The merit of pressure dependent kinetic modelling in steam cracking

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Abstract:

Renewable cracking feedstocks from plastic waste and the need for novel reactor designs related to electrification of steam crackers drives the development of accurate and fundamental kinetic models for this process, despite its large scale implementation for more than half a century. Pressure dependent kinetics have mostly been omitted in fundamental steam cracking models, while they are crucial in combustion models. Therefore, we have assessed the importance of pressure dependent kinetics for steam cracking via an in-depth modelling and experimental study. In particular we have studied the influence of considering fall-off on the product yields for ethane and propane steam cracking. A high pressure limit fundamental kinetic model is generated, based on quantum chemical data and group additive values, and supplemented with literature values for pressure dependent kinetic parameters for β-scission reactions and homolytic bond scissions of C_2 and C_3 species. Model simulations with high pressure limit rate coefficients and pressure dependent kinetics are compared to new experimental measurements. Steam cracking experiments for pure ethane and propane feeds are performed on a tubular bench-scale reactor at 1.7 bara and temperatures ranging from 1058 to 1178 K. All important product species are identified using a comprehensive GC × GC - FID/q-MS. For homolytic bond scissions, the inclusion of pressure dependent kinetics has a significant effect on the conversion profile for ethane steam cracking. On the other hand, pressure dependence of C_2 β-scissions significantly influences conversion and product species profiles for both ethane and propane steam cracking. C_3 β-scissions pressure dependence has a negligible effect in ethane steam cracking, while for propane steam cracking the effect is non-negligible on the product species profiles.

1. Introduction

Steam cracking is the predominant process for converting a wide variety of fossil feedstock (ethane, propane, naphtha's, gas oils, gas condensates, etc.) to chemical building blocks such as ethylene, propylene, butadiene and aromatics. Due to the scale of the ethylene producing industry, there is a large interest in understanding and predicting the chemistry of this process. Over the past decades the modelling of the chemistry has therefore shifted from empirical models to single event kinetic models [1-4]. To this end, several kinetic models have been developed using first principle-based parameters. In many cases, the pressure dependence of these reactions is not accounted for and it is assumed that steam cracking chemistry can be described accurately without the need for pressure dependent rate coefficients and pathways [1, 2, 5-7]. This is in contrast to the combustion kinetic models, where pressure dependence is of key importance [8, 9]. Current commercial software for predicting the steam cracking process, such as SPYRO [2] and COILSIM1D [10] typically do not include pressure dependence, but rather fit key reactions to provide accurate results for a wide range of steam cracking conditions. This approach has provided satisfactory results for decades in the steam cracking industry. However, since these models are fitted at typical pressures for steam cracking, any pressure dependence would be captured by the fitted parameters as long as one remains within the conventional pressure range.

Recently, the shift to renewable feedstocks such as plastic waste pyrolysis oil [11, 12] and biomass derived feeds [13-16] has reinforced the need for accurate, fundamental steam cracking kinetic models, since the fitted commercial models do not accurately describe the pyrolysis of these renewable feedstocks due to the high olefin content and unconventional functional groups and impurities. Furthermore, like most industrial sectors, there is a push for electrification of the petrochemical industry [17]. This push has led to a reassessment of the steam cracking process and the inception of several revolutionary reactor concepts, e.g., the roto dynamic reactor developed by Coolbrook [18]. This reactor is an ineffective compressor that, instead of increasing the pressure, transforms the electrical energy into heat using a rotor and a stator during which shock waves are generated. For such a new reactor design or for a renewable feedstock it is likely that the highly fitted commercial steam cracking models might not be accurate and a pressure dependent fundamental kinetic model will be better suited, since it can capture the effect of the unconventional conditions or feeds. Finally, the increase in computational power of the last decades combined with master equation solvers such as MESS [19] or MESMER [20] provide a more suitable framework for generating pressure dependent fundamental kinetic models [21, 22].

Typically it is expected that the likelihood of fall-off decreases with increasing size of the reactant [23, 24], however, Wong et al. [25] stated that fall-off at a specific pressure is more dependent on temperature and nature of the reaction than on the molecular size. However, since typical steam cracking temperatures are intermediate between atmospheric chemistry, where pressure dependence is negligible, and high temperature oxidation, where pressure dependence is essential for many reactions, the molecular size of the reactant will be an important indicator for predicting fall-off behavior. For example, it is found that C_2 β-scissions are in fall-off at steam cracking conditions, whereas Wong et al. show that the β-scission of the primary butyl (C_4) radical is not yet in fall-off regime at the same conditions [25, 26].

In this work, the role of pressure dependence in micro-kinetic modelling for the steam cracking of both ethane and propane diluted with water is investigated. The in-house developed automatic model generation code, Genesys [27] is employed to generate a single-event, high pressure limit kinetic model for ethane and propane steam cracking. Thermodynamic and kinetic parameters assigned to the developed model are either quantum-chemically calculated at the CBS-QB3 level of theory or estimated using group additivity schemes or rate rules based on accurate ab initio calculations. The influence of the pressure dependence of rate coefficients for unimolecular reactions of small molecules (C_{3-}) is investigated by replacing pressure dependent reactions with the equivalent high pressure limit pathways. Model simulations with high pressure limit and pressure dependent kinetics are compared to experimental yields of key steam cracking products. For this, the steam cracking of ethane and propane are also studied experimentally at temperatures ranging from 1058 – 1178 K at a pressure of 1.7 bara in a bench scale tubular reactor.

2. Methodology

2.1. Experimental method

In order to study the effect of pressure dependence in the model, experimental validation is required. The pyrolysis experiments in this work are performed on a dedicated bench scale unit at the Laboratory for Chemical Technology at Ghent University. A detailed description of this unit has been given in the past, therefore, only a brief description is provided here [28-30]**.** The bench scale steam cracker consists of three sections: the feed section, the reactor section and the analysis section, as can be seen in the schematic representation in Supporting Information.

Ethane or propane is provided to the feed section directly from a cylinder with a fixed flow rate of 0.0361 g/s. The feed is mixed with 0.0144 g/s H_2O and preheated using an electrical heater. Subsequently, the feed enters the reaction section, which consists of a vertical tubular reactor with a length of 149 cm and 0.6 cm internal diameter. This reactor is heated to a desired temperature using a four sectioned electrical furnace. The process gas temperatures are measured by 8 type K thermocouples distributed along the length of the reactor. The measured temperature profiles are provided in Supporting Information. Pressure inside this reactor is set to 1.7 bara using a back-pressure regulator. Pressure drop inside the reactor is negligible and does not exceed 0.05 bar.

After reaction, the effluent is sent to the on-line analysis section that is maintained at high temperatures (above 573 K) to avoid condensation. Two distinct gas chromatographs are available in this section. The refinery gas analyzer (RGA) detects primarily H_2, CO, CO_2 and small hydrocarbons (C_{4-}). The RGA is equipped with a thermal conductivity detector (TCD) and uses a set flow rate of N_2 as an internal standard to quantify light hydrocarbons (C_{2-}) and permanent gasses, i.e. N_2, CO, CO_2 and H_2. The RGA is also equipped with an FID that detects the C_{4-} hydrocarbons in the effluent. This also results in an additional measurement for CH_4, C_2H_6, C_2H_4 and C_2H_2, which is a direct internal validation of the RGA measurements. A second chromatograph is the GC × GC, which is responsible for the quantification of the bulk of components. The GC × GC is equipped with a flame ionization detector (FID) for quantification and a quadrupole mass spectrometer (*q*MS) for identification. The FID signal is quantified using the methane concentration in the effluent as a secondary internal standard, since this was previously quantified in the RGA. The apolar/polar column configuration of the GC × GC, with internal modulation by liquid CO_2, allows separation of the effluent on both boiling point and polarity.

Ethane experiments were carried out under temperatures ranging from 1088 – 1178 K. This results in conversions ranging from 49 – 90 %. Propane experiments were carried out under temperatures ranging from 1058 – 1138 K, resulting in conversions ranging from 58 - 96 %. The spacetime, as calculated based on the inlet temperature of 673 K and pressure of 1.7 bara, is set at 0.6 s. Detailed temperature profiles of all experiments are found in Supporting information. During each experiment, multiple samples are injected on the RGA. Principal component analysis (PCA) is performed on this data using an in-house developed data analysis tool, Quantis [31]. After PCA, outliers for each of the conditions are removed and the remaining product yields are averaged for each of the conditions. The outliers identified by PCA are generally the first injection after a new temperature profile is set and thus it can be assumed that these outliers occur because steady state operation has not been fully reached. For both sets of experiments, the mass and molar balances are closed within 5 % using the internal standard method as described in Van Geem et al. [32]. The uncertainty on the experimental values is determined as 5 % rel. in accordance with previous studies. A summary of experimental conditions and the associated yields as well as the results from the PCA are provided in the Supporting Information.

2.2. Model construction

Before the influence of pressure dependent kinetics are studied, a single-event kinetic model with high pressure limit rate coefficients is developed for the steam cracking of light hydrocarbons. The kinetic model contains only elementary reaction steps and was constructed using the automatic network generation tool, Genesys. The Genesys software tool has been described in detail before [27].

Thermodynamic and kinetic parameters are assigned to all species and reactions. First a database of ab initio calculated values with thermodynamic and kinetic parameters, obtained at the CBS-QB3 level of theory as available in Gaussian 16 [33], is used whenever an entry is available for a specific molecule or reaction. A detailed description of the quantum mechanical method is given elsewhere [34]. If no thermodynamic parameters are available in the database, Benson’s group additivity method [35] is employed. In this work, the group additivity values (GAVs) from Sabbe et al. [36] are used. If no entries are available in the database when assigning kinetic parameters for certain reactions, the kinetic group additivity method developed by Saeys et al. [37] and extended by Sabbe et al. [38-40] can be used. The specific database with group additive values or the estimation method of the kinetic parameters depends on the reaction family as described below.

The user-defined reaction families in Genesys are a description of the molecular rearrangement(s) occurring in a single step from reactant(s) to product(s). For intermolecular hydrogen abstractions by a carbon radical or hydrogen atom, kinetic group additivity values calculated by Sabbe et al. [38, 39, 41] are used. Values for the intermolecular radical addition to olefins and the reverse β-scissions are obtained from the work by Sabbe et al. [40]. The intramolecular hydrogen abstractions or shifts are estimated using the kinetic GAVs as obtained by Van de Vijver et al. [42] in case no quantum chemical calculations were available. Intramolecular radical addition with the formation of a 5- or 6-membered ring is accounted for using kinetic GAVs, regressed on unpublished in-house generated quantum chemical calculations. Rate coefficients from Diels-alder reactions are assigned using a rate rule from literature [43]. Retro-ene reactions are accounted for using an in-house generated set of kinetic GAVs. Finally, because of the barrier-less nature of these reactions, no kinetic values can be calculated at the CBS-QB3 level of theory for radical recombinations and the reverse homolytic bond scissions. For the most important radical recombinations, alkyl radical recombinations forming ethane and propane, literature calculations are used that are performed using a variational reaction coordinate by Klippenstein et al. [44]. For the remaining homolytic bond scissions of single bonded C-C or C-H, the reverse radical recombination reactions are implemented in the kinetic model using a rate rule. The kinetics of those reactions are assumed to be barrier less and close to the collisional rate limit. The rate rule for radical recombination reactions is defined with respect to the recombination of ethyl and methyl to propane, which has a reaction path degeneracy or number of single events equal to four. This results in a high pressure limit single event reaction rate for radical recombination of approximately 0.5×10^{13} $cm^3\,mol^{-1}\,s^{-1}$ at 1000 K according to several experimental [45] and theoretical [46, 47] studies.

Finally, the user must provide constraints to the algorithm to avoid the generation of an unnecessarily large or chemically redundant model. Genesys uses a rule-based constraint strategy for this purpose and applies them to the reaction families and the product species. An important constraint used in this work is to limit the size of products to 7 carbon atoms. This is justified, as the largest carbon number feed used in this work is propane and from the experimental results it is seen that the majority of products (> 98 wt. %) are C_{7-}. Other constraints are related to a specific reaction family, for example radical addition is limited to radicals with 3 heavy atoms or less as larger radicals will typically decompose faster through unimolecular reactions. The generated model contains 915 species and 9384 reactions and can be found in Supporting Information.

2.3. Methodology for assessment of importance of pressure dependence

The single event kinetic model for steam cracking was used for reactor simulations in CHEMKIN PRO [48] using the plug flow reactor implementation and the experimentally measured temperature profile. When selecting the reactions of interest to be included in the pressure dependent model, two criteria were employed: the likelihood that a reaction will demonstrate pressure dependent behavior, and the expected influence of this behavior on predictions of key products for steam cracking models (i.e. ethylene, propylene, acetylene, benzene, butadiene, etc. ...). The pressure dependence of each reaction will be investigated in a case study to assess their influence on the conversion and yield of important steam cracking products. First, a base pressure dependent model is made by defining pressure dependent parameters for the selected reactions in the original high pressure limit model. Subsequently, several cases are defined where the pressure dependence of a subset of the reactions is 'disabled'. Each 'case' is thus a different version of the kinetic model where the rate coefficient of the reaction in question has been set to the high pressure limit. Subsequently a simulation is performed using this specific version of the kinetic model, allowing for a comparison between cases to evaluate the influence of a (combination of) reaction(s). The pressure dependence of both unimolecular homolytic bond scission reactions and β-scission reactions are considered.

2.3.1. Pressure dependent rate parameters for homolytic bond scission

In steam cracking, the role of the homolytic bond scissions is key. Especially the dissociation of the feed has a major influence on the simulated conversion profile and product yields, as it determines the temperature at which the radical mechanism is initiated. This is opposed to combustion mechanisms where the radical mechanism is initiated by reactions with molecular oxygen. For combustion, mainly the reverse (bimolecular) radical-radical recombination reactions are of great importance as it is a source of heat release and plays a key role in soot formation [44]. In general, homolytic bond scission reactions and the reverse radical recombination reactions are key to determine the radical concentration in the system.

Several methods are investigated for the kinetics of homolytic bond scissions. It is important to differentiate between the uncertainty on the kinetic parameters of the bond scissions and the effect of possible pressure dependence. For this reason, two sources are used for high pressure limit parameters of the bond scissions to compare the effect of pressure dependence at steam cracking conditions to the uncertainty in calculating these barrierless reactions. A first approach is to use the high level variable reaction coordinate transition state theory calculations reported by Klippenstein et al. [44]. These calculations result in high pressure limit modified Arrhenius parameters that are valid in the 200-2000 K range. Alternatively, it is possible to investigate the pressure dependence of these reactions by employing the parameters that are available within the AramcoMech 3.0 (AM 3.0) mechanism [9] and the associated high pressure limit.

To study the bond scissions, only the C_2 and C_3 scissions are considered, since the effect is expected to decrease with growing molecular size. This thus includes the $CH_3 + CH_3$ and $CH_3 + C_2H_5$ forming scissions. Note that in the kinetic model these scissions are in fact defined as reversible radical recombination reactions, as found in literature. The rate of bond scissions is then determined by the thermodynamic relation of products and species. The following three cases are defined: high pressure limit variational TST [44] (‘Rec. VTST HP’), pressure dependence AM 3.0 [9] (‘P. dep’) and high pressure limit AM 3.0 [9] (‘Rec. AM HP’). For the remaining recombination reactions, the single event methodology of Genesys is used by default, as mentioned before.

2.3.2. Pressure dependent rate parameters for β-scission reactions

Besides homolytic bond scission reactions, also the pressure dependence of the unimolecular β-scission of weakly bound free radicals is considered. These reactions are typically of interest in combustion chemistry when discussing pressure dependence. Weakly bound free radicals that are of interest in pyrolysis environments are vinyl, ethyl, allyl and other C_3H_5 isomers [49]. The β-scissions of these radicals are considered for this study, as well as the β-scissions of the propyl radical, since this is an important intermediate in propane steam cracking. All other β-scission kinetic parameters are defined in Genesys libraries or calculated using kinetic group additivity based on ab initio calculations. The pressure dependence of the considered reactions have been reported in literature by Klippenstein et al. [50] for ethyl and vinyl, by Miller [51] and Narendrapurapu [52] for allyl and other C_3H_5 isomers and by Miller et al [53] for propyl β-scissions.

Again, a set of different cases are defined to study the influence of pressure dependence on product yields. The ‘P. dep’ case corresponds to the case where all studied β-scissions are defined with pressure dependent parameters as they are found in their respective sources [50-53]. The remaining cases correspond to a model in which one or more reactions have been set at the high pressure limit. Case ‘β-scis. C_2H_5’ , for example, sets the ethyl β-scission in the model to the high pressure limit rate parameters as defined in the respective source [50], while case ‘β-scis. C_3’ sets the propyl [53] and allyl [51, 52] β-scissions to the high pressure limit and so on. When implementing these β-scissions into the model, the “well-skipping” reactions defined in their respective sources are also included in the kinetic model. An overview of the constructed cases is shown in Table 1.

Table 1: Overview of constructed model cases, reactions that are substituted with their corresponding high pressure limit parameters are indicated with 'High P' and the selected parameters for homolytic bond scissions are marked. C_3H_7 and C_3H_5 represent the primary and both secondary radicals with this structural formula. C_3H_4 represents both propadiene and methylacetylene. The complete pressure dependent model is the 'P. dep' case

Reaction	P. dep	Rec. AM HP	Rec. VTST HP	β – scis. C_2H_3	β – scis. C_2H_5	β – scis. C_3H_5	β – scis. C_3H_7	β – scis. C_2	β – scis. C_3
Recombinations									
Variational TST			**X**						
AM 3.0 pressure dependence	**X**			**X**	**X**	**X**	**X**	**X**	**X**
AM 3.0 high pressure limit		**X**							
β-scissions									
$C_2H_5 \leftrightharpoons C_2H_4 + H$					**High P**			**High P**	
$C_2H_3 \leftrightharpoons C_2H_2 + H$				**High P**				**High P**	
$C_3H_7 \leftrightharpoons C_3H_6 + H$							**High P**		**High P**
$C_3H_7 \leftrightharpoons C_2H_4 + CH_3$							**High P**		**High P**
$C_3H_5 \leftrightharpoons C_3H_4 + H$						**High P**			**High P**
$C_3H_5 \leftrightharpoons C_2H_2 + CH_3$						**High P**			**High P**

3. Results and discussion

3.1. Validation of the pressure dependent model

Discussion of the influence of the pressure dependent parameters is only relevant when the overall model achieves good results. The P dep. model contains pressure dependent kinetics for 2 homolytic bond scission reactions, 2 C_2 β-scissions and 8 C_3 β-scissions. The experimental yields and model predictions for feed conversion in ethane and propane steam cracking experiments are shown in Figure 1. Ethane feed conversion is overpredicted at higher temperatures, while propane feed conversion is predicted well across the studied temperature range.

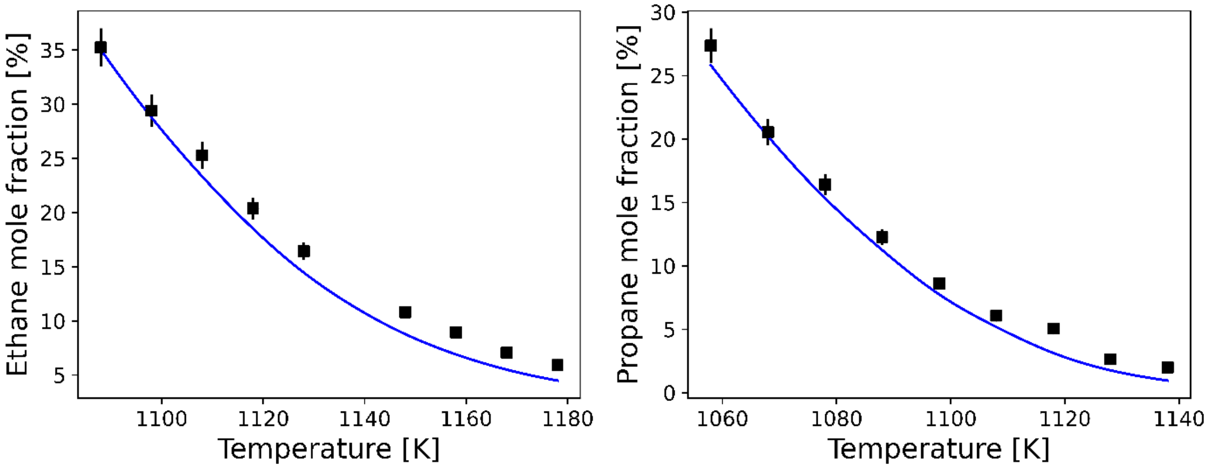

Figure 1: Feed mole fraction as a function of temperature for the steam cracking of ethane (left) and propane (right). Experiments (symbols) and simulation results (lines) are compared. Experimental conditions are 1.7 bara, 0.6 s space time, inlet temperature of 673 K, continuous feed flow of 0.0361 g/s and a steam dilution of 0.4 kg/kg. Simulations are performed with CHEMKIN software using the 1D plug flow reactor option and the new P dep. model.

In Figure 2 the major products of ethane steam cracking are compared to model predictions using the pressure dependent kinetic model. Model predictions are shown as a function of conversion rather than temperature. This serves to isolate the effect of the C_2 and C_3 β-scission pressure dependence in the subsequent study, since any effects these reactions have on conversion can be decoupled from the effect on the model predictions. It also avoids perpetuating the error of conversion prediction at higher temperatures to the product species profiles. Ethylene concentrations are predicted well by the model. For both propylene and 1,3-butadiene, a small overprediction is observed in the model predictions, while acetylene concentrations are considerably overpredicted at higher conversion. Model predictions for propane concentration indicate that the bond scissions and associated reverse recombinations are able to capture the formation of propane in addition to the conversion. Note that the yield of propane in ethane steam cracking is very low (< 0.1 mol%) and a higher experimental uncertainty can be expected for these experimental measurements. Hydrogen, methane and benzene concentrations are also predicted satisfactorily by the model.

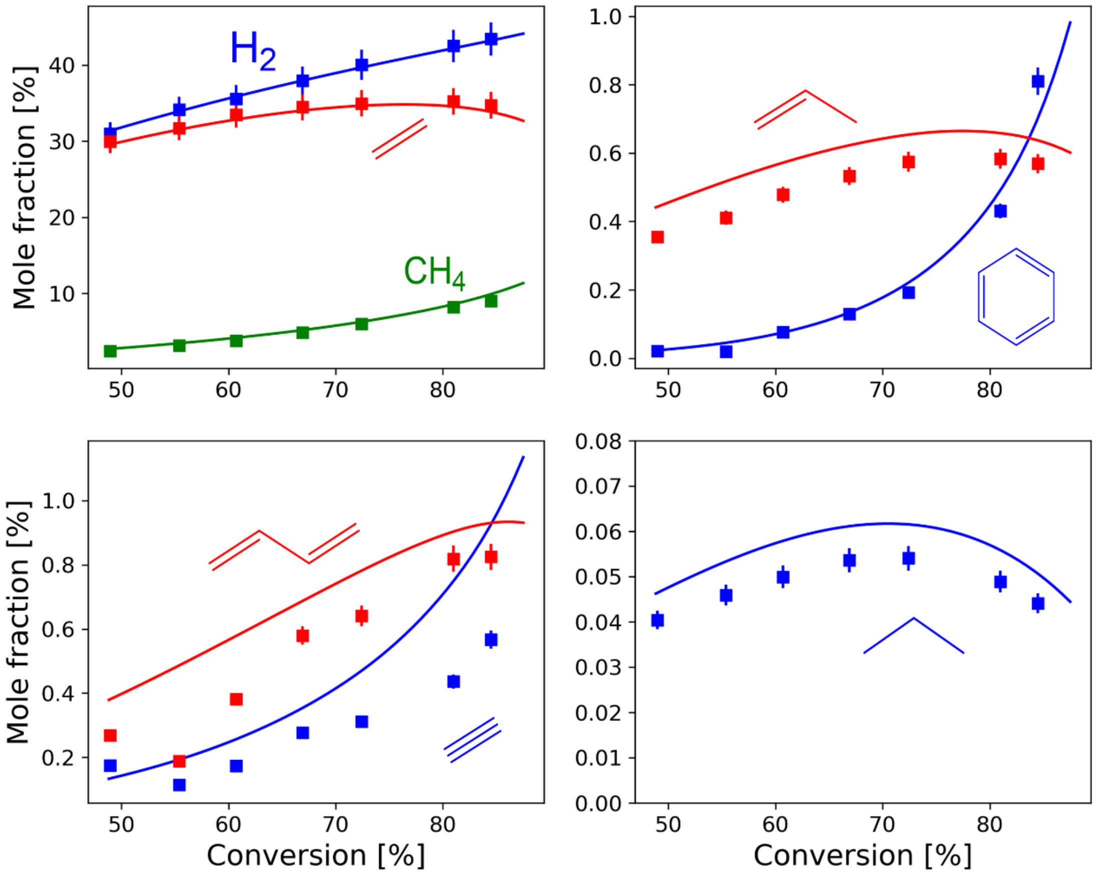

Figure 2: Comparison between major products experimental (symbols) and simulation (lines) results as function of feed conversion for ethane steam cracking. Experimental conditions are 1.7 bara, 0.6 s space time, inlet temperature of 673 K, outlet temperatures of 1088 – 1178 K, continuous feed flow of 0.0361 g/s and a steam dilution of 0.4 kg/kg. Simulations are performed with CHEMKIN software using the 1D plug flow reactor option and the new P dep. model.

Figure 3 shows the model performance of the pressure dependent model on the propane steam cracking experiments. Similar to ethane steam cracking results ethylene and methane yields are predicted accurately by the model. Contrary to the results for ethane steam cracking, propylene and hydrogen concentrations are underpredicted. The accurate prediction for ethane yield again indicates that the pressure dependent bond scission kinetics are able to describe the formation of ethane well in addition to the initiation chemistry. Benzene predictions are good, similar to the ethane results. Butadiene is overpredicted and acetylene is predicted well throughout the entire conversion range.

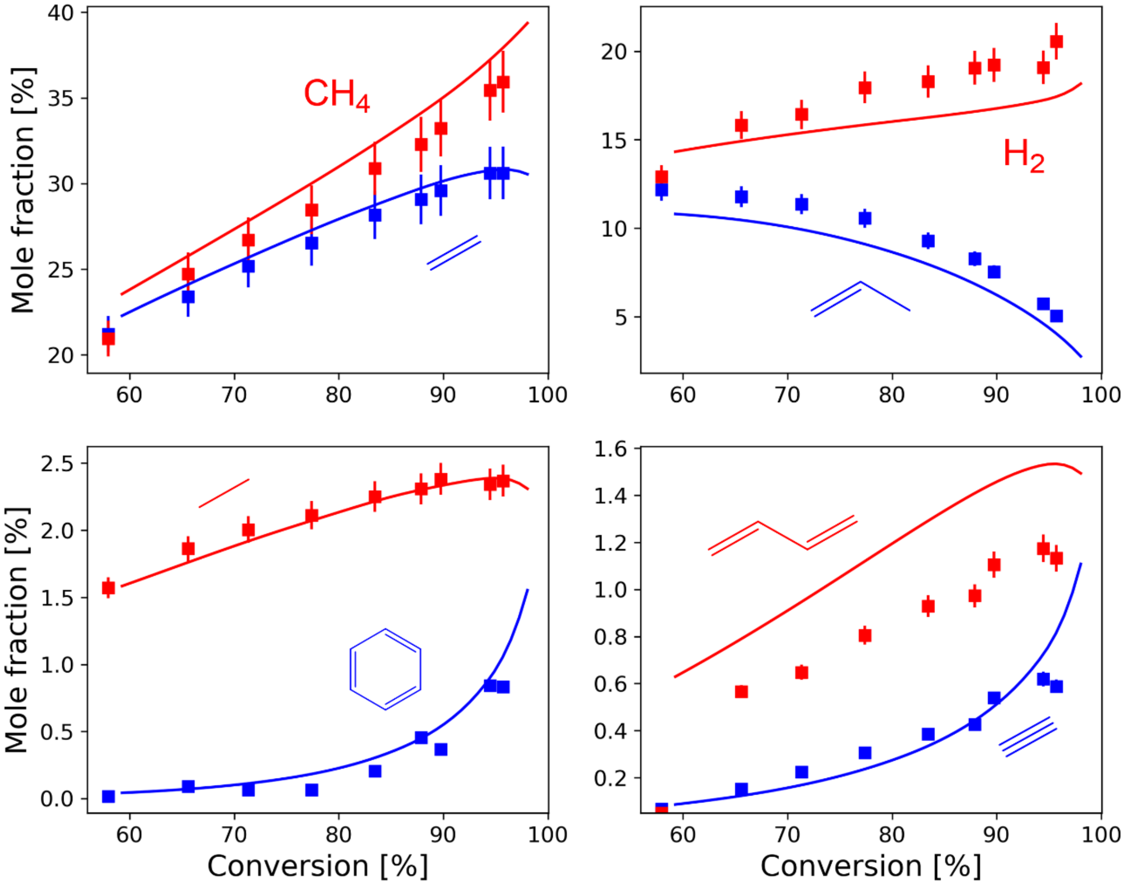

Figure 3 Comparison between major products experimental (symbols) and simulation (lines) results as function of feed conversion for ethane steam cracking. Experimental conditions are 1.7 bara, 0.6 s space time, inlet temperature of 673 K, outlet temperatures of 1058 – 1138 K, continuous feed flow of 0.0361 g/s and a steam dilution of 0.4 kg/kg. Simulations are performed with CHEMKIN software using the 1D plug flow reactor option and the new P dep. model.

The previous results show that the model with the highest degree of pressure dependence, describes the experiments and conversion well. In the subsequent sections it will be explored to what degree this can be attributed to the additional pressure dependent parameters by comparing the model to the different cases defined for the case study.

3.2. Influence of pressure dependence on the feed conversion

The effect of pressure dependence is expected to have a substantial influence on the prediction of the conversion of ethane and propane because of the importance of homolytic bond scissions in the initiation chemistry and β-scissions in the propagation chemistry of the process. Figure 4 shows that indeed conversion predictions vary considerably depending on which case of the model is used.

Comparison of different bond scission parameters, on the left side of Figure 4, shows that these strongly influence conversion predictions. It is clear that high pressure kinetics are not sufficient to describe the bond scissions (Rec. AM HP and Rec. VTST HP) as conversion is overestimated. When using the pressure dependent parameters that are available in AramcoMech 3.0 (P. Dep) it is seen that the conversion is much better described, however, at higher temperatures it is seen that an overestimation still occurs. When these bond scission kinetics are implemented it is always performed for both ethane and propane bond scissions. The comparison on the right side of Figure 4 shows that the pressure dependence of the ethyl β-scission to ethylene and a hydrogen atom has a strong influence on conversion predictions. If this reaction is set to its high pressure limit, the conversion predictions vary considerably at low temperatures (± 5 mol. %), while at the highest temperatures equilibrium is reached and they have no more influence. This reaction is crucial in the propagation chemistry, as it is the dominant path in ethyl consumption. Evidently this reaction exhibits considerable pressure dependence, as the high pressure limit variant of this reaction proceeds markedly faster and thus results in an overprediction of conversion. The same influence is not seen for the vinyl radical β-scission as it predicts identical conversion regardless of the pressure dependence. Overall, the conversion is still overpredicted at higher temperatures.

In commercial steam cracking models these initial bond scissions and β-scissions are fitted to large experimental datasets as these are of critical importance in describing the feed conversion and thus heavily influence the model predictions. When these reactions are fitted, this is typically performed on experiments within a narrow pressure range that represents the industrial steam cracking conditions (1 – 3 bara). Therefore, the pressure dependence is essentially captured for these reactions by fitting and not in a fundamental way. It is seen here that the pressure dependent parameters for the homolytic bond scission of ethane that are found in combustion models, where their main purpose lies in predicting soot and aromatics formation, are not accurate enough at higher conversions for steam cracking of ethane. Note that the uncertainty of other parameters could also contribute to the deviation for conversion predictions, for example hydrogen abstractions on the feed also have a strong influence on conversion and thus the uncertainty on those kinetics could influence model predictions.

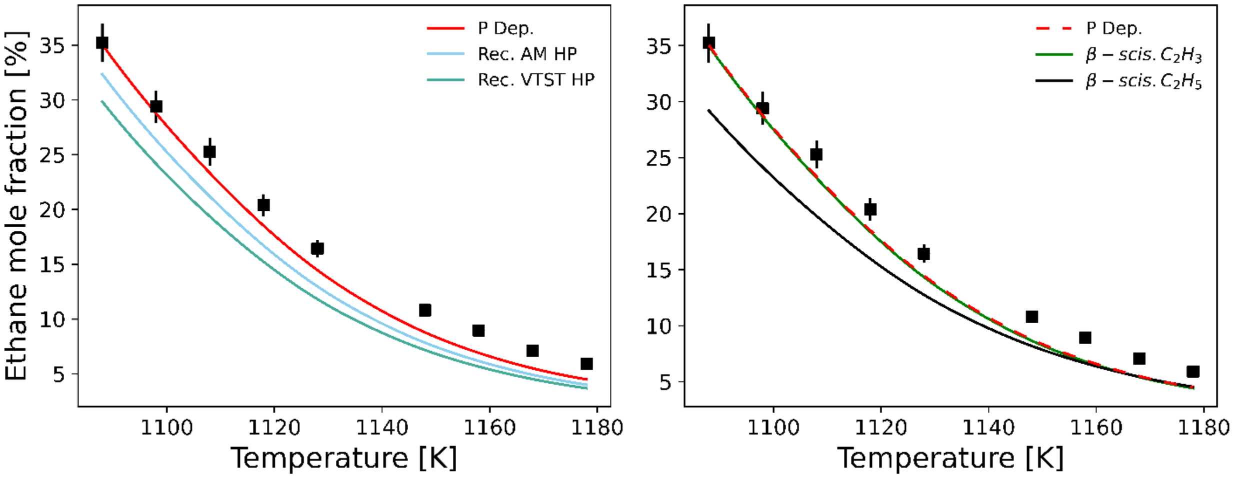

Figure 4: Feed mole fraction as a function of temperature for the steam cracking of ethane. Experiments (symbols) and simulation results (lines) are compared. Experimental conditions are 1.7 bara, 0.6 s space time, inlet temperature of 673 K, continuous feed flow of 0.0361 g/s

and a steam dilution of 0.4 kg/kg. Simulations are performed with CHEMKIN software using the 1D plug flow reactor option and the selected model is indicated in the legend.

A similar study on the influence of pressure dependence on conversion is possible for propane steam cracking experiments. Figure 5 shows the effect of different bond scission rates on conversion and contrary to the case of ethane cracking there is very little influence. The high pressure limit of AM 3.0 parameters (‘Rec. AM HP’) slightly overestimates the conversion, whereas the high pressure limit parameters from variational reaction coordinate calculations (‘Rec. VTST HP’) predicts almost an identical conversion to the pressure dependent parameters found in AM 3.0 (‘P. Dep’). This deviation between two high pressure limit sets of kinetic parameters indicates that the uncertainty on these parameters is certainly not negligible either. The small deviation between all these parameters indicates that the fall-off of the propane homolytic bond scission is barely significant in the typical steam cracking conditions. Since the pressure dependence of bond scission kinetics is expected to decrease as molecule size increases in steam cracking conditions, the effect on conversion for C_{4+} bond scissions in butane or pentane steam cracking is expected to be irrelevant. Furthermore, Figure 5 shows the influence of pressure dependence of β-scissions of C_2 and C_3 radicals on the propane conversion. When removing pressure dependence for propyl β-scissions a very minor effect on conversion can be seen at low temperatures, however, the remaining pressure dependent parameters seem to have no impact on conversion as all remaining cases predict near identical conversion as the pressure dependent model. Even though these reactions are very important in the propagation of propane cracking, it can be seen that inclusion of pressure dependence for these reactions is not substantial when observing conversion.

In short, pressure dependent parameters are a significant improvement over the high pressure limit in ethane steam cracking conversion prediction, while for propane steam cracking their influence is less pronounced.

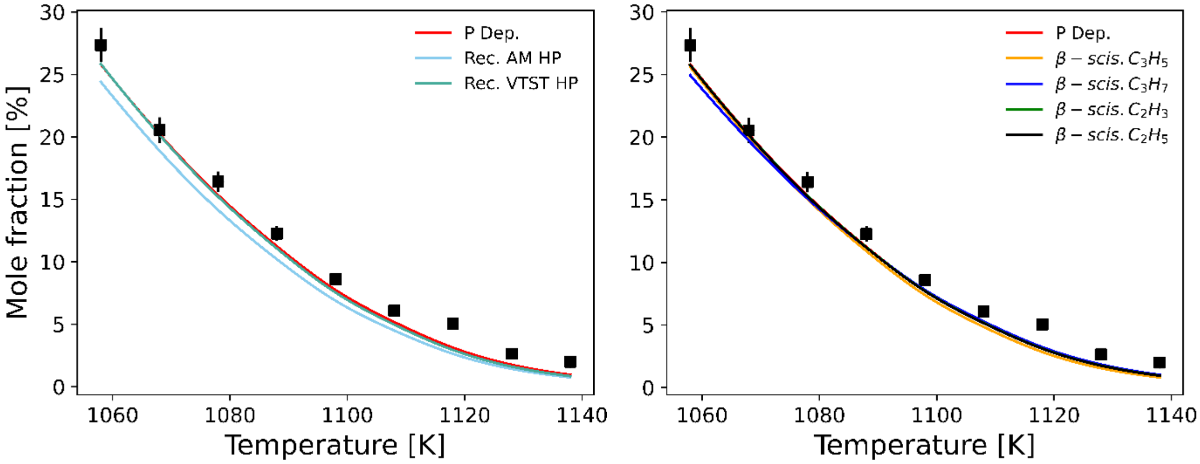

Figure 5: Feed mole fraction as a function of temperature for the steam cracking of propane. Experiments (symbols) and simulation results (lines) are compared. Experimental conditions are 1.7 bara, 0.6 s space time, inlet temperature of 673 K, continuous feed flow of 0.0361 g/s and a steam dilution of 0.4 kg/kg. Simulations are performed with CHEMKIN software using the 1D plug flow reactor option and the selected model is indicated in the legend.

3.3. Influence of pressure dependence on primary decomposition products

The feed conversion is of course not the only feature of interest when modelling steam cracking. The main products considered in this study are: ethylene, propylene, acetylene and 1,3-butadiene as they are considered the most important and valuable olefins among the steam cracking products. Most of those are also the primary products formed through the reactions for which pressure dependent kinetics are considered. For both the ethane and propane feeds these simulated product profiles vary depending on the model case that is used and this indicates the importance of the pressure dependence of each reaction.

In ethane steam cracking it is expected that the pressure dependence of the β-scission reactions will have a large influence on these product species profiles, since most are directly formed via one of these reactions. 1,3-Butadiene is an exception to this statement, nevertheless it is an important steam cracking product and a precursor for aromatics formation. In ethane cracking it is primarily formed by addition of the vinyl radical to ethylene and a subsequent β-scission. Concentrations of the vinyl radical and ethylene are both dependent on the newly introduced pressure dependent parameters, therefore, the study of 1,3-butadiene is expected to give an indication of the indirect effect of these parameters.

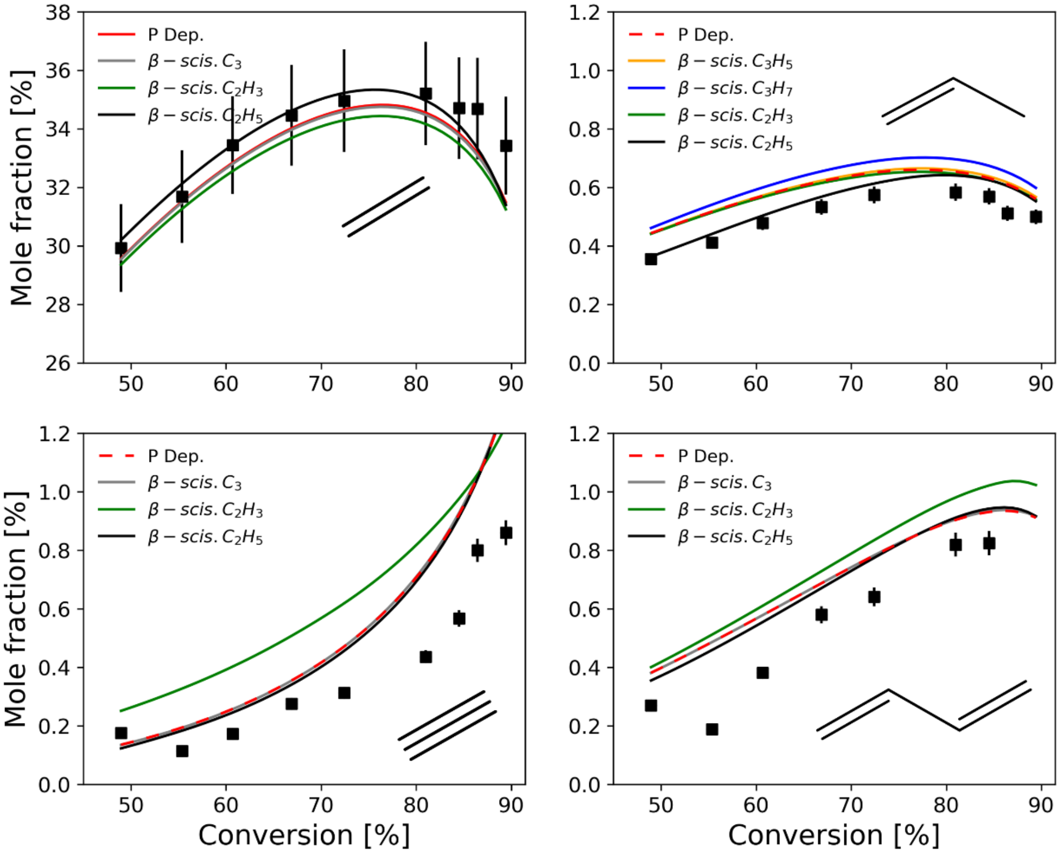

Figure 6: Comparison between major products experimental (symbols) results and model predictions (lines) as a function of ethane conversion for ethane steam cracking experiments. Experimental conditions are 1.7 bara, 0.6 s space time, inlet temperature of 673 K, outlet temperatures of 1088 – 1178 K, continuous feed flow of 0.0361 g/s and a steam dilution of 0.4

kg/kg. Simulations are performed with CHEMKIN software using the 1D plug flow reactor option and the selected model is indicated in the legend.

Figure 6 shows the model predictions for the selected species with varying degrees of pressure dependence. The ethylene, acetylene and butadiene profiles show that C_3 pressure dependent β-scissions have no influence on these predictions as the high pressure limit case for these β-scissions predict identical compositions as the pressure dependent model. The predictions are, however, sensitive to C_2 pressure dependence. Setting ethyl β-scissions to their high pressure limit results in increased ethylene predictions. This can be attributed to the increased consumption of the ethyl radical to ethylene since this reaction rate was considerably reduced by the pressure dependence and thus results in faster ethylene formation when it is set to the high pressure limit. The opposite effect is observed for the vinyl β-scission as this high pressure limit reduces ethylene predictions because the consumption of ethylene to acetylene is artificially accelerated. This can also be seen in the acetylene product profile. The effect on ethylene of the aforementioned reactions is not major, as all model predictions still fall within the 5% relative uncertainty that is associated with the experimental setup. However, in absolute terms this corresponds to around 0.5 mol. % and even such a small deviation can be impactful when considering the large scale of the ethylene industry for which a model such as this is generated.

When discussing propylene concentrations for ethane cracking, one must keep in mind that the $C_3H_7 \leftrightharpoons C_3H_6 + H$ and $C_3H_7 \leftrightharpoons C_2H_4 + CH_3$ reactions have less influence than one would expect, because these reactions are in fact not a major path of propylene formation in ethane cracking. Most propylene is formed via C_4 chemistry that originates from the addition of an ethyl or vinyl radical to ethylene or the recombination of ethyl radicals. Radicals formed in this C_4 mechanism can then decompose into propylene and a methyl radical. The predictions for the propylene concentration show that C_3 pressure dependence does have an influence. The influence of allyl β-scissions is negligible, but when propyl β-scissions are set to their high pressure limit, this result in a higher prediction of propylene. This is because the reverse β-scission is also impacted by this change as all reactions are defined reversibly in the model. Effectively the high pressure limit parameters for propyl β-scissions (more specifically the $C_3H_7 \leftrightharpoons C_2H_4 + CH_3$ reaction) thus result in an increased consumption of ethylene to propylene. The C_2 β-scissions also have a minor influence. Pressure dependence of the vinyl β-scission has no influence, but when the ethyl β-scission is set to the high pressure limit, a decrease in propylene predictions is observed. This is due to the decreased ethyl concentration, as more is converted to ethylene, which results in a lower rate of C_4 radical formation and subsequent reactions to propylene.

The acetylene model predictions show that only the pressure dependence of the vinyl β-scission impacts the acetylene predictions significantly. When this reaction is set to its high pressure limit, acetylene predictions increase as more vinyl radicals are consumed to acetylene. Studying 1,3-butadiene model predictions shows again that only the pressure dependence of the vinyl β-scission impacts the predicted concentration. This is because butadiene is indirectly formed by the radical addition of the vinyl radical to ethylene, which are both influenced by this reaction. However, one would expect that by setting the vinyl radical β-scission to its high pressure limit, 1,3-butadiene predictions should decrease, since less vinyl radicals are available and thus the formation pathway should proceed slower. However, the opposite is observed in this case. This is because the major pathway of 1,3-butadiene consumption is also affected by vinyl radical chemistry, namely, the addition of a vinyl radical to 1,3-butadiene is also slowed down. Of these two effects the reduced consumption of 1,3-butadiene seems to outweigh the reduced formation.

For propane steam cracking product yields, the pressure dependence for C_3 is expected to be more important compared to ethane steam cracking, since the initial propagation step involves the formation of either a primary (C_3H_7-1) or secondary (C_3H_7-2) propyl radical. The pressure dependent kinetic parameters for the decomposition of these radicals is therefore expected to have a more pronounced influence. The same key products are discussed here, namely: ethylene, propylene, acetylene and 1,3-butadiene. The experimental yields and model predictions are shown in Figure 7.

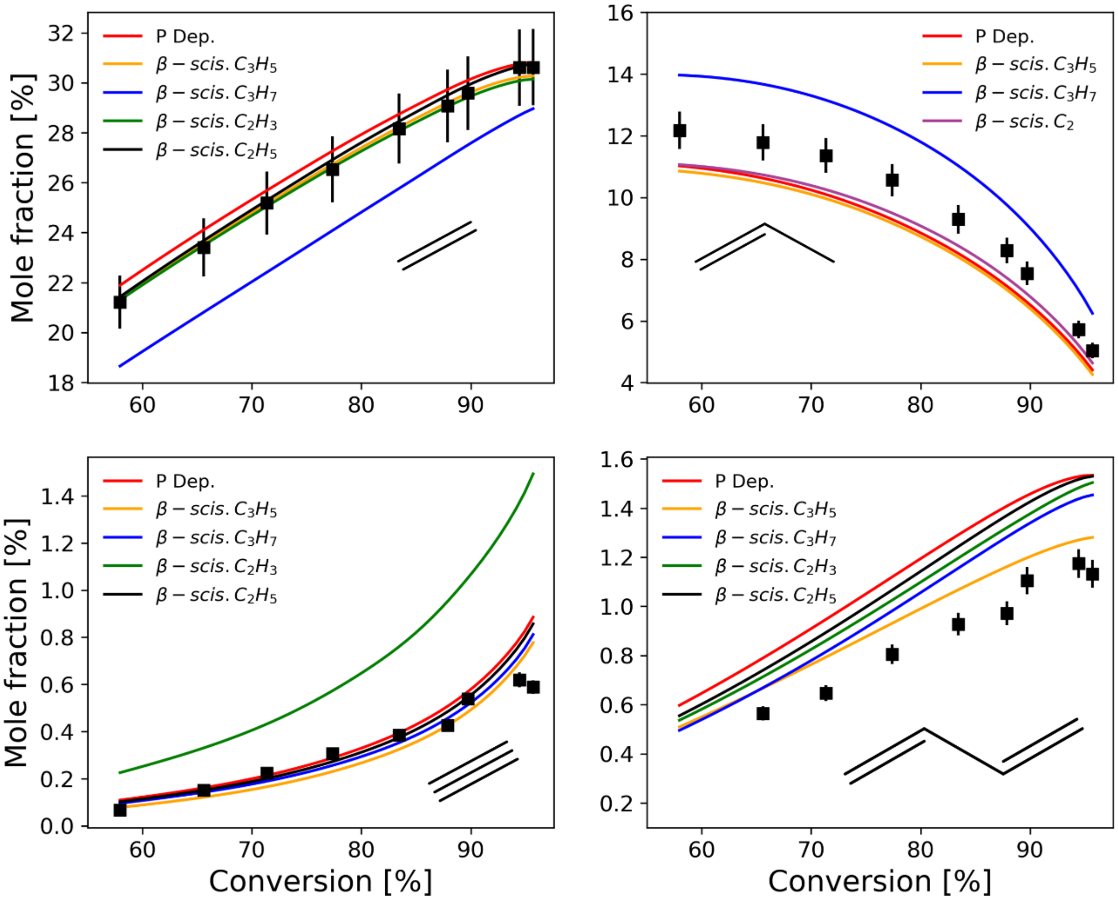

Figure 7: Comparison between major products experimental (symbols) results and model predictions (lines) as a function of propane conversion for propane steam cracking experiments.

Experimental conditions are 1.7 bara, 0.6 s space time, inlet temperature of 673 K, outlet temperatures of 1058 – 1138 K, continuous feed flow of 0.0361 g/s and a steam dilution of 0.4 kg/kg. Simulations are performed with CHEMKIN software using the 1D plug flow reactor option and the selected model is indicated in the legend.

Figure 7, shows that the pressure dependence of the propyl β-scissions is the most important for an accurate prediction of ethylene when considering propane cracking. This case constitutes the decomposition of both the primary and secondary propyl radical to propylene (C_3H_7-1/2 ⇋ C_3H_6 + H) or ethylene and a methyl radical (C_3H_7-1 ⇋ C_2H_4 + CH_3). These two pathways determine the fraction of propane that is converted to propylene and the fraction that is converted to ethylene after the initial hydrogen abstraction from the feed. By introducing high pressure limit kinetics for both reactions, the ratio between these rates changes. The ethylene forming pathway proceeds slower than the competing pathway to propylene and thus less ethylene and more propylene is predicted. This indicates that the propyl β-scission pressure dependence should be accounted for as otherwise the ethylene profile is strongly underpredicted compared to experimental results. The effect of the other β-scissions is less pronounced. The same can be said for propylene predictions, although neither version of the kinetic model results in highly accurate propylene predictions, the deviation is smaller when the pressure dependent model is used.

The acetylene predictions in Figure 7 indicate that here mostly C_2 pressure dependence is of importance, more specifically the consumption of the vinyl radical to acetylene as was discussed for the ethane steam cracking results. The C_3 β-scission pressure dependence has an impact on ethylene concentrations and therefore a minor, indirect impact on acetylene concentrations.

In propane cracking, 1,3-butadiene is mainly formed via 2 pathways as is shown in Figure 8. Either decomposition of 1-butene, which is predominantly formed by recombination of a methyl radical and an allyl primary radical or decomposition of the C_5 radical that is generated by addition of a vinyl radical to propylene. The C_5 pathway is affected by the vinyl β-scission pressure dependence as a decrease in vinyl radical concentration caused by setting this reaction to its high pressure limit results in a lower rate of 1,3-butadiene formation. When the allyl β-scissions are set to their high pressure limit, it can be seen that fall-off is also significant for this reaction because butadiene concentrations decrease markedly. Since the β-scissions of the allyl radical effectively proceed faster in their high pressure limit, the concentration of allyl radicals in the system decreases and less recombination towards 1-butene occurs, impacting another major path of 1,3-butadiene formation.

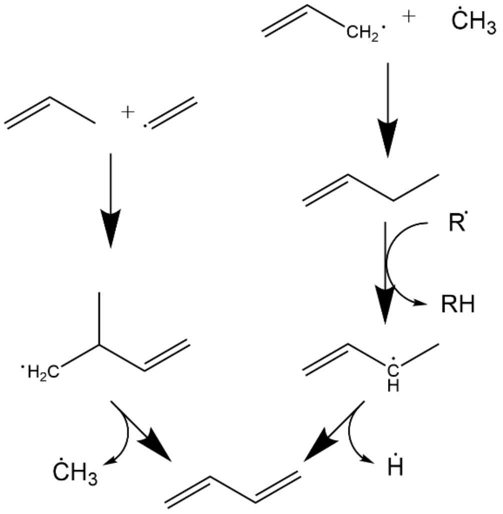

Figure 8: Main 1,3-butadiene forming pathways during the steam cracking of propane feeds.

It is clear that C_3 pressure dependence overall has a much higher influence in propane cracking compared to ethane cracking because the major propagation pathways towards propylene and ethylene are affected by this pressure dependence.

3.4. Influence of pressure dependence on secondary decomposition products

The products discussed in the previous section are all to some degree affected by the introduced pressure dependence into the high pressure limit kinetic model. However, it is also important to assess the influence of the pressure dependent parameters on products of secondary importance. In Figure 9 the model predictions for product species profiles of benzene, ethane, propane, hydrogen and methane are shown with varying degrees of pressure dependence.

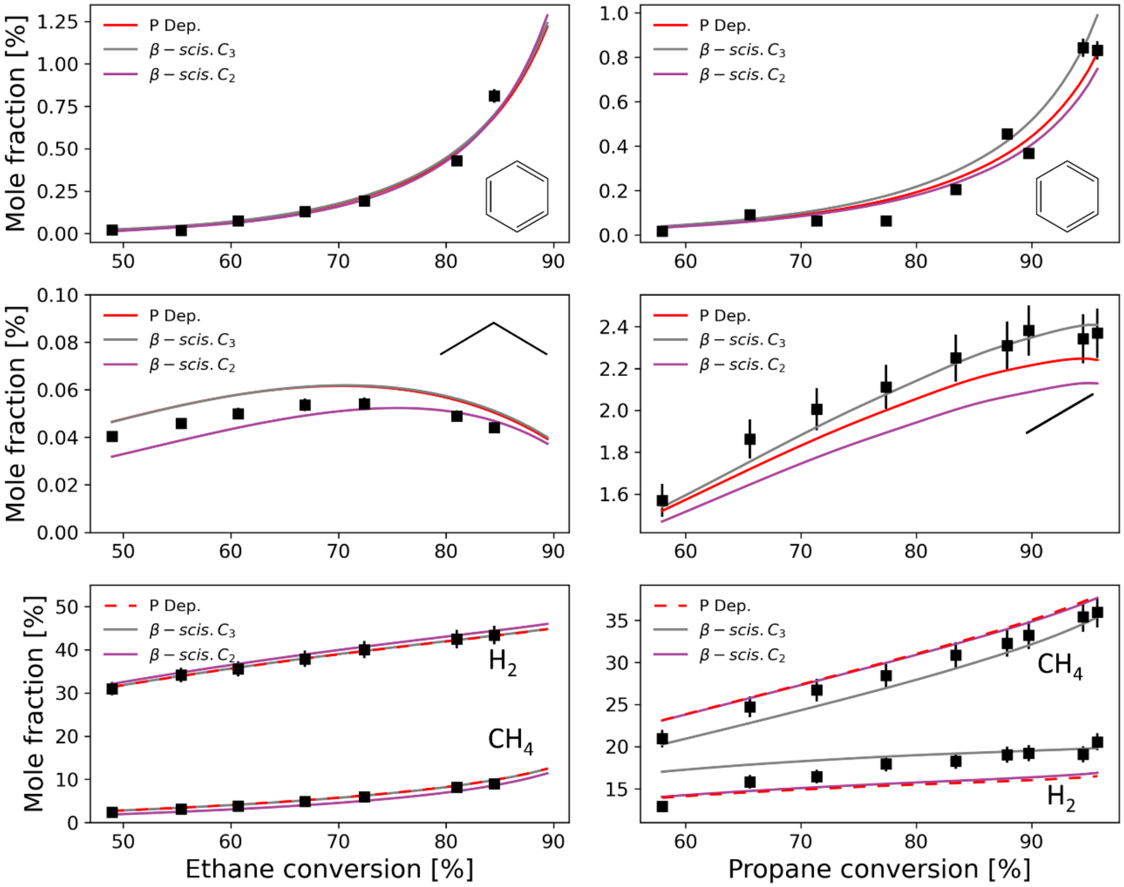

Figure 9: Comparison between major products experimental (symbols) results and model predictions (lines) as a function of conversion for ethane (left) and propane (right) steam cracking experiments Experimental conditions are 1.7 bara, 0.6 s space time, inlet temperature of 673 K, outlet temperatures of 1058 – 1178 K, continuous feed flow of 0.0361 g/s and a steam dilution of 0.4 kg/kg. Simulations are performed with CHEMKIN software using the 1D plug

flow reactor option and the selected model is indicated in the legend.

Benzene concentrations are not sensitive to the pressure dependence in ethane cracking. For propane cracking, a small deviation is seen if C_3 pressure dependence is set to the high pressure limit. This is because in propane cracking most pathways forming benzene and other aromatics originate from radical addition of C_3 radicals to propylene and subsequent ring formation to a cyclic, typically methyl cyclopentadiene, intermediate that forms benzene. The diminishing effect of C_3 pressure dependence on propylene concentrations and thus also C_3 radical concentration was shown in the previous section and thus is likely the main cause for the observed increase in benzene predictions if it is not included. The effect of C_2 β-scissions can be attributed to a secondary pathway for benzene formation that comes from addition of a vinyl radical to 1,3-butadiene resulting in a C_6 radical that forms benzene after ring formation. It was already discussed in the previous section that butadiene formation is reduced if the vinyl β-scission is set to the its high pressure limit, and thus it is logical that the effect is also seen on benzene predictions.

The propane predictions in ethane steam cracking are indicative of the accuracy of the recombination of ethyl and methyl radicals. Only C_2 pressure dependence has an influence on these predictions, as this results in a higher ethyl radical concentration compared to the high pressure limit due to the fall-off in the β-scissions of ethyl. Therefore, the ethyl radical is more likely to recombine with a methyl radical, although the effect is minor. In propane cracking, the ethane concentration is not only dependent on recombination of methyl radicals. The main source of ethane is the abstraction of a hydrogen atom from propane or propylene by the ethyl radical. Setting C_2 β-scissions to their high pressure limit results in an increased rate of ethyl decomposition and thus the bimolecular hydrogen abstraction by this radical is less likely, hence the decreased ethane predictions. If C_3 pressure dependence is disabled, a large decrease in ethylene concentrations and increase in propylene concentrations was observed in the previous section. This results in a higher concentration of C_3 molecules from which the ethyl radical can abstract a hydrogen atom and a slight increase in ethane predictions is the result.

The predictions for methane and hydrogen concentrations in ethane cracking are not sensitive to C_3 pressure dependence and only slightly sensitive to C_2 pressure dependence. This is mainly due to the effect on conversion. In propane cracking, however, a much larger deviation is seen for both molecules if C_3 pressure dependence is disabled. This can be attributed to the decrease in ethylene formation from propyl radicals via the β-scission of propyl to methyl and ethylene, which produces a methyl radical that will eventually recombine with another radical or abstract a hydrogen atom and thus form methane. The decreased methane prediction is complemented by a decrease in hydrogen predictions. C_2 pressure dependence has no influence on methane and hydrogen predictions in propane cracking.

The studied reactions in this work were limited to unimolecular reactions of C_{3-} species. It is expected that for reactions involving more than 3 carbon atoms the influence of pressure dependence will be less significant, however, a future study on these reactions should verify this. Furthermore, the effect is studied using ethane and propane feeds, while it will most likely be less pronounced for naphtha feeds as in that case, the initial propagation reactions will be less affected. To account for this, a future study could use a feedstock representative of naphtha, such as hexane.

4. Conclusions

In this combined experimental and modelling study, the importance of fall-off in steam cracking is investigated. Steam cracking experiments are performed for ethane and propane feedstocks in a range of 1058 – 1178 K and at a pressure of 1.7 bara in a bench scale tubular reactor with a steam dilution of 0.4 g H_2O / g Feed and a spacetime of 0.6 seconds. A new fundamental kinetic model is generated with pressure dependent rate coefficients when appropriate for the most important reactions.

Considering fall-off at steam cracking conditions for homolytic bond scissions is required based on the influence on the conversion profile for ethane cracking. Results for the homolytic bond scission of propane do not lead to the same conclusion for the propane conversion profile; only a minor influence is observed, which reinforces that this effect will most likely be negligible for bond scissions of larger hydrocarbons.

Influence of the fall-off regime for the β-scission of C_2 radicals provides a strong shift in the prediction of the conversion profile for ethane cracking, as well as for the individual product yields like ethylene or acetylene. It can be concluded that C_2 pressure dependence would best be included in a kinetic model that fundamentally describes steam cracking. The pressure dependent parameters for C_3 β-scissions have a relatively minor influence on ethane steam cracking product yields. For propane cracking, it becomes obvious that the pressure dependence of these reactions is in fact important and significantly influence product yields, mainly ethylene and propylene. The observed influence of C_2 and C_3 pressure dependence warrants a future study on C_{4+} pressure dependence on feeds with a higher carbon chain length. On the other hand, the construction of a completely pressure dependent kinetic model is not necessary nor merits the additional computational effort.

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