

## STEAM CRACKING OF BIOMASS-DERIVED C<sub>30</sub>- NORMAL AND BRANCHED ALKANES: AN EXPERIMENTAL AND FUNDAMENTAL KINETIC MODELING STUDY

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Vegetable oils, waste fats/greases and algae are promising green feedstocks for the production of renewable ethene, propene and other valuable chemicals [1]. They have a low oxygen content and can be upgraded through catalytic hydrogenation and isomerization processes. The resulting normal and branched alkanes can be processed in conventional steam crackers (which are designed for pure hydrocarbon feedstocks). In this work, the pyrolysis chemistry of several mixtures containing normal and branched alkanes, produced by Neste through the aforementioned process, was investigated. These mixtures consist of alkanes having less than 30 carbon atoms and contain up to 90wt% of branched alkanes (including methyl-, ethyl-, dialkylated-alkanes).

Pyrolysis experiments of the paraffinic mixtures were performed in a dedicated setup, consisting of a feed section, reactor section and analysis section. The feed section ensures evaporation and a stable feed of hydrocarbons and water (diluent) to the reactor. The reactor is a tubular reactor. Heat is provided by an external electrical furnace. The reactor effluent was analysed on-line using several gas chromatographs, including a two dimensional gas chromatograph with a time-of-flight mass spectrometer and flame-ionization detector. The effect of dilution and reactor temperature on the effluent composition was determined. Pyrolysis of the paraffinic mixtures has high ethene, propene and butene yields. The type and degree of branching of the hydrocarbon feedstocks influences the selectivity's to these alkenes. The yields of products that are formed by bimolecular chemistry, such as aromatics, increase with decreasing dilution, given the higher hydrocarbon partial pressure.

A detailed kinetic model was developed for the pyrolysis of normal and branched alkanes up to 30 carbon atoms using an automatic network generation tool called PRIM-O [1]. Reaction rate coefficients and thermodynamic data were estimated using a comprehensive group-additive framework developed by Marin and coworkers [1]. The developed kinetic model was used to simulate literature-reported pyrolysis experiments of pure branched alkanes [2] and the experiments performed in this work. There is a good agreement between model calculated and experimental product profiles. The model is able to capture the effect of dilution and branching on reactor effluent composition. Reaction path analysis reveals that alkanes are mainly consumed by hydrogen abstraction reactions. Subsequent C-C  $\beta$ -scission reactions results in the formation of the observed small alkenes. The presence and type of branching determines the type of alkene that is formed, e.g. isobutene in the case of C-C  $\beta$ -scission of 2-methyl-2-alkyl radicals. Other products in the reactor effluent, such as aromatics, are formed by secondary reactions. Benzene, the aromatic with the highest yield, is formed by addition of vinyl on 1,3-butadiene, recombination of methyl and 1,3-cyclopentadienyl and self-recombination of allyl followed by hydrogen abstraction. Substituted aromatics, such as toluene, xylenes, ethylbenzene and styrene have comparable formation channels, e.g. toluene is formed by addition of propen-1-yl on 1,3-butadiene, recombination of ethyl and cyclopentadienyl and recombination of allyl and butenyl followed by hydrogen abstraction.

### References:

- [1] R. De Bruycker, J.M. Anthonykutty, J. Linnekoski, A. Harlin, J. Lehtonen, K.M. Van Geem, J. Räsänen, G.B. Marin, *Ind. Eng. Chem. Res.*, 53, pp 18430-18442, 2014.  
 [2] P. Zámotný, Z. Bělohávl, L. Starkbaumová, J. Patera, *J. Anal. Appl. Pyrolysis*, 87, pp 207-216, 2010.

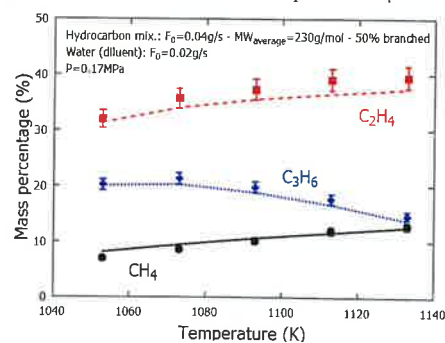


Figure 1 : Experimental (symbols) and model calculated yields (lines) of methane, ethene and propene as a function of reactor temperature