Paper 51F

Bio-Ethylene Production:
Alternatives for Green Chemicals and Polymers

Kevin M. Van Geem

Laboratory for Chemical Technology, Ghent University
Ghent, Belgium

Jinto Manjaly Anthonykutty

VTT Technical Research Centre of Finland
Espoo, Finland

Steven P. Pyl

Laboratory for Chemical Technology, Ghent University
Ghent, Belgium

Ali Harlin

VTT Technical Research Centre of Finland
Espoo, Finland

Guy B. Marin

Laboratory for Chemical Technology (LCT), Ghent University
Ghent, Belgium

1

Production of bioethylene: alternatives for green chemicals and polymers

Prof. Kevin Van Geem
Laboratorium voor Chemische Technologie
Ugent – Ghent University
Technologiepark918
9052 Zwijnaarde
tel: 00 (32) 478573874 - 00 (32) 92645597
fax: 00 (32) 92645824

ABSTRACT:

There is an increasing trend of using bio-polyethylene and bio-polypropylene in Europe for making consumer goods. However there is currently very limited production capacity available for producing these base chemicals that are used in the polymerization processes. This contribution will give an overview of the presently available routes for the production of bio-ethylene and bio-propylene (bio-ethanol to olefins, methanol to olefins, hydrodeoxygenation of biomass followed by steam cracking, fast pyrolysis of biomass) and discuss advantages and disadvantages. The talk will be completed with results obtained from different pilot plant studies starting from tall-oil and waste fats and greases. In a first step these feedstocks are catalytically converted, in a second step they are cracked towards olefins. The total light olefin yield (ethylene and propylene) that has been obtained is in all cases higher than with naphtha and is above 50 wt% depending on process conditions, pretreatment and the biomass origin.

Introduction

Increasing oil prices, and the growing awareness of the detrimental environmental effects related to the use of fossil resources have focused research attention towards alternative routes and feedstocks for the production of light olefins and aromatics[1-3]. These large-volume chemicals such as ethylene, propylene, 1,3-butadiene and benzene are the building blocks for most polymers and the starting materials for many additives, solvents, etc.

Currently, steam cracking of fossil-based feedstocks is responsible for the production of these chemical building blocks, producing over $140 10^6$ tons of ethylene per year with a growth rate of 5.3%[4]. Large capacity crackers are operated all over the world, making the use of biomass-derived feedstocks to complement or even replace fossil feedstocks in existing units an interesting option. Several types of low cost biomass resources are, after effective upgrading, suitable renewable feeds for conventional steam crackers.

Crude tall oil is a viscous liquid obtained as a by-product of the Kraft process for wood pulp manufacture when pulping mainly coniferous trees[5]. It can be fractionated into distilled tall oil (DTO) and tall oil fatty acids (TOFA). These fractions mainly contain long chain fatty acids. DTO also contains significant amounts of rosin acids, i.e. a mixture of organic acids such as abietic acid. Catalytic hydrodeoxygenation (HDO) of both DTO as well as TOFA removes the oxygen in these acids in the form of H_2O, CO and CO_2, producing highly paraffinic hydrocarbon liquids, i.e. HDO-TOFA and HDO-DTO respectively[6].

Similarly, catalytic hydrodeoxygenation of triglyceride based biomass (TGB), such as algae oils or low cost waste greases like poultry fat and yellow grease, also produces paraffinic liquids (HDO-TGB) that are attractive feedstocks for conventional steam crackers.

In order to properly assess the potential of such deoxygenated bio-oils, steam cracking of HDO-TGB and HDO-TOFA was studied in the LCT pilot plant. The dedicated on-line analysis section includes a GC×GC-FID/(TOF-MS) and enables quantitative and qualitative on-line analyses of the entire reactor effluent with high level of detail[7]. The detailed characterization of feedstocks and pilot plant products for varying process conditions allows validation of the single-event microkinetic (SEMK) model, originally developed for steam cracking of fossil feedstocks [8, 9].

Experimental

TGB hydrodeoxygenation

A low value waste grease blend (46 wt% poultry fat, 18 wt% yellow grease 18 wt% brown grease, 9 wt% floatation grease, and 9 wt% grease from prepared foods) was acquired from Tyson Foods (Springdale AR, USA). Preliminary pretreatment involved filtration and washing to remove contaminants such as animal solids, phosphorus, and solubilized alkali/alkaline earth metals. The pretreated greases were subjected to catalytalic hydrodeoxygenation (HDO) in a two stage HDO pilot plant (Syntroleum, Geismar LA, USA). Catalysts were activated according to the Syntroleum sulfiding procedure before introduction of the feed[10, 11]. Bio-Synfining™ catalysts, i.e. commercially available hydrotreating catalysts, and the reactor operating conditions are described in more detail by Abhari et al. [11].

TOFA and DTO hydrodeoxygenation

Commercially available tall oil fractions (Stora Enso Kraft pulping facilities, Sweden) from Norwegian spruce pulping were used as raw materials. SYLVAT® 2 is a tall oil fatty acid (TOFA) with high fatty acid content (96 wt%) and a low content of rosin acids (1.8 wt%) and unsaponifiables (2 wt%). The employed SYLVATAL® 25/30S distilled tall oil (DTO) contained 27 wt% rosin acids, 70 wt% fatty acids and 3 wt% unsaponifiables. In both fractions the main component is oleic acid (C18:1). The main rosin acid in these fractions is abietic acid. Hydrodeoxygenation (HDO) of TOFA and DTO was performed in a fixed-bed reactor system at SINTEF Materials and Chemistry (Trondheim, Norway) aiming to produce 150 liters of product for further processing. The oils were processed as received on a continuous basis for 23 days without any pre-treatment/upgrading. The commercial HT-catalyst (NiMo) was presulfided prior to the experiment and the reactions were conducted in a temperature range of 320-360^0 C at 50.5 bara hydrogen pressure. Bio-oils were fed to the reactor at a constant rate (WHSV = 2 h^{-1}). Additionally, HDO experiments were also performed at VTT Technical Research Center Finland (Espoo, Finland)[6] in a bench-scale reactor in order to contrast the pilot scale and lab scale studies. The same HT-catalyst (NiMo) was used in VTT studies and the presulfidation was carried out by using H_2S/H_2 mixture for 5 hours at 400^oC (H_2S/H_2 = 5 vol %). The experiments were conducted in a temperature range of 325-450 ^{o} C at a hydrogen pressure of 50 bar. The liquid feed was fed in to the reactor with three different feed rates (WHSV= 1, 2 and 0.3 h^{-1}). After a 6-hour stabilization period, liquid sample was collected and fractionated in to organic and aqueous phases.

The organic phase was further analyzed by GC-MS, GC×GC and CHNS-O elemental analyzer[6].

Steam Cracking Pilot Plant

The pilot plant at the Laboratory for Chemical Technology (Ghent University, Belgium), shown in Figure 1, consists of 3 sections: the feed section, the furnace/reactor section and the analysis section[12, 7]. The furnace, built of silica/alumina brick (Li23), is 4 m long, 0.7 m wide and 2.6 m high. It is fired by means of 90 premixed gas burners, mounted with automatic fire checks and arranged on the side walls in such a way as to provide a uniform distribution of heat. The furnace is divided into 7 separate cells that can be heated independently so that any type of temperature profile can be set. 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. These dimensions are chosen to achieve turbulent flow conditions in the coil with reasonable feed flow rates. The reactor outlet pressure is controlled by a computer regulated restriction valve. Twenty thermocouples and five pressure transducers are mounted along the coil to measure the temperature and pressure of the reacting gas.
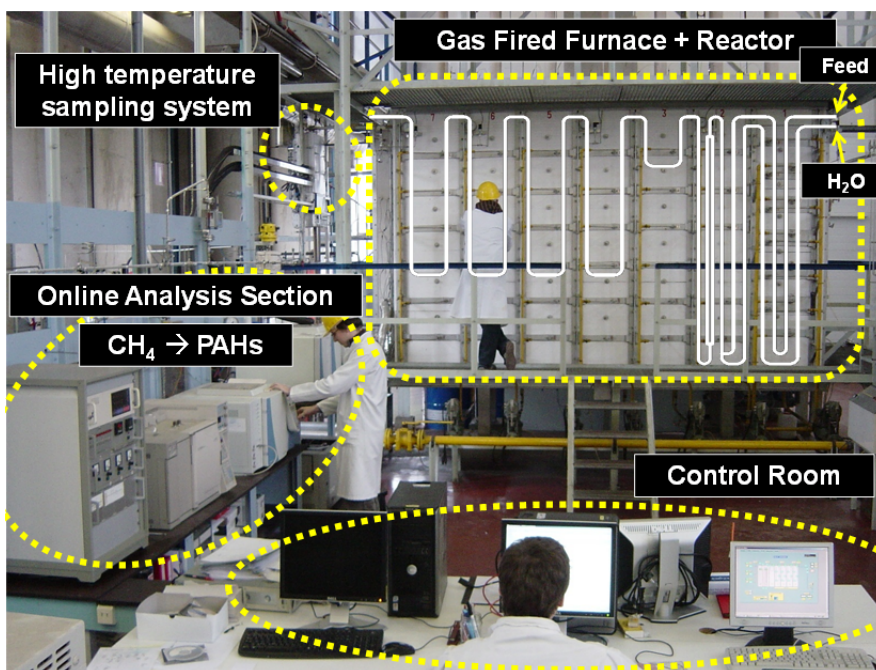

Figure 1: Steam cracking pilot plant[7]

The analysis section of the pilot plant enables on-line qualification and quantification of the entire product stream, i.e. a wide boiling mixture containing H_2, CO, CO_2 and hydrocarbons ranging from methane up to polyaromatic hydrocarbons[9, 7, 3]. The complexity of the effluents calls for several gas chromatographs: a permanent gas analyzer (PGA), a refinery gas analyzer (RGA), a detailed hydrocarbon analyzer (DHA) and a GC×GC-FID/TOF-MS. The pilot plant effluent is sampled on-line, i.e. during pilot plant operation, and at high temperature (400°C-500°C) using a heated valve-based sampling system and uniformly heated transfer lines. A fixed amount of N_2 is continuously added to the effluent, which acts as an internal standard, and permits the determination of absolute flow rates of all effluent components which allows to assess the effect of process conditions on the product distribution.

Single-event Microkinetic Model

Thermal cracking of organic components mainly proceeds through a free radical mechanism[13]. Three important reaction families can be distinguished: (i) bond scission and the reverse radical recombination; (ii) hydrogen abstraction; and (iii) radical addition and the reverse β-scission.

The microkinetic model is divided into two parts: the *µ network*, i.e. an extensive database of sub-mechanisms for the primary decompositions for large species (typically C_{6+}), and the *β network*, i.e. the core of the kinetic model that contains the interactions between smaller (typically C_{5-}) radicals and molecules [14, 15, 8]. A comprehensive group additive framework, i.e. a consistent extension of Benson's group additivity concept to transition state theory, allows automatic calculation of all kinetic parameters using a set of reference reactions and group additive values[16-20]. The SEMK model was originally developed to model steam cracking of fossil-based feedstocks, e.g. light hydrocarbons (ethane, propane, butane), naphtha and gas oils. The model therefore includes a wide range of components, such as paraffins, olefins, mono-, di- and tri-cyclic naphthenes, mono-, di- and tri- cyclic aromatics, and naphtheno-aromatics.

Coupling the microkinetic model to an appropriate reactor model and a solver for the resulting set of DAE's, allows simulation of industrial, pilot scale and bench scale reactors for a wide range of feedstocks[21]. However, as the number of species, and consequently equations and simulation time, increases exponentially with the complexity and average carbon number of the feedstock[22], *a priori* application of the quasi steady state approximation for so-called µ radicals ensures that the number of species and equations remains manageable [14, 15, 8].

Results and discussion

Feedstock Analyses

The detailed composition of the studied feedstocks was determined using GC×GC-FID/TOF-MS[7]. In Figure 2 the group-type compositions of the hydrodexygenated oils are presented as well as the composition of a typical petroleum-derived naphtha, i.e. currently the main steam cracker feedstock certainly in Europe [23]. Compared to this naphtha, the HDO-TGB contains high amounts of n-paraffins in a significantly higher carbon range, i.e. C14-C24 for the HDO-TGB versus C3-C13 for the naphtha. Only small amounts of naphthenes and no more than traces of aromatics were detected in the HDO-TGB. Also the HDO-TOFA and HDO-DTO feeds are highly n-paraffinic mixtures (C14-C24). The rosin acids present in the untreated TOFA and DTO fractions result in significant amounts of tricyclic naphthenes, such as norabietane (C19), and aromatics, such as norabietatriene (C19). In both fractions also some fatty acids methyl esters (FAME) were measured.
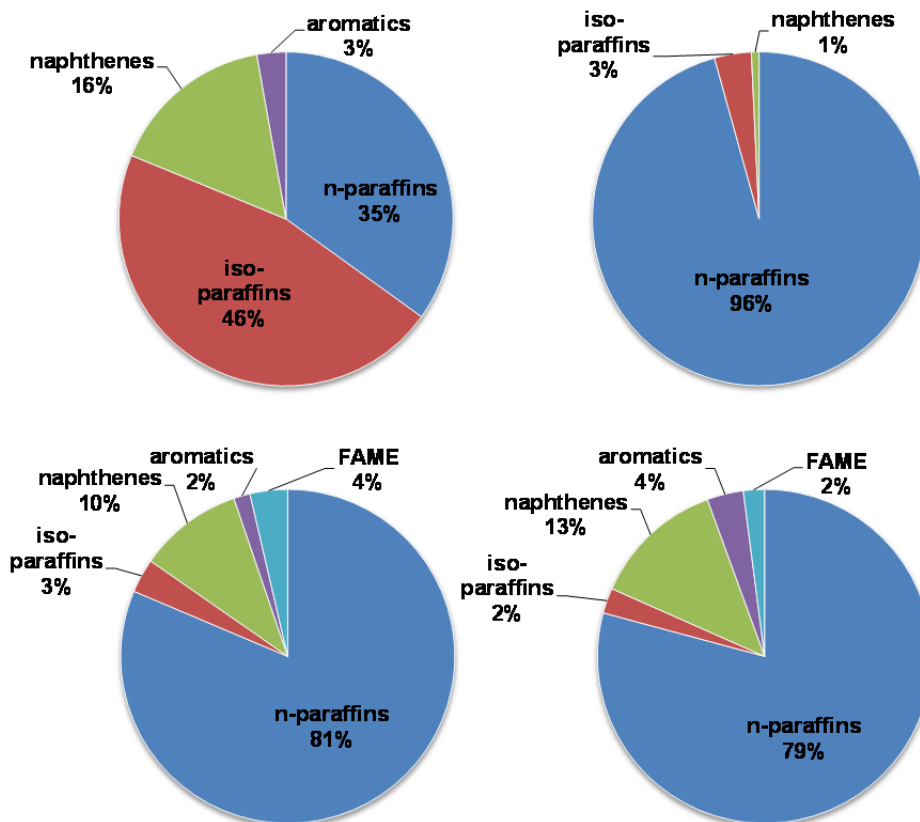

Figure 2: Group-type composition of (a) reference petroleum naphtha (C_3-C_{13}), (b) HDO-TGB (C_{14}-C_{24}), (c) HDO-TOFA (C_{14}-C_{24}) and (d) HDO-DTO (C_{14}-C_{24})

Pilot plant steam cracking

Table 1 gives an overview of the measured product yields for the various studied feedstocks at a coil outlet temperature (COT) of 820 °C and 850 °C respectively.

Table 1: Effect of feedstock composition and coil outlet temperature on product yields [δ = 0.45 kg/kg; τ = 0.3 s, COP = 1.7 bar]

Feed	Naphtha		HDO-TGB		HDO-TOFA	
COT	820 °C	850 °C	820 °C	850 °C	820 °C	850 °C
Methane	12.7	15.6	9.81	12.7	10.4	11.8
CO	0.02	0.03	0.02	0.04	0.13	0.10
CO_2	< 0.01	< 0.01	< 0.01	0.01	0.10	0.03
Ethylene	25.9	29.9	36.0	37.5	35.4	36.9
Propylene	17.8	16.5	19.5	18.1	17.5	15.3
1-Butene	2.37	1.44	4.18	1.63	2.20	1.05
1.3-Butadiene	4.72	5.33	7.45	7.56	4.51	4.92
Benzene	4.48	6.05	4.16	7.02	4.45	6.75
Toluene	2.14	2.47	1.29	1.86	1.42	3.33
Fuel oil	0.60	1.50	0.21	0.88	11.3	2.44

When cracking HDO-TOFA or HDO-TGB, ethylene yields are significantly higher compared to naphtha cracking for these conditions. This can be explained by the n-paraffinic nature of the renewable feeds. However, naphtha cracking results in relatively high methane and propylene yields due to the higher amount of iso-paraffins in the feed.

Cracking HDO-TOFA results in the highest amounts of CO and CO_2 which is in line with the feedstock analysis: the HDO-TOFA feed contains an important amount of esters. At a COT of 820°C quite a lot of unconverted feed was observed resulting in a large amount of so-called fuel oil, i.e. the heavy and low value fraction of the product stream.

Microkinetic Modeling

The combination of detailed feedstock analyses and pilot plant data allows validation of the SEMK model discussed above. This kinetic model was originally developed to model steam cracking of fossil-based feedstocks such as ethane, naphtha and gas oils. Table 2 compares the measured and simulated yields of some important products.

Table 2: Comparison of experimental and simulated product yields [δ = 0.45 kg/kg; τ = 0.3 s, COP = 1.7 bar, COT = 820 °C]

Feed	Naphtha		HDO-TGB		HDO-TOFA	
	Exp.	Sim.	Exp.	Sim.	Exp.	Sim.
Methane	12.7	12.4	9.81	9.48	10.4	9.42
Ethylene	25.9	25.7	36.0	35.5	35.4	33.6
Propylene	17.8	17.9	19.5	20.4	17.5	19.5
1-Butene	2.37	2.81	4.18	4.34	2.20	3.73
1.3-Butadiene	4.72	5.03	7.45	6.51	4.51	6.25
Benzene	4.48	3.32	4.16	5.35	4.45	6.54
Toluene	2.14	1.56	1.29	1.27	1.42	1.83

For the naphtha, the model performance is quite exceptional. Not surprisingly, since the SEMK model was optimized based on an extensive set of pilot plant data, mainly comprising experiments with gaseous and naphtha feedstocks. Nevertheless, the model performance is more than adequate for both HDO-TGB and HDO-TOFA. This, however, after inclusion of retro-ene decompositions for long-chain olefins. Via these concerted path reactions linear α-olefins, i.e. the primary decomposition product of paraffins, are transformed into propylene and a smaller linear olefin. Including these decomposition pathways in the microkinetic model proved to be necessary to more accurately model the measured product distribution of these highly paraffinic feeds.

As discussed above, the HDO-TOFA also contains a small amount of FAME. Since the SEMK model currently does not consider any esters, these components were represented by n-paraffins. This can explain the somewhat larger discrepancies between measured and simulated yields for this feedstock. However, including the decomposition of esters to the SEMK model should result in more accurate predictions.

Conclusions

Catalytic hydrodeoxygenation of tall oils as well as waste greases such as poultry fat and yellow grease produces paraffinic hydrocarbon liquids. These liquids are attractive renewable feedstocks that can be used in conventional steam cracking units.

Pilot plant steam cracking of such hydrodeoxygentaed bio-oils reavealed that, compared to a typical petroleum-derived naphtha, high amounts of light olefins, e.g. up to 40 wt% of ethylene, can be produced.

Acknowledgement

References

1. Ren T, Patel MK, Blok K. Steam cracking and methane to olefins: Energy use, CO2 emissions and production costs. *Energy*. 2008;33:817-833.
2. Carlson TR, Cheng Y-T, Jae J, Huber GW. Production of green aromatics and olefins by catalytic fast pyrolysis of wood sawdust. *Energy & Environmental Science*. 2011;4:145-161.
3. Pyl SP, Schietekat CM, Reyniers M-F, Abhari R, Marin GB, Van Geem KM. Biomass to olefins: Cracking of renewable naphtha. *Chem. Eng. J.* 2011;176-177:178-187.
4. Zimmermann H, Walzl R, *Ethylene*, in *Ullmann's Encyclopedia of Industrial Chemistry*. 2009, John Wiley & Sons, Inc.: New York.
5. Norlin L-H, *Tall Oils*, in *Ullmann's Encyclopedia of Industrial Chemistry*. 2005, John Wiley & Sons, Inc.: New York.
6. Anthonykutty JM, Van Geem KM, Pyl SP, Kaila R, Räsänen J, Penttinen T, Laitinen A, Krause O, Harlin A. *Upgrading of fatty acid containing rosin acids in to high value hydrocarbons via catalytic hydrodeoxygenation*. in *ECCE 8*. 2011. Berlin, Germany.
7. Van Geem KM, Pyl SP, Reyniers M-F, Vercammen J, Beens J, Marin GB. On-line analysis of complex hydrocarbon mixtures using comprehensive two-dimensional gas chromatography. *J. Chromatogr. A*. 2010;1217:6623-6633.
8. Van Geem KM, Reyniers MF, Marin GB. Challenges of modeling steam cracking of heavy feedstocks. *OGST - Rev. IFP*. 2008;63:
9. Pyl SP, Van Geem KM, Reyniers M-F, Marin GB. Molecular reconstruction of complex hydrocarbon mixtures: An application of principal component analysis. *AIChE J.* 2010;56:3174-3188.
10. Abhari R, Tomlinson HL, Havlik PZ, Jannasch NL, *Process for co-producing jet fuel and LPG from renewable sources*. 2008: USA.
11. Abhari R, Havlik PZ, *Hydrodeoxygenation Process*. 2009: USA.
12. Van Damme PS, Froment GF. Putting computers to work - Thermal cracking computer control in pilot plants. *Chemical Engineering Progress*. 1982;78:77-82.

13. Rice FO, Herzfeld KF. The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. VI. The Mechanism of Some Chain Reactions. *J. Am. Chem. Soc.* 1934;56:284-289.

14. Clymans PJ, Froment GF. Computer generation of the reaction paths and rate equations in the thermal cracking of normal and branched paraffins. *Computers & Chemical Engineering*. 1984;8:137-142.

15. Hillewaert LP, Dierickx JL, Froment GF. Computer-Generation of Reaction Schemes and Rate-Equations for Thermal-Cracking. *AIChE J.* 1988;34:17-24.

16. Willems PA, Froment GF. Kinectic modeling of the thermal cracking of hydrocarbons - 1. Calculation of frequency factors. *Ind. Eng. Chem. Res.* 1988;27:1959-1966.

17. Willems PA, Froment GF. Kinectic modeling of the thermal cracking of hydrocarbons - 2. Calculation of activation energies. *Ind. Eng. Chem. Res.* 1988;27:1966-1971.

18. Sabbe MK, Reyniers MF, Van Speybroeck V, Waroquier M, Marin GB. Carbon-centered radical addition and beta-scission reactions: Modeling of activation energies and pre-exponential factors. *ChemPhysChem*. 2008;9:124-140.

19. Sabbe MK, Reyniers MF, Waroquier M, Marin GB. Hydrogen Radical Additions to Unsaturated Hydrocarbons and the Reverse beta-Scission Reactions: Modeling of Activation Energies and Pre-Exponential Factors. *ChemPhysChem*. 2010;11:195-210.

20. Sabbe MK, Vandeputte AG, Reyniers MF, Waroquier M, Marin GB. Modeling the influence of resonance stabilization on the kinetics of hydrogen abstractions. *PCCP*. 2010;12:1278-1298.

21. Froment GF. Kinetics and reactor design in the thermal cracking for olefins production. *Chem. Eng. Sci.* 1992;47:2163-2177.

22. Broadbelt LJ, Stark SM, Klein MT. Computer-generated Pyrolysis Modeling – on-the-fly Generation of Species, Reactions, and Rates. *Ind. Eng. Chem. Res.* 1994;33:790-799.

23. Nizamoff AJ, *Renewable Liquids as Steam Cracker Feedstocks - PERP09/10S12*, in *Chemsystems PERP Program*. 2010.