

Modelling of Naphtha Cracking for Olefins Production

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Abstract

The production of ethylene and propylene from naphtha via thermal cracking is a cornerstone of the chemical industry. This process is carried out in furnaces operating at high temperature, and optimal operation of these furnaces is necessary to maintain profitability.

In the present work, a mathematical model of a naphtha cracking furnace was developed in gPROMS®, in which the main focus was the development of a SRT-VI coil model. This furnace model was used to validate kinetics present in literature against typical data for naphtha cracking. A tuning of the implemented kinetics was carried out, by adding new components, new sets of reactions and tuning the kinetic parameters in the reaction scheme, leading to good predictions, having yield deviations of less than 5% for the main products (light olefins - ethylene and propylene) and around 15% for aromatics.

Keywords: modelling, steam cracking, naphtha, ethane, propane, kinetics, furnace.

1. Introduction

Hydrocarbon steam cracking is one of the most important processes in the petrochemical industry, producing highly valuable olefins such as ethylene, propylene from lower value feedstocks, which usually have fossil fuel origin, ranging from gaseous feedstocks, like ethane and propane to liquid, heavier feedstocks, such as naphtha, gas oil and gas condensates. Naphtha is the most widely used, due to availability, low cost and potential for producing high yields of olefins [1].

Ethylene is the major product of a steam cracking unit. With a world production of around 1.48 million tonnes/year in 2014 [2], and an annual growth at an average rate of 4%, it is the largest volume building block, and it is mainly used for the

production of polyethylene, ethylene oxide, vinyl acetate, and ethylbenzene and ethylene dichloride [3].

Propylene is considered a co-product of this process, reporting 109 million tonnes in 2014. It is used for the production of polypropylene, propylene oxide, cumene and isopropanol [4].

For the optimisation of an olefins plant, the developing of predictive furnace models, capable of describing cracking and coking phenomena, becomes essential, and will be the main focus of the current work.

2. Background

The method for the production of olefins from naphtha is through thermal hydrocarbon cracking reactions, which occur in the presence of steam in the radiant coil of the furnace, at high temperatures ranging from 700°C at the inlet of the coil to 900°C at the outlet.

The cracking reactions occur via free-radical mechanisms, and for the cracking of naphtha, resulting in yields of ethylene between 25 – 35% and propylene between 14 – 18% [1].

2.1 Steam Cracking process

A simplified flowsheet of the steam cracking process that be found in Figure 3. The cracking furnace serves as the reactor and “heart” of the process, thus being the most important unit of the plant. It is comprised of two main sections: the furnace section and the radiant section, as seen in Figure 1.

The hydrocarbon feed enters the furnace in the convection section, where it is pre-heated by heat exchange against flue gases. It is then mixed with dilution steam, up to ratios of Steam:Oil ($kg_{steam}/kg_{hydrocarbon}$) of 0.25 – 0.40 for gaseous feed and 0.40 – 0.55 in the case of naphtha. This reduces hydrocarbon partial pressure, leading to reduced rates of coke formation (thus avoiding decreased heat transfer coefficients and increased pressure drops), being able to increase the run-time of the furnace. The resulting mixture is further heated to temperatures of 500 – 680 °C, which favour the cracking reactions. [1] [3]

This mixture of feed and steam, in the gaseous state, enters the radiant section of the furnace, where radiant coils act as tubular reactors, submitting the hydrocarbons to cracking reactions for periods of 0.1 – 0.5 s. This section of the furnace operates at temperatures between

600 – 860 °C, which are maintained through heat transfer with a firebox, where fuel burners reach temperatures between 1000 – 1200 °C. The heat transfer mechanism is mainly radiation. Due to the endothermicity of the cracking reactions, high heat fluxes are required ($75 – 85 kW/m^2$ of coil) [1]. For the cracking of naphtha, and depending on the operating conditions (which heavily influence the severity of cracking), the product stream is made up of (in wt. %) 25 – 35 % of ethylene, 14 – 18 % of propylene, 4 – 6 % of butadiene as well as ~14 % of methane and 5 – 10 % of aromatics, namely BTX.

Typical cracking coil dimensions are usually 40 – 90 m in length, diameters from 3 – 20 cm. [1]

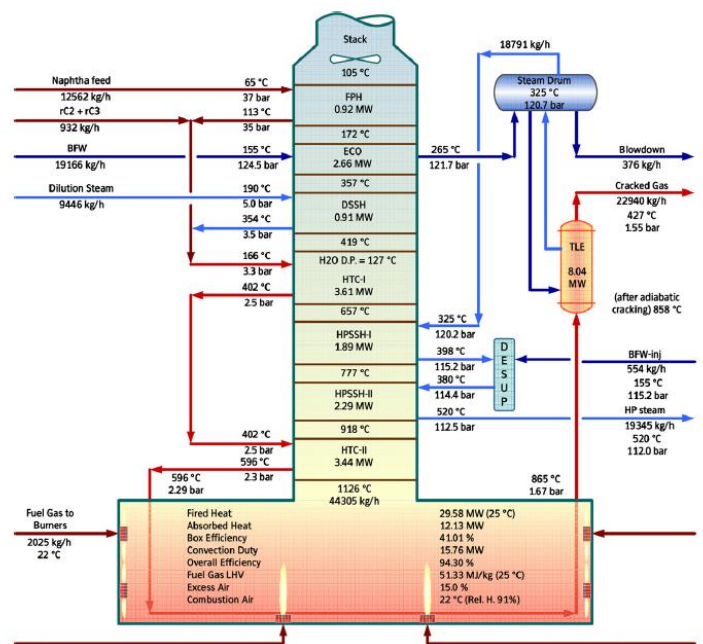


Figure 1- Diagram a steam cracking furnace in a typical olefin plant.



Figure 2- Industrial cracking coil.

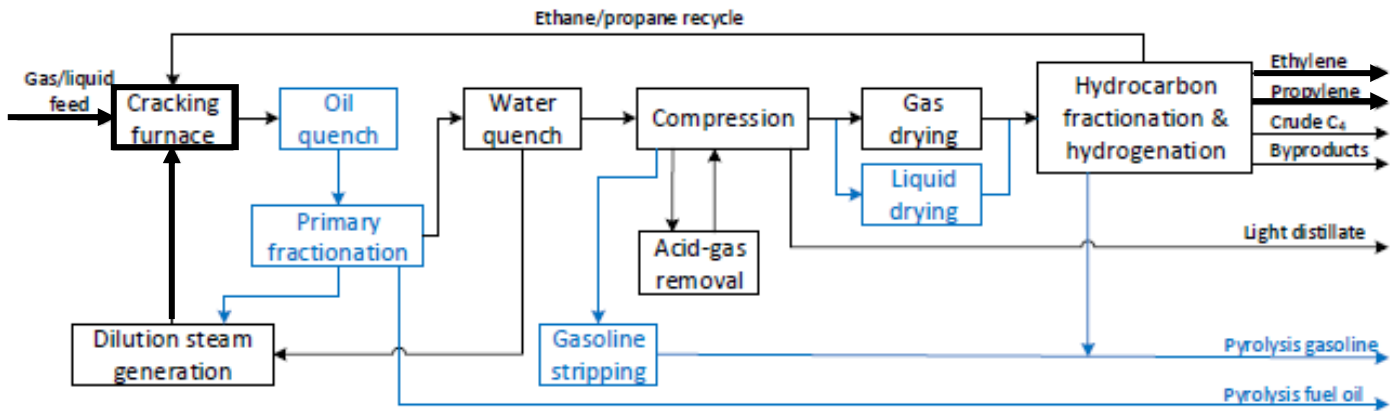


Figure 3- Simplified flowsheet of the steam cracking process.

After exiting the furnace, the resulting stream, in the gaseous phase, and with a high content on light olefins is subjected to a series of treatments to remove condensates, water and other undesired components before the fractionation step.

The cracked gas then leaves the radiant coil at 800 – 860 °C (COT), and is cooled during a period of 0.02 – 0.1 s to 550 – 650 °C to prevent further cracking of valuable reaction products as well the formation of coke. This cooling process occurs in the transfer-line exchangers (TLE), by indirect quenching.

An oil quench follows, which is used to reduce the temperature down to around 230 °C.

Next, a primary fractionator (gasoline fractionator) is used in order to separate the pyrolysis fuel oil (heavier hydrocarbons) from the main stream.

To be further processed, the hydrocarbon product stream is then cooled to near ambient temperature by means of water quench tower, in which it contacts with a large descending water stream.

To compress the cracked gas, a series of 4 to 6 compression stages with inter-stage coolers is used, allowing the cracked gas to reach pressures up to 35 bars, while maintaining temperatures below 100 °C. The condensates, as well as water and other heavier components are removed during this cooling process, alongside with H_2S and CO_2 , which are removed by contacting with an alkaline solution (acid gas removal). [1] [3]

The resulting gas needs to be dried in order to remove water (up to < 1 ppm), in order to proceed for the fractionation equipment.

Finally, the cracked and now purified gas is chilled and separated into its product streams (ethylene, propylene, crude C_4 and pyrolysis gasoline and gas oil), by means of a series of distillation columns.

In order to further increase light olefins yield, hydrogenation reactions occur, in which acetylene, methylacetylene and propadiene are converted to ethylene and propylene in catalytic hydrogenation beds. [1] [3]

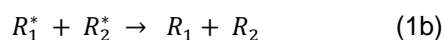
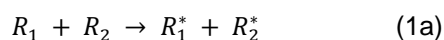
2.2 Steam cracking reactions

It is widely accepted that the largest part of gas phase hydrocarbon pyrolysis occurs through a free radical mechanism, characterized by a vast number of species and reactions.

The kinetic mechanism is summarised by the following reaction classes [5] [6].

1) **Initiation and termination reactions**

These reactions involve either the C-C bond scission, forming two smaller radicals (Eq. 1a), or a new bond (C-C or C-H) as two radicals come together and produce a single molecule (1b).

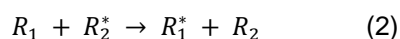


2) **Propagation reactions**

After the initiation step, radical species undergo a series of propagation reactions in which keeping the reaction chain going. These reactions can be of different types:

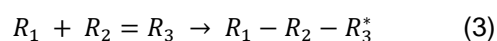
A. Hydrogen abstraction

Smaller reactive radicals abstract a hydrogen atom from another molecule, creating both a new molecule and new radicals.



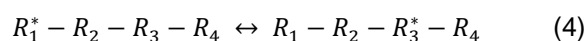
B. Radical addition

Radicals react with olefins, thus forming less saturated compounds and a new radical.



C. Radical isomerisation

Responsible for the transfer of the active radical position within the molecule.



In order to be able to have predictive models, capable of describing the cracking reactions and prediction product distribution, the need arises to develop kinetic models, which describe the cracking phenomena through a series of reactions. In the current work, mechanistic models will be used, based on schemes of free radicals. Two kinetic schemes (available in literature) for the cracking of naphtha will be used: the scheme described by Joo [7], comprising a total of 231 reactions between 79 chemical species up to C_9 ; and the scheme described by Towfighi [8], containing 150 reactions and involving 54 components up to C_8 .

3. **Implementation**

The current work was developed in gPROMS ProcessBuilder®, which was used for model development, flowsheeting and simulation.

An external physical property package was used (Multiflash) as well as a stoichiometric matrix compression scheme (LSKM).

3.1 Model Equations

This section describes the model equations in mathematical furnace model used in this work. The furnace is composed of several sub-models, which together describe all phenomena occurring in the furnace.

For the tube model, which is treated as a PFR, the mass balance is as follows (Eq. 5):

$$\frac{d}{dz} [N_i A] = MW_i A r_i \quad (5)$$

Where N_i represents the mass flux for component i , A is the cross-section area of the tube, MW_i is the molecular weight of component i and r_i is the overall reaction rate (rate of formation/disappearance) of component i .

The reaction rate of a given reaction j , r_j can be related with are the forward and backwards reaction constants for a given reaction j , $k_{f,j}$ and $k_{b,j}$, respectively, and the component molar concentration of the reactants and products by (Eq. 6):

$$r_j = k_{f,j} \prod C_{react} - k_{b,j} \prod C_{prod} \quad (6)$$

The energy balance is as shown in (Eq.6):

$$\frac{d}{dz} [qA] = q_{ext} 2\pi R_{ext} \quad (7)$$

Where $q(z)$ represents the heat flux and R_{ext} represents the outside radius of the tube, through which the heat flux q_{ext} is exchanged, at a rate given by Stefan-Boltzmann law (Eq. 8):

$$q_{ext} = \varepsilon \cdot \sigma (T_{flame}^4 - TMT^4) \quad (8)$$

Which relates the external heat flux with the effective temperature produced by the flames in the furnace burners (T_{flame}) and the tube metal temperature TMT.

4. Steam cracking furnace

A mathematical model of a naphtha cracking furnace with a SRT-VI coil is developed, which will be used to simulate typical operation and to compare the model predictions to data.

Typical geometry and operating conditions of the coil were taken from available literature [9].

Figure 4 shows the coil design.

Table 1 shows the geometry details for the modelled coil (ID and OD represent inner and outer diameter of the coil).

Table 2 shows the main operating conditions for the modelled furnace.

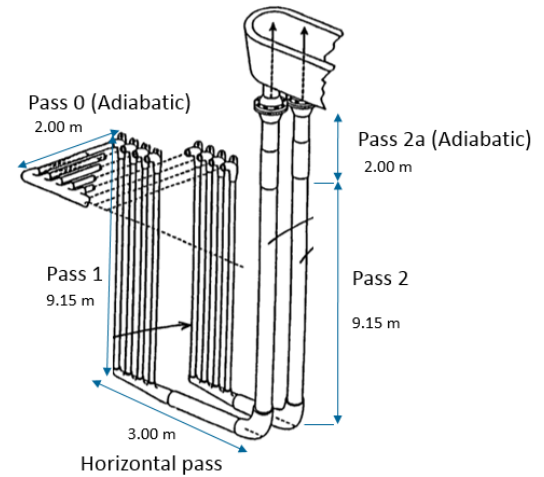


Figure 4 - Schematic of the modelled SRT-VI coil.

Table 1 - Coil geometry details.

Pass	Nº. tubes	ID (cm)	OD (cm)
0	4	5.08	6.34
1	4	5.08	6.35
horizontal	1	10.16	11.43
2	1	10.16	11.43
2a	1	10.16	11.43

Table 2 - Furnace operating conditions.

Furnace operating conditions	Unit	
Number of coils		24
Naphtha feed rate	tonne/h	36.0
Steam:Oil ratio		0.50
Residence time	s	0.22
CIT	°C	620
COT	°C	835
COP	bar abs	1.70
Firing type		Bottoms + Wall

5. Furnace Simulation

The modelled coil is used to validate kinetic mechanisms found in literature [7] [8] and compare the model predictions with typical industrial yields.

Table 3 shows predictions of the furnace model (for both the Towfighi and Joo kinetics) for the yields of the main components and their comparison with typical yields for naphtha cracking units.

Table 3 - Simulation results and comparison with typical yields for naphtha cracking.

Component yields (%)	Typical data	Towfighi	Joo
Hydrogen	0.87	0.25	0.27
Methane	14.36	9.64	9.12
Ethylene	27.62	21.60	25.91
Ethane	3.53	0.10	3.72
Propylene	17.51	6.75	19.70
n-butane	1.35	0	0.35
1-butene	5.77	0.03	11.95
1,3-butadiene	5.70	6.07	4.64
n-pentane	1.10	6.32	1.17
i-pentane	0.97	1.66	2.15
n-hexane	0.48	3.93	1.08
i-hexane	0.43	0.89	3.77
Benzene	5.61	0.98	0.60
Toluene	3.67	1.52	1.87
Xylene	2.80	2.31	2.26
n-nonane	1.87	2.10	5.98

The results show that neither of the kinetics can accurately predict typical yields, but it is noticeable that the kinetics from Joo seem to be a better match, predicting much closer yields than the kinetics from Towfighi.

From the main products, the predictions for benzene and toluene have a significant gap, when compared to typical yields.

5.1 Kinetic tuning

To further improve the yield predictions, the kinetic scheme from Joo (chosen over Towfighi for presenting better predictions for product distribution) is extended by adding additional reactions. The kinetic parameters of few reactions

are tuned, by manually adjusting the pre-exponential factor of certain reactions (multiplying by a tuning factor). The reactions for kinetic parameter adjustment are chosen based on the

mismatch in the yields between the initial model prediction and data. The added reactions are from the kinetic schemes of Towfighi and Belohlav [10].

Table 4 shows the added reactions for acetylene, Table 5 for benzene and Table 6 for toluene.

The reactions whose kinetic parameters were adjusted are from the Joo scheme are from the Joo scheme. Table 7 shows the tuned reactions.

Table 4 - Added reactions for acetylene.

Source	Added Reaction
Towfighi (reaction 103)	$C_2H_2 + H \rightarrow C_2H_3$
Towfighi (reaction 142)	$C_2H_2 + H_2 \rightarrow C_2H_4$
Towfighi (reaction 144)	$C_2H_2 + C_4H_6 \rightarrow C_6H_6 + H_2$
Belohlav (reaction 56)	$C_2H_2 + C_2H_4 \rightarrow C_4H_6$
Towfighi (reaction 74)	$C_2H_3 \rightarrow C_2H_2 + H$
Towfighi (reaction 76)	$C_3H_5 \rightarrow C_2H_2 + CH_3$
Belohlav (reaction 19)	$C_2H_4 \rightarrow C_2H_2 + H_2$

Table 5 - Added reactions for benzene.

Source	Added Reaction
Towfighi (reaction 143)	$C_4H_6 + C_2H_2 \rightarrow C_6H_6 + H_2$
Belohlav (reaction 9)	$C_4H_6 + C_2H_4 \rightarrow C_6H_6 + 2H_2$
Belohlav (reaction 35)	$CH_3 - C_6H_5 + H_2 \rightarrow C_6H_6 + CH_4$

Table 6 - Added reactions for toluene.

Source	Added Reaction
Belohlav (reaction 10)	$C_4H_6 + C_3H_6 \rightarrow CH_3 - C_6H_5 + 2H_2$
Belohlav (reaction 36)	$CH_3CH_3 - C_6H_5 + H_2 \rightarrow CH_3 - C_6H_5 + CH_4$

Table 7 - Tuned reactions from the Joo scheme.

Reaction	Tuned reaction	Tuning factor
34	$1_C_3H_7 \rightarrow C_2H_4 + CH_3$	1.25
67	$1_C_5H_{11} \rightarrow C_2H_4 + 1_C_3H_7$	1.25
79	$i_C_6H_{13} \rightarrow C_2H_4 + 1_C_4H_9$	1.25
95	$1_C_7H_{15} \rightarrow C_2H_4 + 1_C_5H_{11}$	1.50
114	$1_C_8H_{17} \rightarrow C_2H_4 + 1_C_6H_{13}$	2.00
160	$5_MP2 \rightarrow C_2H_4 + i_C_4H_9$	1.50
191	$6_MH2 \rightarrow C_2H_4 + i_C_5H_{11}$	1.50
228	$7_MHP2 \rightarrow C_2H_4 + 5_MP2$	2.00

Table 8 shows predictions of the furnace model (using the improved Joo kinetics) for the yields of the main components and their comparison with typical yields.

A more detailed table (Table 9) will present the yields and their deviations for all the components that were initially considered, as well as the conversion for the most relevant species in the naphtha feedstock.

Table 8 - Simulation results with improving kinetics and comparison with typical yields for naphtha cracking.

Component yields (%)	Typical data	Joo	Yield dev.
Hydrogen	0.87	0.53	-38%
Methane	14.36	11.57	-19%
Ethylene	27.96	27.99	0%
Ethane	3.53	4.74	34%
Propylene	17.51	17.75	4%
n-butane	1.35	0.49	-64%
1-butene	1.83	2.94	50%
1,3-butadiene	5.05	4.85	-5%
n-pentane	1.10	2.82	157%
i-pentane	0.97	1.52	58%
n-hexane	0.48	0.92	90%
i-hexane	0.43	1.41	218%
Benzene	5.61	4.74	-18%
Toluene	3.67	3.50	-4%
Xylene	2.80	2.05	-27%
n-nonane	1.87	1.98	6%

The kinetic tuning has helped to reduce the gap between model prediction and typical data, being capable of predicting ethylene very accurately, as well as the other main olefins, propylene and butadiene with deviations lower than 5%, and also for some other key components, such as the aromatics, greatly improving the initial predictions, now being able to match typical yields within reasonable levels of deviation.

6. Conclusions

In this work a naphtha cracking furnace model with a SRT-VI coil was developed in gPROMS ProcessBuilder.

The modelled furnace was used to validate implemented radical kinetics from Joo and Towfighi against typical yields for naphtha cracking. Initially, the kinetic scheme from Joo

gave better predictions for the yields, but the simulations showed a considerable disagreement with the data, especially for heavier components and aromatics. It was found out that neither of the kinetic schemes took into consideration the cracking of some meaningful heavier components of the naphtha feed (such as n-nonane). To solve this problem, several procedures were taken: lumping of components, addition of new reactions and tuning of the kinetic parameters of certain sets of reactions.

The extended kinetic scheme with adjusted kinetic parameters gave better yield predictions, being able to accurately predict the main yields of olefins within a deviation of 5%

7. Future Work

The furnace model developed in the current work can be further tested using other kinetic mechanisms and validated against more available data from industry. Using formal parameter estimation techniques in gPROMS can in order to can optimise the kinetic parameters to better predict typical yields for naphtha cracking.

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References

- [1] H. Zimmermann and R. Walzl, "Ethylene", in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2012.
- [2] ICIS Chemical Business, vol. 287, nos. 4,9,10,11,15, 2016.
- [3] "Petrochemical industry ethylene plant", <http://www.usa.siemens.com/processanalytics>, [Online; Accessed: 2016-05-12].
- [4] P. Eisele and R. Killpack, "Propene," in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
- [5] M. Dente, E. Ranzi, and A. Goossens, "Detailed prediction of olefin yields from hydrocarbon pyrolysis through a fundamental simulation model (SPYRO)," *Computers & Chemical Engineering*, vol. 3, 1979.
- [6] M. Dente, E. Ranzi, S. Barendregt, and P. Cronin, "Steam cracking of heavy liquid feedstocks: cracking yields rigorously predicted," in *AIChE Spring National Meeting*, USA, 1986.
- [7] E. Joo, *Modelling of Industrial Naphtha Thermal Cracking Furnaces*, PhD thesis, Korea Advanced Institute of Science and Technology, 2000.
- [8] J. Towfighi and R. Karimzadeh, "Development of a mechanistic model for pyrolysis of naphtha," in *Sixth Conference of the Asia-Pacific Confederation of Chemical Engineering*, vol. 3, (Melbourne, Australia), Sept. 1993.
- [9] Patent US8163170B2 "Coil for pyrolysis heater and method of cracking", 2012
- [9] Z. Belohlav, P. Zamostny, and T. Herink, "The kinetic model of thermal cracking for olefins production", *Chemical Engineering and Processing: Process Intensification*, vol. 42, no. 6, pp. 461 – 473, 2003.
- [10] J. Moreira, "Steam Cracking: Kinetics and Feed Characterisation," Master's thesis, Instituto Superior Técnico, November 2015.

Table 9 - Simulation results using the tuned Joo kinetics.

Components	Feed Composition (wt. %)	Plant data yield (%)	Simulation yield (%)	yield dev.	yield dev. (%)	Plant data conversion (%)	Simulation conversion (%)
Hydrogen	0	0.87	0.53	-0.3	-38%	-	-
Methane	0	14.36	11.57	-2.8	-19%	-	-
Ethylene	0	27.96	27.99	0.0	0%	-	-
Ethane	0	3.53	4.74	1.2	34%	-	-
Propylene	0	17.51	17.75	1.0	4%	-	-
Propane	0	0.48	0	-0.5	-100%	-	-
n-butane	6.64	1.35	0.49	-0.9	-64%	79.6	81.7
1-butene	0	1.83	2.94	1.0	50%	-	-
1,3-butadiene	0	5.05	4.85	-0.2	-5%	-	-
i-butene	0	2.91	1.27	-1.7	-58%	-	-
n-pentane	11.48	1.10	2.82	1.7	157%	90.4	75.5
i-pentane	9.78	0.97	1.52	0.6	58%	90.1	83.7
n-hexane	9.13	0.48	0.92	0.4	90%	94.7	90.4
i-hexane	10.83	0.43	1.41	1.0	218%	96.1	88.7
methyl-cyclohexane	13.32	0.27	0.06	-0.2	-93%	-	-
Benzene	0.61	5.61	4.74	-0.9	-18%	-	-
Toluene	1.91	3.67	3.50	-0.2	-4%	-	-
Xylene	2.31	2.80	2.05	-0.7	-27%	-	-
n-heptane	5.31	0.15	0	-0.2	-100%	97.1	100
i-heptane	7.79	0.17	0	-0.2	-100%	97.9	100
n-octane	4.12	0.07	0	-0.1	-100%	-	-
i-octane	6.39	0.08	0	-0.1	-100%	-	-
n-nonane	6.10	1.87	1.98	0.1	6%	-	-