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Correct Molecular Reconstruction of Cracking Feeds: a Need for the Accurate Predictions of Ethylene Yields

Eliseo Ranzi*[a], Sauro Pierucci[a], Mario Dente[a], Marco van Goethem[b], Dirk van Meeuwen [b], Eric Wagner[c]

[a]CMIC Department Politecnico di Milano, Italy.
[b]Technip Stone & Webster Process Technology, Zoetermeer, The Netherlands.
[c]Technip Stone & Webster Process Technology, Inc., Claremont, CA, USA
Eliseo.Ranzi@polimi.it

Liquid feedstocks of ethylene crackers are complex hydrocarbon mixtures containing a huge number of different chemical species. Accurate characterization of petrochemical feeds plays a crucial role in describing the different reaction pathways and reactivity of the various isomer species. Thus, this knowledge becomes a need when it comes to develop comprehensive kinetic models of steam cracking process able to select the optimal design and operation of pyrolysis coils. For this reason, several efforts are recently spent to improve feedstock characterization and analytical separation techniques. The high potential of GC×GC combined with MS detection is a clear example of these efforts. Despite recent advancements of analytical techniques, these methods give only a partial molecular reconstruction of the feedstocks and it is a need to rely also on different bases. The Shannon's entropy criterion correctly describes the boiling curves and molecular weight distributions of different hydrocarbon classes, but this is only a first step and not the very critical one. As a matter of facts, more than the molecular weight distribution and the proper distillation curve, the isomer distribution is proved to have a critical role. Isomers with almost identical physical properties, such as the isomers of branched alkanes and cyclo-alkanes, can exhibit very different cracking behaviors, and hence, a poor estimate of their internal distribution can significantly affect the ethylene yields. Thus, the horizontal lumping becomes more critical than the vertical one, and isomer distribution needs to be characterized in a different way. This paper aims at emphasizing the role of the probability of methylation and alkylation inside the families of homologous hydrocarbons. For the first time, it is highlighted the importance of the internal distribution in the molecular feedstock reconstruction. On these bases and for these purposes, SPYRO® kinetic model is revised and extended to more than 500 species, covering a large detail of feed components, and it is now able to suitably show and quantify the effect of isomer distribution.

1. Introduction

Liquid feedstocks of ethylene crackers are usually complex hydrocarbon mixtures containing a huge number of different chemical species. Detailed hydrocarbon analysis of petrochemical feeds has great importance in describing the different reaction pathways and reactivity of the various isomer species. Thus, this knowledge becomes critical when it comes to develop comprehensive micro-kinetic models of steam cracking process useful for the selection of optimal design and operation of pyrolysis coils and the optimal feed stock selection. For this reason, several efforts are spent to improve feedstock characterization and analytical separation techniques. The high potential of GC×GC, combined with flame ionization detectors (FID) or time of flight mass spectrometers (TOFMS), is a clear example of these efforts [Lissitsyna et al., 2014]. Since its introduction in the 1990s, comprehensive two-dimensional gas chromatography has demonstrated very promising perspectives for the analysis of complex hydrocarbon mixtures. The main reason lies in the higher peak capacity obtained with the combination of two chromatographic columns that develop complementary selectivities so that the entire sample is analysed with two orthogonal separations [Vendeuvre et al., 2005]. Despite recent advancements of analytical techniques (Gieleciak and Fairbridge, 2013), a satisfactory

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molecular description cannot be obtained simply from these methods and the molecular reconstruction of the feedstocks needs to rely also on other bases. Reconstruction methods for the petroleum fractions allow characterizing with a detailed but simplified molecular composition the original complex mixture from analytical data and from expert knowledge of the process under study. Since the very initial research activities on the kinetics of liquid feed pyrolysis, Dente et al. (1979, 1992) proposed naphtha and gasoil feedstock reconstruction methods based on typical commercial indices, such as the specific density, the PIONA (paraffin, isoparaffin, olefins, naphthenes, aromatics weight fractions), the H/C-ratio, and the ASTM boiling curve. This approach allows reducing the number of degrees of freedom from several thousands, corresponding to the molar fractions of the compounds, to a limited number of parameters associated with the analytical constraints. More recently, a special attention was addressed to the reconstruction method based on Shannon's entropy criterion (Van Geem et al. 2007; Hudebine and Verstraete, 2011). This method allows determining the molar fractions of a predefined set of chemical compounds by maximizing an entropic criterion, satisfying the boundary conditions corresponding to the commercial indices of the liquid mixture. Hudebine and Verstraete (2004 and 2010) deeply discussed the available approaches for constructing the molecule libraries ranging from the structural oriented lumping (Quann and Jaffe, 1996) to experimental or stochastic methods (Neurock et al, 1994). The Shannon's entropy criterion properly describes the boiling curves and molecular weight distributions of different hydrocarbon classes, but this is only a first step and not the very critical one.

2. Feed reconstruction and internal distribution parameters

As already discussed in previous papers (Dente and Ranzi, 1983; Dente et al., 2007), it is possible to observe a relative regularity in the internal distribution of the isomers inside the different fractions of virgin feedstocks (Mango, 1997). Thus, for the different isomers of branched-alkanes with eight C atoms, only a few isomers describes the whole fraction: three mono-methyl-heptanes, ethyl-hexane and four dimethyl-hexanes with a tertiary C structure. In spite of the different origins of these feeds, there is clear regularity with regard to their composition. In fact, monomethyl-heptanes prevail on dimethyl-hexanes and monoethyl-hexanes. Trimethyl-pentanes are less abundant and quaternary C atoms are of very limited importance. On this basis, it was possible to derive an internal distribution of the isomer mixture, simply based on the probability of methylation, and or different alkyl substitutions along the carbon chain.

Mango (1997) observed that only oils sharing a common source rock (genetically related oils) show similar distribution of isomers, while different distributions are present in different source rock types. Thus, these internal distributions are a first and rough approximation, and are a peculiarity of the specific virgin fractions. Moreover, they can drastically change after thermal or catalytic refinery processes. Thus, it seems quite difficult to further confirm these assumptions and approach in the literature. In fact, accurate and detailed analyses of different isomers for branched alkanes with more than 10 C-atoms are very scarce. Nevertheless, GC analysis of heavy naphtha, kerosene and light gasoils indicates the prevailing presence of poly-isoprane structures characterized by an average probability of methyl substitution of about 0.20-0.30 (Altgelt and Boduszynski, 1994). In their selection of surrogates for jet fuels, Zhang et al. [2009] carefully investigated the average distribution of substituents in iso-paraffins, cyclo-paraffins and aromatics, based on literature data complemented by NMR analysis. This study indicates a higher methylation probability for the isoparaffins compounds, as well as for the aromatic fractions. The NMR data provided constraints on the number of side chain substitution on aromatic carbons, as well as on the length and branching of the substituents. Their suggested surrogate composition of aromatics with 10 C atoms, all substituents but one being methyl, was about 20% ethyl-toluene, 5% propyl-toluene, 55% ethyl-xylene, and 20% propyl-xylene. This study confirm the importance of highlighting a limited number of intrinsic parameters useful for the proper characterization of the internal distribution of isomers, inside the different hydrocarbon classes. Beside the probability of methylation and different alkylations on the carbon chain, the average number and length of side substitutions on the rings, also the relative presence of cyclo-hexane and and cyclo-pentane structures (as well as the one of tetraline and indane) constitutes a further degree of freedom, mainly dependent on the origin of the feed (Mango, 1997). As also observed by Van Geem et al. [2007], this approach restricts the range of applications of the kinetic model. All these considerations suggest to remove the boundary of fixed isomer distributions, extending in this way the capabilities of the kinetic model. For instance, it is possible to individually investigate the decomposition behaviour of a particular structural isomer, previously lumped into a single equivalent pseudo-component. Due to the current computer facilities, it is now convenient to enlarge the kinetic scheme explicitly including several individual isomers, still maintaining the empirical distribution rules, when analytical and detailed data are not available. Furthermore, this extension in the individual structural isomers could better fit the model to future improvements in characterization of petroleum cuts.

3. Automatic generation of primary lumped reactions (MAMA Program) and extension of the SPYRO kinetic scheme

The extension of SPYRO® kinetic model to a large number of feed components took a great advantage by the use of MAMA program (Pierucci et al., 2005; Dente et al., 2007). This mechanism generator evaluates the set and weights of the end-products obtained by the isomerization and decomposition of heavy alkyl radicals. Starting with an initial radical, the propagation path includes isomerization, decomposition, and dehydrogenation reactions with the formation of final products. Due to the large number of components that can be involved in a propagation path, the lumping of components (or classes of components) becomes a critical item. Despite the possible computing time requirements, the resulting generated pathway of a specific radical is independent on the formation mechanism of the radical itself and therefore all the reaction paths are stored and recorded in a database.

On these bases and with purposes to analyse the effect of the internal isomer distributions, SPYRO® kinetic model has been extended to more than 500 species, covering a large detail of feed components, and it is able to properly show and quantify the effect of isomer distribution.

4. Kinetic mechanism and lumping procedures

The usual practice in the kinetic modeling of steam cracking reactions is to lump all the isomers of large hydrocarbon species into a single lumped or equivalent component. It is strictly required that lumped species react in a similar way, therefore their internal distribution remains almost unchanged with the reactions [Wei and Kuo, 1969]. De-alkylation and dehydrogenation reactions of branched alkyl radicals generate all the different branched alkenes. In order to avoid an unnecessary number of species, a large number of alkene isomers formed during the pyrolysis of heavy alkanes are conveniently grouped and considered as a single lumped compound. The clear advantage of the automatic generation is that the internal splitting of the real components is stored and properly accounted for evaluating the impact on the final product distribution. Let's define as 'horizontal lumping' this grouping of species with the same molecular weight. On the contrary, we can define as 'vertical lumping' the lumping of homologous species with different molecular weights.

Figure 1 shows the yields of major products from pyrolysis of n-paraffins from n-hexane up to n-eicosane. As expected, rising with carbon number there is a regularity and continuity in the formation of several major and minor products. Therefore, the pyrolysis behavior of intermediate species can be reasonably obtained through an appropriate average of reference species. In other words, instead to include inside the kinetic model all the heavy homologous species, it is convenient to select only a few reference components, for instance, only the ones with 20, 25, 30 and 35 C atoms. The reactivity and the product distribution of intermediate species can conveniently be estimated with a linear combination of the reactivity and product distribution of the homologous adjacent species. Thus, the pyrolysis products of n-$C_{28}H_{58}$ can be properly predicted as the weighted sum of the products of the reference components with 25 an 30 C atoms. With the linear lever rule, the weight of the pyrolysis products of n-$C_{25}H_{52}$ is 40%, while the remaining 60% is the weight of the pyrolysis products of n-$C_{30}H_{62}$. This 'vertical lumping' of heavy homologous species is clearly justified, due to the observed and natural continuity of the pyrolysis mechanism, both in terms of reactivity and in terms of product distribution.

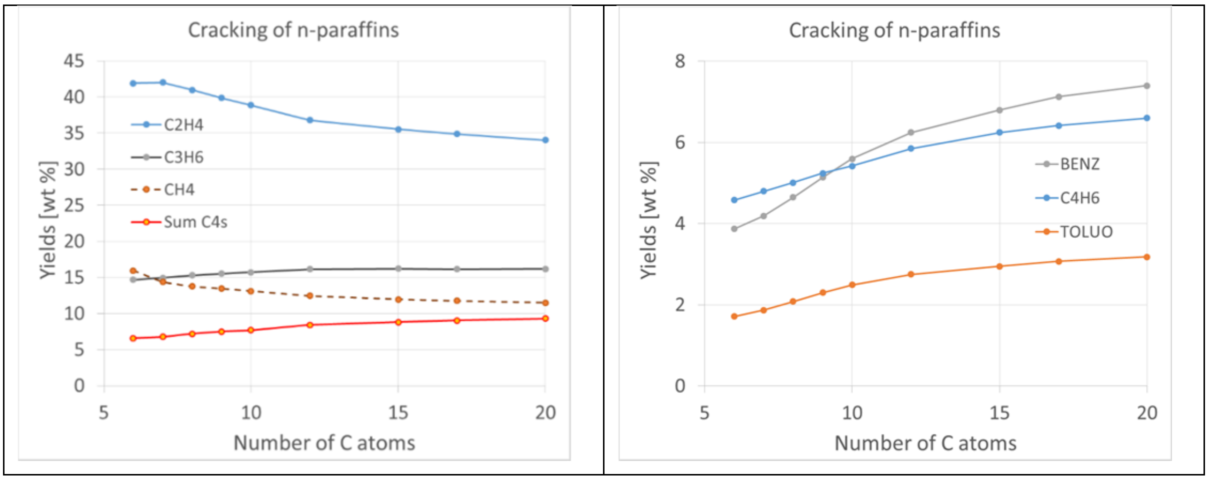

Figure 1. Yields of major products from pyrolysis of n-paraffins from n-hexane up to n-eicosane at usual cracking conditions.

The pyrolysis products of six isomers of the branched paraffins C10 are analysed and compared in Table 1, and clearly shows some limits of the ‘horizontal lumping’. Namely, the following isomers have been selected:

- 2-methyl-nonane (2Me-C9)
- 2,3 di methyl-octane (23diMe-C8)
- 2,7 di-methyl octane (27diMe-C8)
- 2,3,4 tri-methyl-heptane (234triMe-C7)
- 3,4,5 tri-methyl-heptane (345triMe-C7)
- 2 methyl- 3ethyl-heptane (2Me-3Et-C7)

For this analysis, it was first necessary to extend the kinetic scheme and to evaluate with MAMA program the primary decomposition and propagation reactions of the different species. Thus, the kinetic generator directly provides the following reactions for 2-methyl-nonane:

```
C9ME2=  0.02288618 H     + 0.27796584 M     + 0.38144332 E     + 0.35921252 IP    +
    *  0.52725339 NP    + 0.17821006 IBP   + 0.25302884 NBP   + 0.51581907 C2H4  +
    *  0.31019577 C3H6  + 0.10272671 B1    + 0.12886302 IB    + 0.00028093 B1M2  +
    *  0.04206936 B1M3  + 0.10130551 P1    + 0.00085509 P2    + 0.05422898 ES1   +
    *  0.01233325 ES2   + 0.00033794 ES3   + 0.00191558 P1M2  + 0.01246737 P1M4  +
    *  0.00075985 P2M2  + 0.00009604 P2M4  + 0.02771141 AOLC7 + 0.02807620 EPT1  +
    *  0.00252412 AOLC8 + 0.00397231 OCT1  + 0.00232627 AOLC9 + 0.00082235 NON1
R+C9ME2=RH+  0.02747141 H    + 0.14712963 M    + 0.16893637 E   + 0.17807241 IP    +
   *  0.26221180 NP    + 0.08955719 IBP   + 0.12662123 NBP   + 0.28014964 C2H4  +
   *  0.28130448 C3H6  + 0.11890339 B1    + 0.22353639 IB    + 0.00012429 B1M2  +
   *  0.08934201 B1M3  + 0.08446787 P1    + 0.00040237 P2    + 0.07133398 ES1   +
   *  0.00691114 ES2   + 0.00029721 ES3   + 0.00099192 P1M2  + 0.05679748 P1M4  +
   *  0.00039346 P2M2  + 0.00004973 P2M4  + 0.07045432 AOLC7 + 0.11280774 EPT1  +
   *  0.05367221 AOLC8 + 0.08369244 AOLC9 + 0.02496300 NON1  + 0.01730166 OLC10
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Similar reactions are derived for the remaining species and, including all these reactions in the overall kinetic scheme, it is possible to evaluate the product distributions reported in Table 1. As expected, the ethylene selectivity is drastically different for the different isomers, being about 30 % when considering mono-methyl nonanes, and only 20 % for the tri-methyl-heptane.

Table 1. Product yields from the pyrolysis of different branched C10 alkanes at usual cracking conditions in conventional pyrolysis coils.

Yields (wt%)	**2Me-C9**	**23diMe-C8**	**27diMe-C8**	**234triMe-C7**	**345triMe-C7**	**2Me-3Et-C7**
H_2	0.81	0.81	0.84	0.83	0.79	0.86
CH_4	15.82	17.94	17.45	18.97	20.63	18.07
CO	0.35	0.35	0.35	0.35	0.35	0.35
CO_2	0.09	0.09	0.1	0.09	0.1	0.09
	17.08	19.19	18.73	20.24	21.86	19.37
C_2H_2	0.41	0.42	0.4	0.42	0.43	0.42
C_2H_4	29.93	26.39	22.16	22.48	20.11	26.23
C_2H_6	4.23	4.09	2.99	3.67	3.67	4.7
	34.57	30.89	25.54	26.57	24.21	31.35
aC_3H_4	0.38	0.38	0.52	0.41	0.44	0.34
pC_3H_4	0.27	0.27	0.36	0.29	0.31	0.24
C_3H_6	16.22	15.1	17.6	15.93	14.45	13.63
C_3H_8	0.59	0.56	0.6	0.55	0.34	0.59
	17.47	16.32	19.07	17.18	15.53	14.8
C_4H_6	4.85	5.47	4.2	5.92	6.48	5.52
C_4H_8	5	3.74	8.56	4.32	4.04	3.37
C_4H_{10}	0.1	0.09	0.11	0.08	0.07	0.09

Table 1. Product yields from the pyrolysis of different branched C10 alkanes at usual cracking conditions in conventional pyrolysis coils. (Cont.d)

Yields (wt%)	**2Me-C9**	**23diMe-C8**	**27diMe-C8**	**234triMe-C7**	**345triMe-C7**	**2Me-3Et-C7**
C_4&lighters	79.2	75.88	76.39	74.5	72.44	74.66
C5s	3.87	4.29	4.12	4.38	4.68	4.26
Benzene	6.74	7.39	7.42	7.76	7.83	7.79
Other C6	0.78	0.79	1.13	0.81	0.9	0.74
Toluene	3.28	3.75	3.87	3.95	4.2	3.9
Other C7	0.23	0.2	0.31	0.21	0.19	0.19
O-Xylene	0.24	0.31	0.32	0.34	0.42	0.29
M-Xylene	0.38	0.49	0.53	0.55	0.68	0.47
P-Xylene	0.18	0.23	0.24	0.25	0.32	0.22
Ebenzene	0.11	0.12	0.1	0.12	0.12	0.14
Styrene	0.69	0.87	0.71	0.88	1.04	0.94
Other C8	0.02	0.03	0.03	0.03	0.03	0.02
C9s	1.37	1.73	1.42	1.92	2.15	1.92
C10s	1.86	2.49	2.14	2.67	3.07	2.83
C11s	0.39	0.5	0.49	0.56	0.65	0.55
C12+	0.65	0.93	0.77	1.06	1.28	1.08
	100	100	100	100	100	100

The ‘horizontal lumping’ of branched isomers $C_{10}H_{22}$ into a single equivalent component is indeed convenient, but certainly reduce the possibility of the kinetic model. It is evident that, is these conditions, the horizontal lumping can become more critical than the vertical one, and isomer distribution needs to be characterized in a different way.

While Table 1 shows that the cracking behavior of the different C10 isomers are significantly different, it is of interest to analyse the effect of different internal distribution of the whole fraction of the branched alkanes $C_{10}H_{22}$. By individually considering the different isomers inside the overall kinetic scheme, it is possible to analyse the effect of different internal distributions, as a function of a limited number of feedstock parameters, such as the methylation and alkylation probability, the average number and length of side substitutions, and so on. Panel a) of Figure 2 shows the internal distribution of branched alkanes C10 in terms of the relative amounts of methyl-nonanes, di-methyl-octanes, ethyl-octanes, and tri-methyl-heptanes as a function of the methylation degree. There is a clear increase of poly-methylated compounds, with a decrease of the mono substituted species. Note that these distributions refer to a fixed probability of ethyl substitution of 10%. Panel b) of the same figure shows the predicted cracking yields, as obtained in the same conventional pyrolysis coil in standard operation conditions. As expected, the increase of the methylation degrees corresponds to a net decrease of ethylene yields with a parallel increase of methane, propylene, and C5+ components. These significant differences in ethylene yields justify the efforts of a better investigation of the effect of the internal distribution of different isomers, not only inside the branched paraffins, but also with respect to the cyclo-paraffins, where the internal ratio between 5- and 6-membered rings constitutes a further parameter for the correct internal isomer distribution.

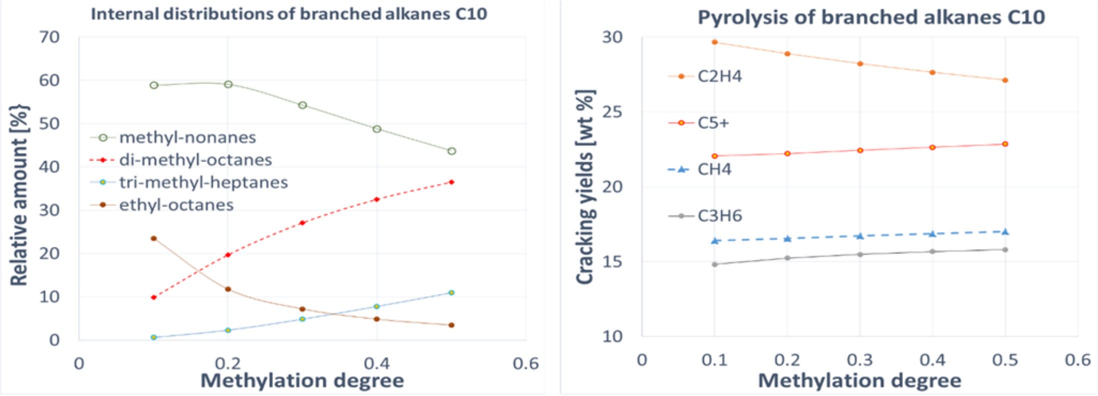

Figure 2: Panel a) Internal distribution of branched alkanes C10 vs the methylation degree. Panel b) Effect of the internal distributions of branched alkanes C10 on the cracking yields

5. Conclusions

The SPYRO® kinetic model has been extended to more than 500 species, covering a large detail of feed components, and it is now able to properly show and quantify the effect of isomer distribution. In this way, the importance of the internal isomer distribution in the molecular feedstock reconstruction is highlighted. Further advancements in combined GCxGC analysis are expected to reveal in the near future more detailed chemical structures, which could assist in a more comprehensive identification of a few freedom degrees useful for the molecular reconstruction of liquid feeds. They are not simply adaptive or empirical factors, but intrinsic characterization parameters, a molecular fingerprint of the different petroleum fractions.

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