	time-of-flight mass spectrometer
FID	flame ionization detector	WHSV	weight hour space velocity [h ⁻¹]
GC × GC	comprehensive 2 dimensional gas chromatograph	δ	steam dilution [kg _{steam} /kg _{hydrocarbons}]
HDO	hydrodeoxygenation	θ	residence time [s]
HDO–DTO	hydrodeoxygenated distilled tall oil		
HDO–TOFA	hydrodeoxygenated tall oil fatty acids		

feeds for conventional steam cracking (Kubičková and Kubička, 2010; Pyl et al., 2011a). For example, crude tall oil, a viscous liquid obtained as a by-product of the Kraft process for wood pulp manufacture (Norlin, 2005), can be fractionated into tall oil fractions called distilled tall oil (DTO) and tall oil fatty acids (TOFA). These fractions mainly contain long chain acids such as oleic and palmitic acids, and a certain amount of rosin acids, i.e. a mixture of organic acids such as abietic acid. Globally about 2 million tons of crude tall oil are refined annually in plants with a typical capacity of 100000 t/a (Norlin, 2005). These tall oil fractions therefore meet the criteria of an economically desirable and readily available feedstock. However, removal of oxygen present in these fractions prior to steam cracking is crucial because separation sections of current steam cracking units are not designed to handle substantial amounts of oxygenated components. Additionally, these components are considered to be the cause of safety issues related to fouling and gum formation in downstream processing (Kohler, 1991). Catalytic hydrodeoxygenation (HDO), using existing hydrotreatment technology and catalysts, of both DTO as well as TOFA removes the oxygen in the fatty and rosin acids in the form of H₂O, CO and CO₂, producing highly paraffinic liquids, i.e. HDO–TOFA and HDO–DTO, respectively (Anthonykutty et al., 2011; Harlin, 2012; Mäki-Arvela et al., 2011; Rozmysłowicz et al., 2010; Sunde et al., 2011). Such paraffinic liquids are commonly considered very desirable feedstocks for steam cracking due to the high light olefin yields they tend to attain (Kubičková and Kubička, 2010; Pyl et al., 2011a).

To properly assess the potential of such hydrodeoxygenated tall oil fractions, steam cracking of HDO–TOFA was studied in a gas-fired pilot plant equipped with a dedicated on-line analysis section. The latter includes a comprehensive 2D gas chromatograph (GC × GC) and enables quantitative and qualitative on-line analyses of the entire reactor effluent with high level of detail.

Furthermore, a pilot plant coking experiment was performed to qualitatively assess the coking tendency of the renewable feed at typical process conditions. Finally, because the enormous operating scale of industrial steam cracking requires vast amounts of feedstock, co-cracking of HDO–TOFA as well as HDO–DTO with petroleum-derived naphtha, the current the most common liquid steam cracker feedstock, was investigated.

2. Experimental

2.1. Wood-derived feedstocks

The renewable liquids used as feedstock in the pilot plant steam cracking experiments were produced by hydrodeoxygenation (HDO) of commercially available tall oil fatty acid (TOFA) and distilled tall oil (DTO) fractions (Stora Enso Kraft pulping facilities,

Sweden), obtained from Norwegian spruce pulping. The raw TOFA had a high fatty acid content (92.6 wt.%) and a low content of rosin acids (1.3 wt.%) and unsaponifiables (6.1 wt.%). The DTO contained 23 wt.% rosin acids, 71.3 wt.% fatty acids and 5.7 wt.% unsaponifiables. The detailed acid composition and elemental composition of these tall oil fractions is presented in Table 1. The main fatty acids in both fractions were oleic (C_{18:1}) and linoleic acids (C_{18:2}). The main rosin acids in DTO were abietic acid and dehydroabietic acid.

Hydrodeoxygenation of TOFA and DTO was performed in a fixed-bed reactor system at SINTEF Materials and Chemistry (Trondheim, Norway), producing 150 liters of product for further processing (Anthonykutty et al., 2011; Harlin, 2012). The tall oil

Table 1
Elemental and detailed acid composition of tall oil fatty acid (TOFA) and distilled tall oil (DTO).

	TOFA	DTO
<i>Elemental composition [%]</i>		
Carbon	76.8	77.4
Hydrogen	11.6	11.1
Nitrogen	<0.1	<0.1
Sulfur	–	0.05
Oxygen	11.6	11.5
<i>Detailed acid composition [wt.%]</i>		
Free Fatty Acids (FFA)	92.6	71.3
(16:0) Palmitic acid	0.40	0.20
(17:0) Margaric acid	0.80	0.30
(18:0) Stearic acid	0.90	0.70
(18:1) Oleic acid	27.4	15.3
(18:1) 11-Octadecenoic acid	0.70	0.50
(18:2) 5,9-Octadecadienoic acid	0.50	0.30
(18:2) Conj. octadecadienoic acid	6.00	8.30
(18:2) Linoleic acid	23.1	24.3
(18:3) Pinolenic acid	8.00	4.4
(18:3) Linolenic acid	4.30	0.60
(18:3) conj. octadecatrienoic acid	0.20	1.80
(20:0) Arachidic acid	0.80	0.40
(20:3) 5,11,14-Eicosatrienoic acid	7.90	7.60
(22:0) Behenic acid	1.30	0.60
Other fatty acids	10.3	6.00
Rosin Acids	1.30	23.0
8,15-Isopimaradien-18-oic acid	0.1	0.5
Pimaric acid	0.7	4.8
Sandaracopimaric acid	–	0.3
Diabietic acid	–	0.5
Palustric acid	–	2.2
Isopimaric acid	–	1.1
13-B-7,9(11)-abietic acid	–	0.4
8,12-Abietic acid	0.1	0.3
Abietic acid	–	7.7
Dehydroabietic acid	–	3.6
Neoabietic acid	–	0.4
Other rosin acids	0.4	1.3

fractions were processed as received, without any pre-treatment or upgrading. The commercial HT-catalyst (NiMo) was presulfided and the reactions were conducted in a temperature range of 320–360 °C at 50.5 bara hydrogen pressure. Tall oil fractions were fed to the reactor at a constant rate (WHSV = 2 h⁻¹). The hydrodeoxygenated TOFA and DTO were analyzed using a comprehensive 2D gas chromatograph (GC × GC), equipped with both a flame ionization detector (FID) and a time-of-flight mass spectrometer (ToF-MS), which has been discussed in detail previously (Pyl et al., 2011b; Van Geem et al., 2010).

2.2. Yields experiments

The main part of the pilot plant for steam cracking (Ghent University, Belgium) is a gas-fired furnace which is 4 m long, 0.7 m wide and 2.6 m high (Van Damme and Froment, 1982; Van Geem et al., 2010). Inside the furnace a tubular reactor is mounted, in which the feedstock is evaporated, mixed with steam and subsequently cracked, at temperatures ranging from 600 to 900 °C. The cracking coil, made of Incoloy 800HT, is 12.8 m long and has an internal diameter of 9 mm. Twenty thermocouples and five pressure transducers are mounted along the coil to measure temperature and pressure of the reacting gas. Steam cracking of pure HDO-TOFA was studied at a coil outlet pressure (COP) of 1.7 bara, a dilution (δ) of 0.45 kg_{steam}/kg_{HDO-TOFA}, and at coil outlet temperatures (COT) of 820 and 850 °C. Cracking of mixtures of HDO-TOFA (15 vol.%) and naphtha (85 vol.%) as well as HDO-DTO (15 vol.%) and naphtha (85 vol.%) was studied at a coil outlet pressure (COP) of 1.7 bara and a dilution (δ) of 0.45 kg/kg. Experiments were conducted at coil outlet temperatures (COT) of 820, 850 and 880 °C for the HDO-TOFA mixture and at 820 and 850 °C for the HDO-DTO mixture. In all these experiments, the coil inlet temperature remained fixed at 600 °C, and the temperature increased linearly along the reactor.

The dedicated analysis section of the pilot plant enables on-line qualification and quantification of the entire product stream. The latter was analyzed by a permanent gas analyzer (PGA), a refinery gas analyzer (RGA), a detailed hydrocarbon analyzer (DHA) and a GC × GC-FID/TOF-MS (Van Geem et al., 2010). The pilot plant effluents were sampled on-line, i.e. during pilot plant operation, and at high temperatures (400–500 °C) using a heated valve-based sampling system and uniformly heated transfer lines. This permitted to analyze the entire product streams, i.e. from methane up to PAHs, in a single run of the GC × GC and DHA and avoided separate condensate and gas-phase analyses. In order to determine absolute flow rates of all effluent components, a fixed flow of N₂, which acts as an internal standard, was continuously added to the reactor effluent. Accordingly, mass balances can be verified after identification and quantification of all detected components. Only experiments that resulted in a mass balance between 95 and 105 wt.% were retained. Subsequently, component mass fractions were normalized to 100 wt.%.

2.3. Coking experiments

A pilot plant coking experiment consists of 2 stages (Dhuyvetter et al., 2001). Here, the first stage involved continuous cracking for a period of 6 h at a coil outlet temperature of 850 °C, a dilution of 0.45 kg/kg, and a coil outlet pressure of 1.7 bara. During this stage cokes is deposited on the inner wall (0.35 m²) of the reactor. The product composition was analyzed regularly to ensure steady state operation. In the second stage, decoking of the reactor was performed by feeding a steam (0.28 g/s)/air (0.23 NI/s) mixture and increasing the reactor temperature uniformly to 900 °C. During this stage the CO/CO₂ content of the effluent was monitored in real time by an infra-red gas analyzer. A vortex gas flow meter

continuously measured the volumetric gas flow rate. Decoking was stopped when the amount of CO₂ in the effluent dropped below 0.01 vol.%. Finally, the acquired data were used to calculate the total amount of carbon deposited on the entire inner wall of the reactor during the first stage.

3. Results and discussion

3.1. Feedstock analyses

In Table 2, group-type composition and distillation data of the hydrodeoxygenated tall oils are presented as well as those of a typical petroleum-derived naphtha and natural gas condensate, i.e. common liquid feedstocks for current steam crackers (Zimmermann and Walzl, 2009).

Overall, approximately 100 components were measured in these mixtures, including paraffins, naphthenes, aromatics and methyl-esters. Fig. 1(a) shows the GC × GC-FID chromatogram of HDO-TOFA, indicating that it mostly contained *n*-octadecane (71.2 wt.%) and *n*-heptadecane (15.6 wt.%), which are the HDO products of the fatty acids present in the untreated TOFA. HDO-DTO (Fig. 1(b)) had a similar composition, but contained a lower amount of *n*-paraffins, including 50.7 wt.% *n*-octadecane and 10.5 wt.% *n*-heptadecane. However, compared to the fossil feedstocks in Table 2, both HDO-TOFA and HDO-DTO contained high amounts of these paraffins in a significantly higher carbon range, i.e. C₁₄–C₂₄ for the tall oil fractions versus C₃–C₁₃ for the naphtha and C₃–C₂₀ for the natural gas condensate. The latter also contained some long chain paraffins, but in lower amounts (Table 2).

The rosin acids present in the untreated TOFA and, especially, DTO resulted in certain amounts of tricyclic naphthenes, such as norabietane isomers (C₁₉), and aromatics, such as norabietatriene isomers (C₁₉). In both fractions also the fatty acids methyl esters (FAME) methyl palmitate (C_{16:0}) and methyl oleate (C_{18:1}) were also detected. Oxygenates are generally avoided in steam cracker feedstocks and product streams because they are believed to

Table 2

Group-type composition and distillation data of HDO-TOFA and HDO-DTO used in the pilot plant experiments, compared to a petroleum-derived naphtha and a natural gas condensate.

Feedstock	Naphtha	Natural gas condensate	HDO-TOFA	HDO-DTO
<i>Group-type composition [wt.%]</i>				
<i>n</i> -Paraffins	35.0	14.6	91.2	75.4
<i>n</i> -heptadecane	–	0.14	15.6	10.5
<i>n</i> -octadecane	–	0.10	71.2	50.7
iso-Paraffins	46.3	14.5	3.17	2.90
Naphthenes	16.0	35.8	5.29	15.9
Norabietane isomers	–	–	0.91	11.8
Aromatics	2.80	35.2	0.13	4.17
Norabietatriene isomers	–	–	0.13	4.17
Methyl-esters	–	–	0.22	1.68
Methyl palmitate	–	–	0.02	0.05
Methyl oleate	–	–	0.04	0.03
Carbon range	C ₃ –C ₁₃	C ₃ –C ₂₀	C ₁₄ –C ₂₄	C ₁₄ –C ₂₄
<i>Simulated distillation [°C]</i>				
Initial boiling point	–	–	71.2	99.0
5%	30.0	–	–	–
10%	36.6	31.0	302.1	303.4
30%	60.4	69.0	–	–
50%	68.0	97.0	316.7	316.4
70%	88.6	139.0	–	–
90%	116.0	233.5	344.6	316.7
95%	141.7	–	–	–
Final boiling point	189.5	414.0	392.2	323.1

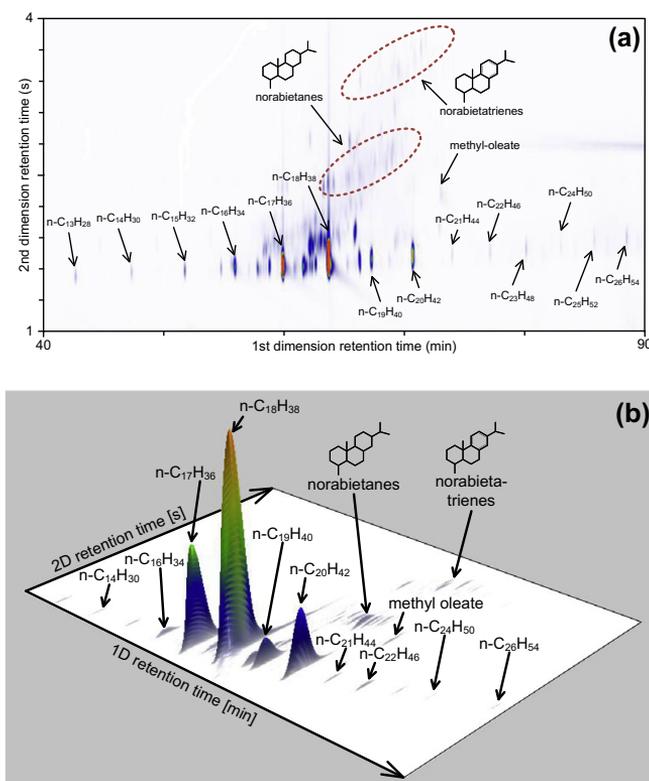


Fig. 1. (a) GC × GC-FID chromatogram (contour plot representation) of HDO-TOFA, and (b) GC × GC-FID chromatogram (3D representation) of HDO-DTO indicating the most important components (norabietane and norabietatriene isomers are represented by a single structural isomer).

contribute to fouling in the downstream separation section. HDO-TOFA contained 0.22 wt.% of methyl-esters, but the total oxygen content (0.02 wt.%) is even lower because of the long hydrocarbon chain in these molecules. Moreover, thermal decomposition of these long-chain esters is quite fast, even at lower temperatures, and most of the oxygen ends up in the form of CO and CO₂ (Pyl et al., 2011b, 2012), which are not believed to contribute to fouling issues in downstream separation.

3.2. HDO-TOFA steam cracking

3.2.1. Yields experiments

Approximately 150 different chemical components were identified and quantified in the pilot plant effluents. In Table 3 a summary of the product yields at the different process conditions is presented. The results are compared to the product distribution when cracking naphtha and natural gas condensate at similar conditions. Fig. 2(a and b) show the GC × GC chromatograms of on-line sampled reactor effluent when cracking naphtha and HDO-TOFA respectively at a COT of 850 °C. These chromatograms illustrate the similarity in the spectrum of chemicals for both effluents, which contain hydrocarbons ranging from light olefins and alkanes (C₄-), to so-called pyrolysis gasoline (e.g. benzene, toluene and xylenes), and up to so-called pyrolysis fuel oil (e.g. naphthalene and phenanthrene).

However, as shown in Table 3, light olefin yields, and in particular ethene yields, were significantly higher for HDO-TOFA than naphtha or gas condensate cracking. This is explained by the high

amount of *n*-paraffins in the renewable feed. Thermal cracking of these long-chain molecules proceeds through a free radical mechanism, resulting in rapid decomposition by successively splitting of ethene molecules (Billaud et al., 1991; Herbinet et al., 2007). In contrast, naphtha cracking results in relatively high methane, propene and iso-butene yields due to the high amount of iso-paraffins in the feed, i.e. 46 wt.% (Table 2).

Due to unwanted steam reforming, catalyzed by Ni in the reactor metal, small amounts of carbon oxides are produced, even when cracking typical hydrocarbon feeds like naphtha. However, Table 3 shows that steam cracking of HDO-TOFA resulted in somewhat higher amounts of CO and CO₂. This is also in line with the feedstock analysis, since HDO-TOFA contained a small amount of esters, and decomposition of the carboxyl-group in these esters results in the formation of additional CO and CO₂ (Pyl et al., 2011b, 2012).

Higher amounts of naphthenes and aromatics in the natural gas condensate resulted in higher pyrolysis gasoline yields, and in particular high benzene and toluene yields. Pyrolysis gasoline yields are quite low when cracking HDO-TOFA mainly because, unlike naphtha and gas condensate, the renewable feed did not contain components in this carbon range. Nevertheless, at a COT of 820 °C certain amounts (Table 3) of unconverted HDO-TOFA feed components, such as heavy paraffins, norabietane and norabietriene isomers, and their primary decomposition products were observed in the product stream. This resulted in a large amount of so-called pyrolysis fuel oil, i.e. the heavy and low value fraction of the product. These components were also mainly responsible

Table 3
Effect of feedstock composition and coil outlet temperature (COT) on product yields [wt.%] [$\delta = 0.45$ kg/kg; COP = 1.7 bara].

COT	Reference feedstocks						Renewable feedstocks						
	Naphtha			Natural gas condensate			HDO-TOFA		85 vol.% Naphtha + 15 vol.% HDO-TOFA		85 vol.% Naphtha + vol.% HDO-DTO		
	820 °C	850 °C	880 °C	800 °C	820 °C	840 °C	820 °C	850 °C	820 °C	850 °C	880 °C	820 °C	850 °C
P/E [kg/kg]	0.68	0.55	0.42	0.70	0.62	0.53	0.51	0.44	0.65	0.57	0.40	0.66	0.56
Permanent gasses [C0–C1]	13.6	16.7	19.1	10.4	12.5	14.2	11.2	12.6	13.2	15.8	19.0	13.1	16.4
H ₂	0.91	1.07	1.23	1.01	0.91	1.20	0.61	0.70	0.72	0.92	1.24	0.71	0.92
CH ₄	12.6	15.6	17.8	9.40	11.6	13.0	10.4	11.8	12.4	14.8	17.7	12.4	15.4
CO	0.02	0.03	0.06	0.02	0.05	0.02	0.11	0.09	0.03	0.05	0.07	0.03	0.04
CO ₂	0.01	0.01	0.01	<0.01	<0.01	0.01	0.08	0.03	0.01	0.01	0.01	0.03	0.02
Light alkenes [C2–C4]	55.6	57.1	54.0	44.4	47.4	47.2	63.4	61.9	57.4	59.0	54.3	56.5	58.1
Ethene	26.0	30.0	32.2	19.6	22.6	24.6	35.4	36.9	27.4	30.0	33.3	27.0	29.6
Propene	17.8	16.5	13.4	13.7	14.0	13.0	18.2	16.3	17.7	17.1	13.4	17.8	16.5
1-Butene	2.29	1.44	0.57	2.01	1.40	0.92	2.20	1.06	2.69	1.53	0.51	2.50	1.52
Iso-butene	3.18	2.75	1.65	2.32	2.38	1.86	0.22	0.23	3.16	2.84	0.84	2.74	2.76
1,3-Butadiene	4.71	4.62	4.34	4.79	5.18	4.70	6.41	6.11	4.56	5.19	4.48	4.49	5.29
Others	1.60	1.75	1.81	1.69	1.47	1.65	0.98	1.32	1.47	1.97	1.31	1.79	2.08
Light alkanes [C2–C4]	4.74	4.66	4.00	3.42	3.98	3.64	5.50	4.92	4.82	4.69	4.16	5.03	4.58
Pyrolysis gasoline [C5–C9]	25.4	19.2	20.2	39.7	34.0	32.0	11.1	18.4	21.7	17.9	19.9	21.1	18.5
Benzene	4.58	6.05	8.07	6.54	7.96	8.91	4.35	6.75	3.56	6.03	8.28	3.79	6.14
Toluene	2.05	2.47	3.01	7.03	6.67	6.87	1.42	3.33	1.46	2.49	3.11	1.54	2.50
Xylenes	0.60	0.60	0.51	4.02	3.23	3.14	0.26	0.48	0.38	0.68	0.49	0.60	0.55
Others	18.2	10.0	8.59	22.1	16.2	13.1	5.07	7.88	16.3	8.74	8.03	15.2	9.27
Pyrolysis fuel oil [C10–C30]	0.46	1.34	2.40	1.99	2.06	2.92	8.73	1.94	2.96	2.51	2.59	4.23	2.51
Naphthalene	0.17	0.41	0.76	0.59	0.73	1.07	0.57	1.01	0.25	0.69	0.99	0.43	0.55
Methyl-naphthalenes	0.11	0.18	0.52	0.42	0.40	0.55	0.19	0.35	0.11	0.32	0.65	0.37	0.26
Other PAH's	0.19	0.75	1.12	0.89	0.82	1.21	0.66	0.84	0.23	0.86	0.95	0.34	0.89
Heavy paraffins and olefins	–	–	–	0.09	0.10	0.08	2.79	0.02	1.07	0.02	<0.01	0.83	0.09
Heavy naphthenes	–	–	–	–	–	–	3.58	<0.01	1.04	0.49	<0.01	1.47	0.52
Heavy naphtheno-aromatics	–	–	–	–	–	–	0.94	<0.01	0.25	0.13	<0.01	0.80	0.21

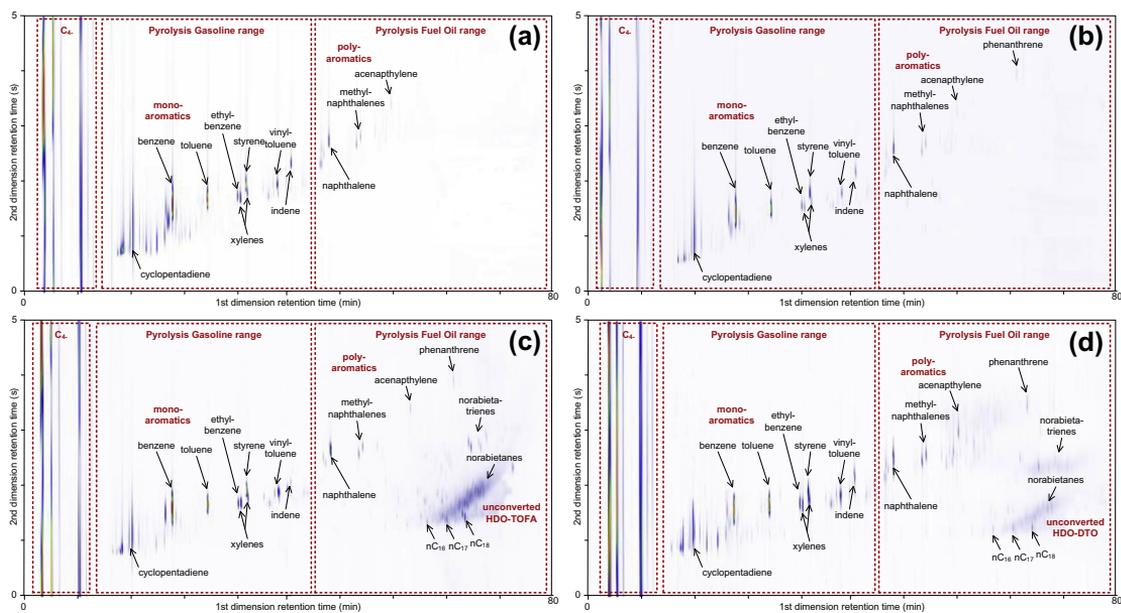


Fig. 2. GC × GC-FID chromatograms (contour plot representation) of on-line sampled reactor effluents during (a) naphtha cracking; (b) HDO-TOFA cracking; (c) naphtha/HDO-TOFA cracking; (d) naphtha/HDO-DTO cracking [COT = 850 °C; $\delta = 0.45$ kg/kg; COP = 1.7 bara].

for the somewhat higher naphthalene and PAH yields, since their conversion involves rapid dehydrogenation into aromatics through a succession of hydrogen abstractions and β -scission reactions (Bounaceur et al., 2000; Oehlschlaeger et al., 2009). At 850 °C

nearly no remaining feed components could be measured. However, this COT resulted in so-called over-cracking which should be avoided in industrial practice. Over-cracking, i.e. cracking at too high temperatures, promotes secondary condensation

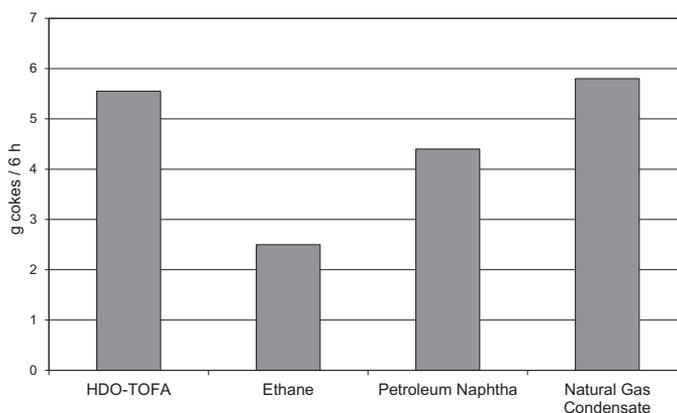


Fig. 3. Measured coke deposition during a 6-h coking experiment with HDO-TOFA [COT = 850 °C; δ = 0.45 kg/kg; COP = 1.7 bar] and reference feedstocks (ethane, naphtha and natural gas condensate) at similar process conditions.

reactions and results in reduced total light olefin yields, in favor of less valuable aromatics such as benzene toluene and naphthalene, as shown in Table 3. An optimal COT would result in high conversion of the feed and maximal light olefin yields. For the studied COP (1.7 bar), dilution (0.45 kg/kg) and flow rates (4 kg/h), this optimal COT was located between 820 and 850 °C. The issue of over-cracking is also observed for naphtha cracking as the total amount of light olefins went through a maximum while pyrolysis gasoline and also fuel oil yields go through a minimum at a temperature between 850 and 880 °C.

Furthermore, an important design specification for industrial units is the yield ratio of propene to ethene (P/E-ratio) (Van Geem et al., 2005). As shown in Table 3 HDO-TOFA cracking at a COT of 820 °C resulted in a desirable P/E-ratio of 0.5. A similar P/E-ratio was obtained at a COT between 850 and 880 °C for the naphtha and at a temperature just above 840 °C for the gas condensate. These results demonstrate that, compared to naphtha and gas condensate cracking, less heat input is required when cracking HDO-TOFA to obtain a similar P/E-ratio.

3.2.2. Coking experiments

Fig. 3 shows that the total amount of coke deposited on the inner wall of the reactor during a 6-h coking experiment at a COP of 1.7 bara, a dilution of 0.45 kg_{steam}/kg_{HDO-TOFA} and a COT of 850 °C was 5.55 g_{cokes}/6 h. For comparison, the results of a similar coking experiment using ethane, naphtha, and natural gas condensate cracked at similar process conditions are also presented.

These results indicate that reasonably long run-lengths can be expected with HDO-TOFA, i.e. comparable to cracking natural gas condensate. However, these process conditions resulted in over-cracking of HDO-TOFA, as discussed in Section 3.2.1. To maximize light olefin yields, an industrial unit could be operated at a lower COT, which would have a beneficial impact on run-length.

3.3. HDO-tall oil/naphtha co-cracking

In Table 3 an overview of the measured product yields is presented for steam cracking of mixtures of HDO-TOFA (15 vol.%) and naphtha (85 vol.%) as well as HDO-DTO (15 vol.%) and naphtha (85 vol.%).

Cracking of HDO-TOFA/naphtha mixtures resulted in slightly higher yields of light olefins compared to cracking of pure naphtha. Furthermore, pyrolysis gasoline yields were also lower, but fuel oil yields were higher. However, the positive impact on olefin yields

decreased with increasing COT. As discussed in Section 3.2.1, so-called over-cracking has an unfavorable impact on olefin yields. Because of the significantly different carbon ranges of naphtha (C₃–C₁₃) and tall oils (C₁₄–C₂₄), optimal process conditions will have to be a compromise between the optimum for naphtha cracking and the optimum for and HDO-TOFA/HDO-DTO cracking. Since industrial steam crackers are usually a combination of a number of furnaces coupled to a single downstream separation section, an alternative to co-cracking is so-called segregate cracking. In this approach the majority of the furnaces can be used to crack naphtha, while one or more furnaces are used to crack renewable feedstocks, depending on their availability. The results presented in Table 3 indicate that this could be a better option, since it allows to optimize process condition in each furnace depending on the employed feed.

This is also illustrated in Fig. 4, which shows the yields of ethene, propene, ethane and 1,3-butadiene for different mixtures of HDO-TOFA and naphtha at a COT of 820 and 850 °C. These products are economically the most valuable products, with ethane being converted to ethene with a selectivity of typically 80% in a separate furnace. To better visualize the trends for these products as function of the amount of HDO-TOFA added to the naphtha, simulation results have been added to complement the experimental data. These simulations were performed with COILSIM1D. This program, discussed in detail previously (Van Geem et al., 2004, 2008), simulates the controlling free-radical chemistry using a microkinetic model that allows to properly account for non-linear mixing effects that have been reported when cracking mixtures (Froment et al., 1976, 1977). COILSIM1D has been validated extensively for gaseous and naphtha feedstocks (Pyl et al., 2011a; Van Geem et al., 2004). Also for the present set of experimental data a reasonable agreement is observed (Fig. 4). It is clear that from an economic point of view it is preferable to run the furnaces on pure TOFA, because this results in maximum ethene and 1,3-butadienes yields, while propene yields are only slightly affected. Fig. 4 shows that co-cracking of naphtha and HDO-TOFA does not lead to significant positive or negative synergetic effects on the yields. For these four products nearly linear mixing rules are a reasonable approximation, in particular for ethene and 1,3-butadiene. Deviations were observed for propene and ethane, which are in line with earlier work carried out on ethane/propane mixtures (Froment et al., 1976, 1977).

Another disadvantage of co-cracking of naphtha and HDO-TOFA is illustrated in Fig. 2(c). This Fig. shows the GC × GC chromatogram

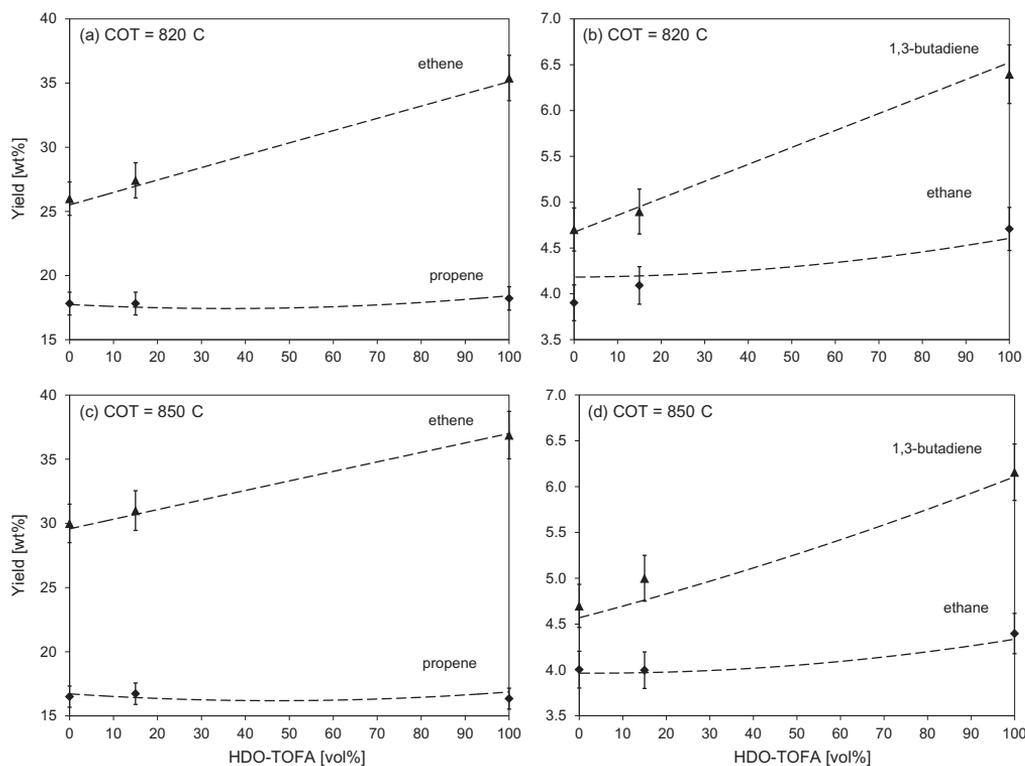


Fig. 4. Influence of the amount of HDO-TOFA in the feedstock on the yields of ethene, propene, 1,3-butadiene and ethane for a COT of 820 and 850 °C [$\delta = 0.45$ kg/kg; COP = 1.7 bar] (dashed lines: simulated using COILSIM1D, symbols: experimental values with 5% rel. error bars).

grams of on-line sampled reactor effluent when cracking naphtha/HDO-TOFA a COT of 850 °C. This Fig. and the values in Table 3 show that, when cracking HDO-TOFA/naphtha mixtures, some residual feed components were present in the product, even at a COT of 850 °C. This phenomenon did not occur with pure HDO-TOFA cracking, as conversion was observed to be complete at this COT (Fig. 2(b)). Similarly, conversion was also not complete when cracking HDO-DTO/naphtha at a COT of 850 °C (Fig. 2(d)). Overall, the HDO-DTO/naphtha mixture resulted in slightly higher light olefin yields at a COT of 820 °C compared to naphtha cracking. However, at a COT of 850 °C olefin yields were somewhat lower, while the amounts of fuel oil was higher due to higher amounts of norabietane and norabietatriene isomers in the HDO-DTO fraction.

4. Conclusions

Catalytic hydrodeoxygenation of tall oil fractions produces paraffinic liquids. These liquids are attractive renewable feedstocks that can be used in conventional steam cracking units for the production of green olefins. Compared to typical petroleum- or natural gas-derived feedstocks, high amounts of ethene and propene can be obtained. Moreover, reasonably high run-lengths can be expected. Co-cracking of HDO-TOFA with naphtha will require a compromise between optimal process conditions, because of the significantly different carbon range of these feeds. Alternatively, segregate cracking would allow to optimize process conditions in each furnace separately, depending on the feedstock.

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