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Thermal reactions of the major hydrocarbon components of biomass gasification gas

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Turku/Åbo 2014

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Rome wasn't build in a day.
- But they were laying bricks every day
Even if the dream is big and sometimes seemingly unreachable,
just do your daily work and don't lose the sight of your dream

Preface

This work was done between February 2008 and December 2013 at the Laboratory of Industrial Chemistry and Reaction Engineering, Department of Chemical Engineering at Åbo Akademi University. The research is a part of activities of the Åbo Akademi Process Chemistry Centre (PCC), a centre of excellence financed by Åbo Akademi University.

I would like to express my gratitude to my supervisor, Professor Tapio Salmi for his guidance which has been irreplaceable for writing this thesis. Likewise, the help of Dr. Pekka Simell (VTT) and Dr. Matti Reinikainen (VTT) is greatly appreciated. Also, invaluable help has been provided by Dr. Kari Eränen with instrumentation and experimental work.

I would like to thank all my colleagues from the Laboratory of Industrial Chemistry and Reaction Engineering. It has been a privilege and great opportunity to work with all of you. A special thank to Dr. Teuvo Kilpiö for sharing his knowledge and thoughts about modeling.

Last but by no means least, I would like thank my family members for their patience during past years. Thank you Hanna and my parents. And of course my aunt Leila.

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Åbo, November 2014

Petteri Suominen

Abstract

Gasification of biomass is an efficient method process to produce liquid fuels, heat and electricity. It is interesting especially for the Nordic countries, where raw material for the processes is readily available. The thermal reactions of light hydrocarbons are a major challenge for industrial applications. At elevated temperatures, light hydrocarbons react spontaneously to form higher molecular weight compounds. In this thesis, this phenomenon was studied by literature survey, experimental work and modeling effort.

The literature survey revealed that the change in tar composition is likely caused by the kinetic entropy. The role of the surface material is deemed to be an important factor in the reactivity of the system. The experimental results were in accordance with previous publications on the subject. The novelty of the experimental work lies in the used time interval for measurements combined with an industrially relevant temperature interval.

The aspects which are covered in the modeling include screening of possible numerical approaches, testing of optimization methods and kinetic modelling. No significant numerical issues were observed, so the used calculation routines are adequate for the task. Evolutionary algorithms gave a better performance combined with better fit than the conventional iterative methods such as Simplex and Levenberg-Marquardt methods.

Three models were fitted on experimental data. The LLNL model was used as a reference model to which two other models were compared. A compact model which included all the observed species was developed. The parameter estimation performed on that model gave slightly impaired fit to experimental data than LLNL model, but the difference was barely significant.

The third tested model concentrated on the decomposition of hydrocarbons and included a theoretical description of the formation of carbon layer on the reactor walls. The fit to experimental data was extremely good. Based on the simulation results and literature findings, it is likely that the surface coverage of carbonaceous deposits is a major factor in thermal reactions.

Referat

Termiska reaktioner av låga kolväten med låga molekylvikter

Förgasning av biomassa erbjuder en effektiv process för produktion av bränsle, värme och elektricitet. Speciellt användbar är processen för de nordiska länderna som är rika på råmaterial med tanke på denna process. De termiska reaktionerna framför en stor utmaning för hela processen. Vid höga temperaturer, kolväten med låga molekylvikter reagerar spontant och producerar tyngre molekyler. I denna avhandling har detta fenomen studerats genom litteratursökning, experimentellt arbete samt matematisk modellering.

Litteraturarbetet avslöjade att skillnaderna i tjärans sammanfattning beror på kinetisk entropi. Ytmaterialet är en viktig variabel i reaktiviteten för systemet. De experimentella resultaten överensstämmer med tidigare publicerade data. Nyheten i det experimentellt arbetet ligger i det använda intervallet för reaktionstiderna samt industriellt relevant temperaturintervall.

De synpunkter som täcks av matematisk modellering är analys av möjliga numeriska problem, test av olika optimeringsmetoder samt kinetisk modellering. Inga betydande numeriska onoggrannheter observerades och de använda beräkningsrutinerna ansågs vara tillfredsställande. Evolutionära algoritmer fungerade effektivare och gav bättre anpassning till mätdata jämfört med de konventionella iterativa metoder så som Simplex- och Levenberg-Marquardt-metoder.

Tre olika modeller anpassades till experimentella data. LLNL modellen användes som referensmodell för de två övriga modeller. En kompakt modell som innehåller alla observerade komponenter utvecklades. Parameterestimering visade att anpassningen till experimentell data var en aning sämre än för LLNL -modellen men skillnaden var inte avsevärd.

Den tredje testade modellen koncentrerade sig på sönderfall av kolväten och inkluderade en teoretisk beskrivning av formation av kolskikt på reaktorväggarna. Anpassningen till experimentella data var ytterst bra. På basis av simuleringar och litteraturarbete, kan man konstatera högst sannolikt att ytans täckningsgrad av kolrester är en betydande faktor i högtemperaturreaktioner.

Articles & manuscripts

This thesis is a monography based on the following articles and manuscripts.

I. Thermal Reactions of the Main Hydrocarbon Components in Gasification Gas, submitted
II. Parameter Estimation of Complex Chemical Kinetics with Covariance Matrix Adaptation Evolution Strategy, MATCH, Communications in Mathematical and in Computational Chemistry 68 (2012) No. 2, 469-476
III. A reduced reaction mechanism for light hydrocarbon thermal reactions, submitted
IV. Peak Function as a Correction Term for Radical Reaction Kinetics, submitted
V. Modeling of thermal reactions of methane-ethene-hydrogen mixture in quartz glass reactor, submitted

Articles I-V were written and edited by the author. All the experiments, coding and modeling was made by the author.

Conference presentations related to thesis

A reduced reaction mechanism for light hydrocarbon thermal reactions – oral presentation

EU COST Action CM0901 Annual Meeting 2011 Zaragoza, Spain

Parameter Estimation of Complex Chemical Kinetics with Covariance Matrix Adaptation Evolutionary Strategy – oral presentation, Advanced Computational Methods in Engineering 2011 Liége, Belgium

Other scientific work

Hydrogenation of sugars – combined heat and mass transfer

Kilpiö, T., Suominen, P., Salmi, T., Sugar hydrogenation – combined heat and mass transfer, Computer Aided Chemical Engineering, 32 (2013), 67-72

Mass Transfer in a Porous Particle – MCMC Assisted Parameter Estimation of Dynamic Model under Uncertainties

Suominen, P., Kilpiö, T., Salmi, T., Mass Transfer in a Porous Particle – MCMC Assisted Parameter Estimation of Dynamic Model under Uncertainties, Computer Aided Chemical Engineering, 33 (2014), 277-82

Mass Transfer in a Porous Particle – MCMC Assisted Parameter Estimation of Dynamic Model under Uncertainties – accepted for oral presentation

24th European Symposium on Computer Aided Process Engineering 2014 Budapest, Hungary

Hydrogenation of sugars – combined heat and mass transfer – poster presentation

23rd European Symposium on Computer Aided Process Engineering 2013 Lappeenranta, Finland

Contents

1 Introduction

1.1 Biomass gasification

Gasification is a process which converts carbon-containing feedstock at high temperature to syngas. Optimal syngas is a mixture of hydrogen and carbon monoxide with a minor amount of carbon dioxide. The difference between combustion and gasification is in the amount oxygen. In gasification, the amount of oxygen is very small compared to combustion.

The gasification process consists of five principal processes. Dehydration, pyrolysis, combustion, gasification and water-gas shift reaction. During dehydration, water in the gasified material is evaporated. The second step, pyrolysis, produces volatiles and char. After the pyrolysis, resulting char, which can be up to 70 % lighter than the raw material, is gasified and partially burnt. The simplified reaction mechanism for combustion is presented in Eq. 1. Carbon containing compounds (CCC) react with oxygen to produce carbon dioxide and other oxides depending on the composition of the feedstock. Simultaneously, char (CHAR) is gasified by steam. The reaction is given in Eq. 2. The water-gas shift reaction presented in Eq. 3. is a reversible reaction and it alters the carbon monoxide – hydrogen ratio of syngas depending on the process conditions. In practice, syngas contains besides the desired components also methane and other light hydrocarbons. A reaction which produces methane is given in Eq. 4. A subsequent reaction producing ethane is shown in Eq. 5.

$$\mathrm{CCC} + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} \qquad (1)$$

$$\mathrm{CHAR} + \mathrm{H_2O} \rightarrow \mathrm{H_2} + \mathrm{CO} \qquad (2)$$

$CO + H_2O \leftrightarrow H_2 + CO_2$ (3)

$4\ CO + 2\ H_2O \rightarrow CH_4 + 3\ CO_2$ (4)

$CH_4 + CH_4 \rightarrow C_2H_4 + 2\ H_2$ (5)

Gasification as such is an old process. First industrial-scale applications are from the 19th century as town gas was produced either by gasification or carbonization. In 1920's, applications to manufacture synthetic chemicals were introduced and during World War I and II, the production of liquid fuels was an important application of gasification. The renaissance of gasification began in 1990's when the awareness of the green-house effect was increased. The gasification of biomass offers an carbon-neutral way to produce energy.

The total use of biomass for energy production is globally approximately 52 EJ/a[1]. This is one tenth of the total global energy supply. Almost two thirds of this amount is consumed in developing countries for cooking and heating. However, gasification as a process for the utilization of biomass is still quite a minor application. Less than 5 MWth of synthesis gas is produced globally[2].

Gasification of biomass is an efficient alternative for liquid fuel production via Fischer-Tropsch-synthesis or for power and heat production. The gasification process has attended a large global attention and is particularly important for Nordic countries which are rich in woody biomass per capita.

One of the biggest challenges in the gasification of biomass is accompanied with tar formation. This is an obstacle specific to biomass treatment as the gasification of coal does not produce these components. Tar formation has been studied intensively but it still remains a challenge[3]. Tar components cause problems in several steps of the process, for instance, during cleaning and reforming processes[4] by blocking the pipelines. To overcome this big problem, fundamental knowledge about the tar formation and decomposition is needed. This implies that the reaction mechanisms and kinetic models of the radical and catalytic reactions involved should be determined.

At elevated temperatures, hydrocarbons undergo thermal reactions, which include rearrangement reactions, polymerizations, redistribution reactions and numerous decomposition reactions[5]. Even if the amount of tar components formed during the gasification could be suppressed, the lighter hydrocarbons, such as methane and ethene continuously react to produce tar throughout the process, provided that the temperature is sufficiently high. Tar can block pipelines and cause catalyst deactivation. Therefore, an accurate model of the cleaning and reforming processes must include even thermal reactions. In order to develop a model for these steps, it is necessary to understand the various reactions, which produce tar out of lighter hydrocarbons and to reveal how the tar components decompose.

The thermal reactions of the two major hydrocarbons in the gasification gas, ethene[6] and methane[7,8,9], have been investigated previously. There has been published even a study on a ethene-methane mixture but the pressures investigated were below atmospheric, the temperature range was narrower and the residence times used in the experiments were several magnitudes larger than in this work[10].

Thermal reactions of hydrocarbons have been discussed traditionally in the context of crude oil cracking[11]. The thermal reactions are mostly considered to be reactions between radicals, but some important reaction routes between a radical species and a molecular species[12,13] have been suggested, too. The reaction mechanisms are in general very complex.

A particular challenge in modeling this phenomenon is the high uncertainty in published parameter values. Several articles give uncertainties of up to an order of magnitude. This has lead to much debate in scientific community about the accurate values of the kinetic values and in many cases modeling efforts concentrate in fine-tuning a certain part of a large reaction mechanism.

1.2 Aim and scope of this thesis

The aim of this thesis was to investigate how the main hydrocarbon components in gasification gas react under the conditions of gasification gas reforming. The scope of the thesis is limited to atmospheric pressure in order to exclude the pressure from the variable list. The modeling part of the thesis concerns parameter estimation of complex systems appearing in the gasification gas, and discusses the reliability of the literature data of kinetic parameters.

2 Experimental section

2.1 Materials

The reactive gases C_2H_4 (99.995 %), CH_4 (99.995 %), H_2 (99.999 %) and balance gas N_2 (99.999 %) were obtained from AGA Oyj (Finland). All gases were used without further purification. Quartz glass was chosen to the reactor material to avoid possibly catalytic materials present in stainless steel reactors. Two mixtures, the compositions of which are presented in Table 1, were investigated thoroughly. The experiments were conducted between 500 °C and 1000 °C with steps of 100 °C. The residence times were within the range of 10 milliseconds to over 1 second. The amount of samples was in 10 samples at each of temperatures which were six total. The same applies for both mixtures. There were 13 analyzed and quantified species. This was considered to be enough for a reliable kinetic modeling.

Table 1. Gas mixture compositions used in this thesis.

Mixture	Ethene (mol-%)	Methane (mol-%)	Hydrogen (mol-%)	Nitrogen (mol-%)
1	2	10	0	88
2	2	10	35	53

The mole fractions of the reactive components in the gas mixture compositions were selected to correspond to realistic values for a gasification gas originating from biomass.

2.2 Reactor system

A tubular reactor (i.d. 9 mm, length 300 mm) operating in upflow mode was placed in a tubular oven (Carbolite Furnaces MTF 12/25A) for heating. The gas flows were controlled by mass flow controllers (Brooks 5850). The stainless steel tubesbetween the reactor and the analyzer, gas chromatograph (Hewlett-Packard 6890N) (GC), were heated to 170 °C by electric coils to avoid condensation of high molecular weight products. The pressure in the system was monitored on-line and kept at the atmospheric level by withdrawing samples by a continuously running vacuum pump after the GC. This allowed higher flow rates as only a small portion of the total flow passed the narrow GC lines. If the whole flow would have been directed through the GC, the pressure in the system would have raised up to 2 atm. The reactor system is illustrated in Figure 1. The experimental setup is similar to ones used in many literature sources. None of the experimental setups in literature use a vacuum pump for sampling which enabled higher flow rates and lower residence times than are typically used in studies of this phenomenon.

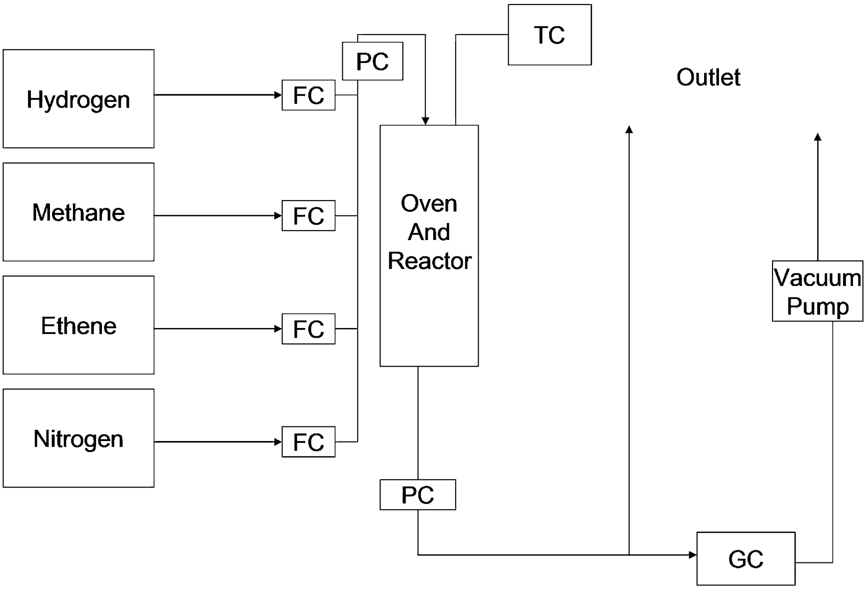

Figure 1. Flowsheet of experimental apparatus.

2.3 Analytical procedure

The products were analyzed by an on-line GC (Hewlett-Packard 6890N) with two columns in series: Porapak HP-Plot Q (length 30 m, i.d. 0.53 mm, film 25 μm) and HP-Mol Sieve (length 30 m, i.d. 0.53 mm, film 40 μn). Hydrogen and the lightest hydrocarbons were allowed to pass both columns but heavier hydrocarbons passed the first column only.

The main hydrocarbons, C1-C4 alkanes, alkenes, alkynes and 1,3-butadiene were calibrated against an internal standard. Off-line GC-MS (Agilent 6890N with Agilent 5973Network mass detector) was used to identify the unknown compounds. The hydrocarbon concentrations were quantified by flame ionization detector (FID) and hydrogen concentration by a thermal conductivity detector (TCD).

The calibration gas mixtures which were used in the calibration have relative uncertainties, which influences the accuracy of the analysis results. These effects were calculated and they all were below 0.1 %. The repeatability of the analysis was checked by doing parallel measurements at randomly selected temperatures and residence times. For each point tested the relative standard deviations were below 1.0 %.

3 Modeling aspects

Modeling the thermal reactions of light hydrocarbons is in general a very tedious task. There are basically two possible directions where to proceed; either large, detailed models varying from several hundreds of reactions[14,15] to over 16000 elementary reactions[16] and everything in between[17] or, alternatively engineering models based on the few non-elementary reactions can be considered.

For industrial applications, models based purely on hydrocarbon reactions are not sufficient as there are minor and trace compounds present in the gasification gas, for instance ammonia, NO_x, hydrogen sulfide, and SO_x, in product mixtures which affect the product distributions. Therefore, detailed models become even larger. They are needed to gain insight in the mechanisms of soot formation. As the models grow larger, their applicability to practical cases which require rapid solutions, is reduced.

Engineering models have their advantages as well as their disadvantages. Their computational cost is much lower, but they do not offer any mechanistic explanation to the physical phenomena behind the soot formation. They are also restricted to a quite narrow operating window. New parameters must be estimated always when the operating conditions are altered. The issue is that the new parameters might significantly differ from the old ones which makes the parameter estimation task harder. This kind of model has always a strongly adaptive character.

The parameter estimation, which is a numerical optimization problem, becomes more and more challenging as the dimensionality of the system increases. This is mainly because the choice of the initial parameter values becomes harder and harder as the amount of local minima increases in the objective function. Another issue in the parameter estimation is presented in Figure 2. If the shape of the minimum is highly oblong, the path which an iterative method such as a Newton or a quasi-Newton algorithm takes may become long and the maximum allowed number of iterations is reached before the absolute minimum is reached.

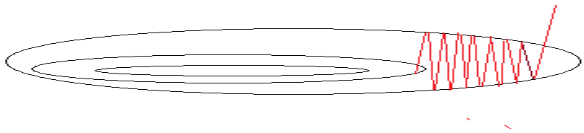

Figure 2. Badly chosen initial value for a gradient-based method.

3.1 Optimization approach

Stochastic optimization methods such as evolutionary algorithms (EA), swarm algorithms, simulated annealing, quantum annealing and many others offer a way to overcome to some extent the previously presented problems related to the dimensionality of the optimization problem. A recent review article was written by L. Elliott et al.[18]

The main challenge in using classical Newton and quasi-Newton algorithms is the need of finding suitable initial values for the algorithm. If suitable initial values are found, iterative methods outperform the stochastic methods. In recent years, hybrid algorithms[19] have gained popularity to combine the advantages of the both optimization method classes.

An interesting idea was presented by L. Elliott et al.[20]. In their work, they combined the parameter estimation with the mechanism reduction scheme. The results obtained by this method in their study are comparable to those obtained by commonly used mechanism reduction methods.

As a working hypothesis, it was assumed that a probable cause for the inaccuracies in model predictions could be the challenges in optimization. For that reason, a state-of-art, stochastic optimization algorithm, evolutionary strategy with covariance matrix adaptation(CMA-ES)[21] was tested in this study.

The detailed models of tar formation from light hydrocarbons are very complex, consisting of several hundreds of reactions. As the amount of estimated parameters can be as high as three times the amount of reactions, parameter estimation of chemical kinetics for tar formation is a practical example of an optimization problem, for which conventional gradient/derivative based algorithms are difficult to implement. It has been proposed that the limit above which stochastic optimization methods outperform the gradient based methods is as low as ten dimensions.

After noticing that the problem was not in optimization, a more easily applicable stochastic optimization routine build around the PyEvolve[22] package was used.

3.1.1 Evolution algorithms in general

Evolution algorithms are effective and robust methods for optimization. Their biggest disadvantage is the poor convergence performance and therefore they are most efficient in global optimization problems that have many local optima. They have been used in parameter estimation of complex chemical kinetics, but have not gained popularity over conventional gradient/derivative based methods, which are computationally lighter in simpler parameter estimation tasks. In large parameter estimation tasks, however, evolution algorithms have a clear advantage as the choice of initial parameter values is by far simpler task as it is for gradient/derivative based methods.

Evolution algorithms can be divided in different techniques based on the implementation details. These techniques include genetic algorithm, genetic programming, evolution programming, neuroevolution and evolution strategy. For this paper, an evolution strategy (ES) was chosen for parameter estimation. The selection process in evolution strategies is based on the fitness rankings rather than the actual fitness values and it is deterministic. This is one of the main reasons for the robustness of ESs. Besides selection, mutation is used as a search operator. The step-size of mutation is often governed by self-adaptation to keep the progress in the evolution window. Another technique to ensure the convergence to the optimum of a function is cumulative step size adaptation.

Evolution strategies have been previously used in parameter estimation of complex chemical kinetics by Polifke et al[23]. In that work, a simple $(\mu + \lambda)$-ES by Rechenberg et al[24]. was used. Some improvements to this work has been proposed by Elliott el al[18]. including addition of recombination operation, which is occasionally used in evolution strategies to prevent the algorithm to stuck on local optima. Other types of evolution algorithms, mainly genetic algorithms, and also other types of stochastic algorithms, such as particle swarm and differential evolution (DE) have also been applied to parameter estimation in chemical kinetics.

3.1.2 Evolutionary strategy with covariance matrix adaptation

To our work, an evolution strategy with covariance matrix adaptation (CMA-ES) by Hansen and Ostermeier[21] was chosen. Hansen and Ostermeier depict the step to CMA-ES from an ES with isotropic mutation distribution as comparable to a step from a simple gradient-based method to a quasi-Newton method, e.g. a step from local gradient to approximation of inverse Hessian matrix. CMA-ES has already been applied to many real-world search problems. The advantage of CMA-ES over the conventional ESs is the added invariance properties.

3.1.3 In-house stochastic optimization routine based on the PyEvolve

For parameter estimation of the surface corrected model, a stochastic optimization routine was programmed. The software utilizes the PyEvolve package[22]. The algorithm behind the package is not as sophisticated as the CMA-ES but much more easier to implement in practice and actually just as effective. The code of the our implemantion is presented in Appendix 2.

3.2 Parameter estimation software

The parameter estimation software mostly used in our laboratory, Modest[25], was soon deemed too cumbersome to be applied in this kind of work. The reason for this is that many of the published models are available as a Chemkin[26] input file which is completely different from Modest input files. Therefore, a new parameter estimation software was designed and programmed. The software is presented in detail in Appendix 1. It is based on the Chemkin II software[26] which was distributed as a source code. The parameter estimation software utilized the pre-processor and Senkin modules of the Chemkin II to simulate the reaction scheme. The CMA-ES parameter estimation software was used to find the optimal values for kinetic parameters. The software includes also an in-house driver and post-processor. The software is schematically presented in Figure 3.

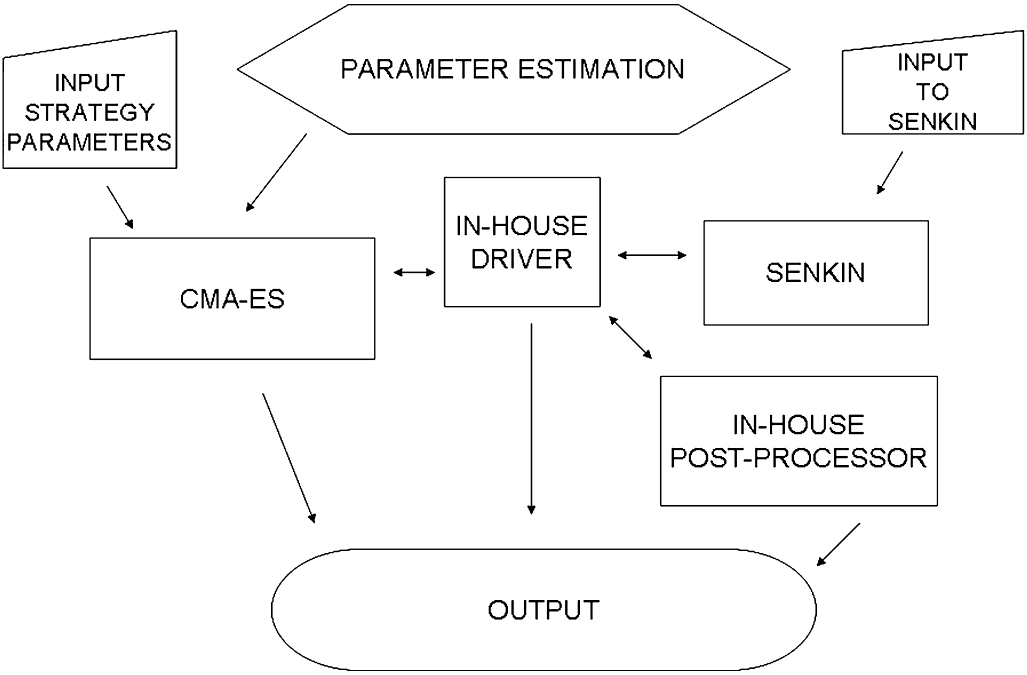

Figure 3. A schematic view of the parameter estimation software use in this work.

The initial strategy parameters are manually inserted to CMA-ES algorithm. Likewise, the model is written to an input file to the SENKIN module of the CHEMKIN II software package. The parameter estimation is started and CMA-ES sends the proposed coefficients for parameters to in-house driver program. The SENKIN module simulates the model with parameter values, which are calculated to be the product of the proposed coefficient and literature value of the respective kinetic parameter. After a successful simulation, the in-house driver starts the in-house post-processor, which calculates the sum of squares of the simulated values and our experimental results. The post-processor returns this value to driver which returns it to CMA-ES algorithm as a fitness value. At the same time, both in-house modules record the all-time best values. CMA-ES then proposes new values for coefficients, which undergo the same process until a termination condition is met. When a termination condition is met, CMA-ES produces the results of its workings. The in-house driver produces a CHEMKIN input file with best found parameter values and post-processor gives results in a form, which can easily be plotted graphically.

3.3 Key reactions

The reaction network for this kind of system is complex. Figure 4 presents the possible reactions of hydrogen radicals with ethyne, ethene and ethane. There are two principal reactions: abstraction and addition. A radical species is created in both cases. The same applies for ethane and ethyne.

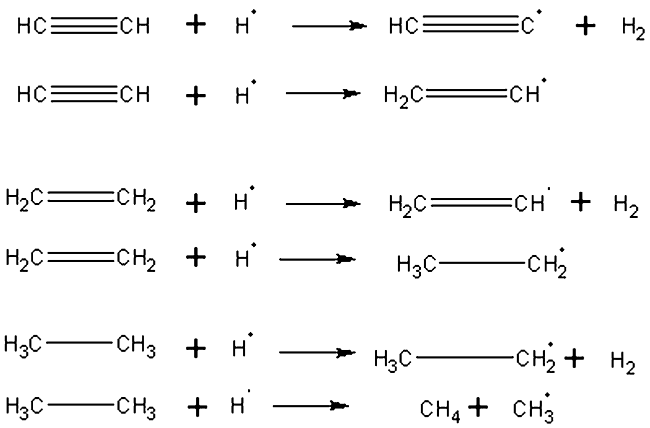

Figure 4. Hydrogen radical attack on ethyne, ethene and ethane.

The situation increases rapidly in complexity as illustrated in Figure 5. The number of possible reactions is now five as the length of hydrocarbon increases by one carbon atom. If similar figures would be drawn for even longer hydrocarbon species, the amount of reactions would increase further.

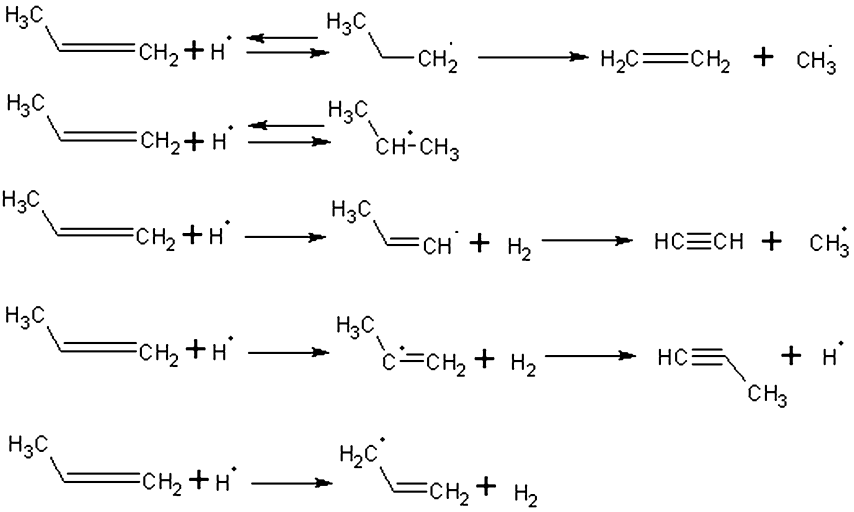

Figure 5. Hydrogen radical attack on propene.

It is worth noticing that at elevated temperatures, a variety of energetically strained radicals can exist which additionally increases the size of the reaction system.

Obviously, the hydrocarbons do not necessarily react solely with hydrogen radicals. It is totally possible that the opposite occurs, that is, hydrogen molecule reacts with hydrocarbon radicals, and the hydrocarbon-hydrocarbon reactions are also possible. The only limitation is that the molecule-molecule reactions are much slower than the molecule-radical reactions. Radical-radical reactions can also occur but the low concentrations of the radical species make these reactions less probable.

Campbell et al[27] have studied the methyl radical coupling in the presence of catalytic materials. They concluded that at least 40 % of the ethane formed is a result of gas-phase reactions, not surface reactions. Cho et al.[28] concluded that the formation of hydrocarbon radicals cannot be solely a gas-phase process. Grubbs and George[29] have studied the effect of different reactor materials on the hydrogen radical concentrations and their results show that there is a clear difference in the concentrations depending on the reactor material.

It seems that even though the formation of radicals occurs in large extent on the surfaces of the reactor, even on the catalytically inactive ones, the radicals react in gas phase. Therefore, the physical properties of the surfaces in the reactor vessel affect strongly the product distributions. To further complicate the issue, the carbonaceous deposits formed in the reactor have different surface properties than the reactor materials which results in time-dependent sorption effects.

The results obtained by Kopinke et al.[30] show that the formation of carbon layer depends on the reactor material. The process on steel surface is highly erratic. Some unsteady behavior can be observed also on quartz surfaces but the experimental data show that the process proceeds in S-curve like fashion.

The erratic characteristics of the carbon layer formation on steel surfaces is an unfortunate effect in modeling industrial applications. Fortunately, the surface area-to-volume ratio[31] in industrial applications is such that the importance of the surface reactions is likely to be less than in a laboratory scale.

3.4 Entropy contributions

In an *ab initio* study, Li and Brenner[32] calculated rate constants and analyzed the enthalpy and entropy effects on them. Based on quantum chemical calculations, they concluded that at temperatures relevant to this study, the entropy is an important variable when considering the product distributions. The translational entropy increases the probability of the β-scission reaction, which is illustrated in Figure 6, compared to the addition of a hydrogen atom to an unsaturated hydrocarbon. These calculations are in accordance with experimental results of Rye[33] and Balooch and Olander[34]. Similar results were also obtained by Frenklach[35] by numerical simulations.

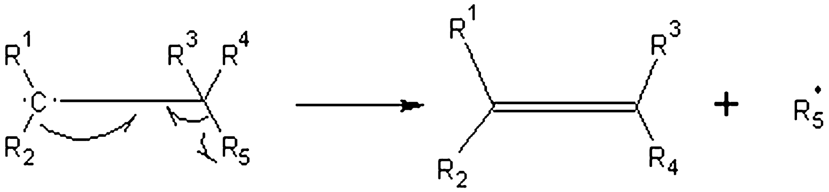

Figure 6. Beta-scission reaction.

Rotational entropy favors hydrogen abstraction reactions. Perhaps the most notable consequence of the entropy considerations is how the β-scission is favored over the hydrogen addition reaction at higher temperatures. This was experimentally observed by Rye[33] and similar results were obtained by Li and Brenner[32] by quantum chemical calculations. Without taking the entropy effects into account, addition reactions would dominate over β-scission even at high temperatures. Interestingly, the tar formed in lower temperatures is aliphatic but aromatic tar is formed at higher temperatures. The results obtained by Spence and Vahrman[36] show that over 10 % of dry tar can consist of paraffins and olefins. There is no literature about significant amounts of aliphatic compounds present in tars from high-temperature gasification processes.

Surface chemical studies would be highly interesting in estimating the role of entropy in the tar formation. A possible explanation to different kinds of tar produced in different temperatures is the reduction of rotational and translational entropy for molecules in an interaction with a surface. This would cause different products for pure gas-phase systems as well as catalyzed, Eley-Rideal and Langmuir-Hinshelwood types of reaction systems. Studying this would require experimental work to determine at which temperatures surface reactions are possible on pure quartz and on carbonaceous deposits.

3.5 Modified Arrhenius equation – thermodynamic explanation for challenges in modeling

An interesting aspect in modelling the chemistry related to combustion and gasification processes is a modified Arrhenius equation presented in Eq. 6. The resemblence to an expression used in transition state theory (TST), which is shown in Eq. 7, is apparent.

$$k = A \cdot \left(\frac{T}{T_{ref}} \right)^{n} \cdot \exp^{\frac{-E_a}{R \cdot T}} \tag{6}$$

$$k = \frac{k_b \cdot T}{h} \cdot \exp^{\frac{\Delta S_c^{\circ,\mp}}{R}} \cdot \exp^{\frac{-\Delta H_c^{\circ,\mp}}{R \cdot T}} \tag{7}$$

Based on the literature findings presented in previous chapter, it is clear that the entropy contributes to the product distributions of the thermal reactions. This leads intuitively to think that the exponential temperature dependency in modified Arrhenius equation in this application, actually depicts the entropy contribution of the reaction. If this thought is developed further, a probable cause for deviation of the predictions by detailed reaction mechanisms can be worked out. There are namely problems with applying transition theory to high temperature radical reactions.

First, the transition theory assumes that all the intermediate species can reach a Bolzmann distribution of energies. That is, the intermediate species are enough stable and therefore being enough long-lived. If this is not a case, then the momentum of reaction trajectory from reactants to intermediates can be transferred to products, which affects the product distributions. As many of the hydrocarbon radical species are short-lived, there is a good chance that the product distributions differ from the theoretical ones even though the kinetic constants would be correctly defined for every elementary reaction in mechanism.

Second, the transition state theory fails if the atomic nuclei do not behave according classic mechanics. In quantum mechanics, for every barrier with finite amount of energy exists a possibility that a particle can tunnel across. Many of the activation energies are low in radical species reactions. Therefore, probability for tunneling increases and again, the product distributions may differ from the ones predicted by classical kinetics.

Third, according to transition state theory the reactions proceed through the lowest energy saddle point at potential energy surface. This is the case for reactions at low temperatures but at high temperatures, higher energy vibrational modes are populated. This leads to more complex behavior of the molecules and ultimately to transition states which are far away from the energetic minimum. And even this phenomenon increases the deviation from the predicted product distributions.

3.6 Positive and non-positive activation energies

Conventionally, the activation energy of a reaction is considered to be equivalent to the energy barrier between two minima of the potential energy. The value of activation energy is positive for both exo- and endothermic reactions. In some cases the activation energy can be non-positive. The theoretical background for this phenomenon has been published by Houk and Rondan[37] and Mozurkewich and

Benson[38]. The background is most easily presented by the Tolman interpretation of the activation energy[39] presented in Eq. 8.

$$E_{act} = \langle E \rangle_{TS} - \langle E \rangle_{R} \qquad (8)$$

The activation energy (E_{act}) is a difference of the average energies of the transition state ($\langle E \rangle_{TS}$) and reactants ($\langle E \rangle_{R}$). Three cases are possible.

In the first case, the transition state is a tight one. Some of the degrees of freedom are transformed to vibrational modes as the reactants are transformed to the transition state. Generally, this has a very minor effect on the average internal energy by the decrease in the kinetic energy and the increase in the potential energy by the breaking and forming of the bonds is much larger. In this case, which is also the most common one, the activation energy is positive.

The second alternative is that the transition state is loose. Neither the changes in the potential energy or the kinetic energy are significant and the activation energy is very close to zero.

A negative activation energy is the consequence of the third alternative. This can happen if the reaction which is assumed to be elementary is not truly elementary but proceeds via a stable intermediate. In this case, the types of the transition states between the reactants and the intermediate, and the intermediate and the products together with the magnitudes of their energy thresholds dictate the sign of the activation energy.

3.7 The models used

3.7.1 LLNL model

The LLNL model[40] is a classical detailed reaction mechanism for gas-phase reactions of light hydrocarbons. It includes 687 reversible reactions and has been validated for n-butane, propane, ethyne, ethane and methane. It was chosen to be the standard model to which the other tested models were compared.

3.7.2 A compact model

In many literature sources, it is stated that some of the kinetic parameters for detailed mechanisms of gasification and combustion are not estimable at all or only in order of magnitude. The assumption was made that a reduction of the dimensionality of the model would result in easier parameter estimation tasks. Therefore, a compact model which includes all the observed species, was designed. The reaction mechanism consists of 37 reversible reactions and 30 species. This model is presented in Table 2.

Table 2. Rate constant parameters after the parameter estimation. Units are cm, mole, cal, K and Pa. Reference is for the publication from which the reaction has been taken.

	reaction	A	n	E_a	Ref
1	$C_2H_4 + C_2H_4 \leftrightarrow C_2H_5^{\bullet} + C_2H_3^{\bullet}$	4.72E14	0.00	7.13E4	[41]
2	$C_2H_4 + CH_4 \leftrightarrow C_2H_5^{\bullet} + CH_3^{\bullet}$	1.41E9	0.00	1.00E3	[14]

3	$H_2 \leftrightarrow H^\bullet + H^\bullet$	6.55E4	0.00	1.02E5	41
4	$C_2H_4 + H_2 \leftrightarrow C_2H_5^\bullet + H^\bullet$	1.03E13	0.00	6.82E4	41
5	$CH_4 \leftrightarrow CH_3^\bullet + H^\bullet$	6.26E20	0.00	1.02E5	41
6	$C_2H_3^\bullet + C_2H_4 \leftrightarrow C_4H_6 + H^\bullet$	4.98E11	0.00	7.31E3	41
7	$C_2H_4 + H^\bullet \leftrightarrow C_2H_3 + H_2$	7.00E13	0.00	2.87E3	41
8	$C_2H_4 + C_2H_5^\bullet \leftrightarrow C_2H_3^\bullet + C_2H_6$	1.38E13	0.00	2.19E4	41
9	$C_2H_5^\bullet + H_2 \leftrightarrow C_2H_6 + H^\bullet$	2.56E12	0.00	1.30E4	41
10	$C_2H_5^\bullet + C_2H_5^\bullet \leftrightarrow C_4H_{10}$	1.07E13	0.00	0	41
11	$C_2H_4 + C_2H_5^\bullet \leftrightarrow C_4H_9^\bullet$	2.83E11	0.00	8.06E3	41
12	$C_4H_9^\bullet \leftrightarrow C_4H_8 + H^\bullet$	9.71E13	0.00	3.84E4	42
13	$C_2H_2 + C_4H_9^\bullet \leftrightarrow C_3H_5^\bullet + C_3H_6$	7.22E11	0.00	9.00E3	43
14	$C_4H_9^\bullet \leftrightarrow C_3H_6 + CH_3^\bullet$	1.97E13	0.00	3.00E4	14
15	$C_2H_4 + CH_3^\bullet \leftrightarrow C_3H_7^\bullet$	3.34E11	0.00	7.71E3	14
16	$C_3H_7^\bullet + C_2H_3^\bullet \leftrightarrow C_3H_8 + C_2H_2$	1.22E12	0.00	0	44
17	$CH_3^\bullet + CH_3^\bullet \leftrightarrow C_2H_5^\bullet + H^\bullet$	1.05E13	0.00	1.07E4	45

18	$C_2H_3^\bullet \leftrightarrow C_2H_2 + H^\bullet$	7.74E16	0.00	3.61E4	41
19	$C_2H_3^\bullet + H^\bullet \leftrightarrow C_2H_2 + H_2$	9.73E13	0.00	0	41
20	$C_2H_4 + H^\bullet \leftrightarrow C_2H_3^\bullet + H_2$	2.99E14	0.00	1.54E4	41
21	$CH_4 + H^\bullet \leftrightarrow CH_3^\bullet + H_2$	1.84E14	0.00	1.25E4	41
22	$CH_3^\bullet + C_2H_3^\bullet \leftrightarrow C_2H_2 + CH_4$	3.92E11	0.00	0	41
23	$C_3H_6 + H^\bullet \leftrightarrow C_3H_5^\bullet + H_2$	3.14E13	0.00	5.63E3	46
24	$C_2H_4 + M \leftrightarrow C_2H_2 + M + H_2$	4.00E15	0.00	9.03E4	41
25	$C_4H_6 + H^\bullet \leftrightarrow C_4H_5^\bullet + H_2$	3.40E12	0.00	6.00E4	47
26	$C_4H_5^\bullet + H^\bullet \leftrightarrow C_3H_3^\bullet + CH_3^\bullet$	9.81E13	0.00	0	14
27	$C_3H_3^\bullet + C_3H_3^\bullet \leftrightarrow C_6H_5^\bullet + H^\bullet$	2.96E12	0.00	0	48
28	$C_3H_3^\bullet \leftrightarrow C_3H_2^\bullet + H^\bullet$	4.96E12	0.00	7.84E4	14
29	$C_3H_3^\bullet + C_3H_2^\bullet \leftrightarrow C_6H_5^\bullet$	4.93E13	0.00	0	14
30	$C_6H_5^\bullet + CH_3^\bullet \leftrightarrow C_7H_8$	3.95E12	0.00	0	14
31	$C_4H_6 + C_3H_5^\bullet \leftrightarrow C_5H_5^\bullet + C_2H_6$	9.74E12	0.00	2.26E4	14
32	$C_6H_5^\bullet + H_2 \leftrightarrow C_6H_6 + H^\bullet$	3.95E12	0.00	7.89E3	14

33	$C_6H_5^\bullet + C_2H_2 \leftrightarrow C_8H_6 + H^\bullet$	3.95E12	0.00	1.01E4	[41]
34	$C_8H_6 + H^\bullet \leftrightarrow C_8H_5^\bullet + H_2$	2.51E14	0.00	1.60E4	[41]
35	$C_8H_5^\bullet + C_2H_2 \leftrightarrow C_{10}H_7^\bullet$	4.09E13	0.00	1.01E4	[41]
36	$C_{10}H_7^\bullet + H_2 \leftrightarrow C_{10}H_8 + H^\bullet$	1.02E14	0.00	7.89E3	[41]
37	$C_5H_5^\bullet + C_5H_5^\bullet \leftrightarrow C_{10}H_8 + H^\bullet + H^\bullet$	9.83E10	0.00	8.00E3	[41]

The presented reaction mechanism is based on the literature survey. Main source of reaction and kinetic data is the kinetic database of National Institute of Standards and Technology (NIST). The species in the model were chosen based on our experimental work. After the selection of the species, some well-known reactions were chosen as a backbone of the model. Then several combinations of different published reactions were tested and the combination which gave the best fit to experimental data was chosen. During the whole process of selecting reactions, the different stages of chain reaction were considered, so that the necessary branching was obtained.

The goal of the modelling was to keep to the number of reactions to the minimum, with reasonable accuracy, so that the model could be implemented to engineering environment tools where computational effort is required to other calculations as well. The model was also limited to gas-phase reactions at the moment. Different surface reactions are of even greater interest than the gas-phase reactions but the analysis of such reactions would require a new experimental setup.

The mechanism is initiated by the reactions 1-5 forming the hydrogen, methyl, vinyl and ethyl radicals. The first molecular product formed is 1,3-butadiene by the Reaction 6. Also C2-species, ethyne and ethane are formed in the early phase of the reaction scheme. There are several reactions leading to these species. They are needed to obtain the necessary form of the chain reaction with enough branching reactions compared to inhibiting ones. Combination reactions between C2-species form the C4-species and C3-species are formed mainly from the rearrangement reaction between C2-species and C4-species or by decomposition reactions of C4-species, although one reaction, number 15, between a C2-species and methyl leads to formation of propyl radical.

1,3-butadiene is an important intermediate to the formation tar and soot precursors. Consecutive reactions with hydrogen radicals form a propargyl and propadienylidene radicals which form phenyl radical by the Reactions 30 and 32. Another route to cyclic compounds which was chosen to model proceeds also via 1,3-butadiene. Together with allyl radical it forms cyclopentadienyl which can react to other cyclic and polycyclic compounds. Ethyne is an important species for the growth of the aromatic compounds and the consecutive addition of ethyne to phenyl yields naphthalene according to Reactions 33-36. Naphthalene is also the heaviest compound in our model.

Hydrogen radicals are the driving force in the chain reaction. They are formed in 14 different reactions and consumed in 8 reactions. This explains also the importance of the form of the reaction mechanism. The mechanism needs to be constructed so that the formation rate of hydrogen radicals is equivalent to the formation rate of hydrogen radicals in the reactor. In a way, this may seem obvious but in constructing a reduced reaction mechanism which depicts the formation of tar and soot from the lighter hydrocarbons, it is not necessary to model every reaction and species. Some of the reactions and species have very little or even no effect on the outcome of the model. These can be identified by mathematically analysing the equation system.

3.7.2.1 Sensitivity analysis of the reduced reaction mechanism

The sensitivity analysis was performed by SENKIN part of the Chemkin 2 software package. The results of these analyses were used to identify the most dominant parameters in the system. The sensitivity coefficients were calculated to the reactants: hydrogen, methane and ethene. Besides these, benzene was investigated by sensitivity analysis. This is unfortunately only a theoretical investigation as no experimental data is available for benzene. Benzene is among the unwanted species and therefore interesting compound for the sensitivity analysis. A positive coefficient indicates that the reaction enhances the species production and a negative one is a sign of opposite effect.

3.7.2.1.1 Methane

In the presence of hydrogen, methane at 1000 °C was sensitive to three reactions. Its production was enhanced by the Reactions 27 and 30. The Reaction 33 competes with the Reaction 30 and therefore methane production was negatively influenced by it. At 900 °C, the same reactions were important but two new important reactions appeared. Reaction 22 consumes methane and Reaction 24 forms methane. At 800 °C, methane is no longer sensitive towards Reactions 24 and 33. As temperature is lowered to 700 °C and 600 °C, only Reaction 27 remains influential on the methane concentration. At 500 °C, methane is not sensitive to any of the reactions. This according to literature findings which propose that methane works as a radical transfer species. Our experimental work does also support this as methane is neither formed nor consumed at lower temperatures. It seems that methane does have a minor role in the formation aromatic compounds but otherwise it only affects the overall reactivity of the system.

In comparison, if the mixture did not contain hydrogen methane sensitivity was considerably lower at lower temperatures. On contrary, high temperatures exhibit a different behaviour. Methane sensitivity is higher if no initial hydrogen is present in the mixture. The probable cause is the formation of hydrogen from the methane by direct decomposition which is reported to happen at temperatures above 875 °C. At high temperatures, aromatic compounds are forming and as with previous mixture, methane is slightly affected by the Reactions 27, 30, 33, 34 and 37 at 900 °C and 1000 °C. Likewise, at 800 °C is still high enough temperature for the formation of aromatic compounds and methane was sensitive to Reactions 30, 33 and 34. Reactions 30 and 34 lower the methane concentration and Reactions 37, 33 and 27 increase it. At 700 °C, there is a clear difference to hydrogen containing mixture. Methane was sensitive to Reactions 30 and 33 instead of 27 and interestingly Reaction 30 affects negatively the concentration of methane rather than positively as it was the case in the hydrogen containing mixture. This depends most likely on the fact there is very little hydrogen in the system competing for the methyl radicals as the formation of hydrogen begins at temperatures over 700 degrees in hydrogen free mixtures. At 600 and 500 °C methane was even more passive than in the presence of hydrogen.

3.7.2.1.2 Hydrogen

Initially hydrogen free mixture produces hydrogen at elevated temperatures. The sensitivity analysis of this mixture at 1000 degrees shows that many reactions affect the system. Reactions 18, 24, 27, 33 and 37 enhance the consumption of hydrogen and Reactions 22, 30 and 34 produce hydrogen. Termination Reactions 22 and 30 cause the increase in hydrogen production as the amount free radicals in the system diminishes and this increases the probability hydrogen radicals abstract hydrogen from molecular species. The Reaction 27 increases the concentration of phenyl radicals which then react with hydrogen and Reaction 24 produces precursor to this pathway. At 900 °C Reaction 21 is also sensitive for the hydrogen concentration and produces hydrogen. At 800 °C, same reactions were detected. Difference is that Reactions 18, 33 and 37 have a positive effect on the hydrogen concentration whereas Reaction 22 starts consuming hydrogen. At temperature below 800 °C, only traces of hydrogen were observed in the experiments. This does not though affect the sensitivity analyses. Same reactions are sensitive as a new reaction, Reaction 15 becomes relevant. This indicates that the radical transfer properties of methane are important. As temperature is lowered by another 100 °C to 600 °C, same reactions are still important, but also Reaction 25 becomes important. This would indicate that 1,3-butadiene plays some role also in the formation of aliphatic tar and not just in the formation of aromatic tar and soot compounds. At the lowest temperature in our work, the amount of relevant reactions increases. This suggests that hydrogen has an important role in the formation aliphatic tar compounds.

There were plenty of important reactions in the initially hydrogen free mixture but the case is different for hydrogen containing mixture. At 1000 °C and 900 °C only 3 reactions are sensitive. These are numbers 27 and 30 which consume hydrogen and number 33 which forms hydrogen. At 800 °C two more hydrogen consuming reactions are found, numbers 21 and 22. This is caused most likely by the radical transfer properties of methane. At 700 °C Reaction 33 produces hydrogen and Reactions 15, 20 and 22 consume it. At 600 °C and 500 °C only hydrogen consuming reactions were of some importance, namely 20 and 22.

3.7.2.1.3 Ethene

Ethene has the highest conversions of the initial compounds. At 1000 °C without initial hydrogen its consumption is enhanced by the Reactions 33 and 37 and production is enhanced by the Reactions 30 and 34. At 900 °C the same reactions are enhancing the production but there are more reaction affecting the consumption, namely Reactions 18, 21, 22, 24, 25, 33 and 37. One hundred degrees lower, at 800 °C still the same reactions are responsible for the enhancement of production rate but the consuming reactions alter again. This time the Reactions 21, 27, 33 and 37 were analysed. Even in the context of ethene reactivity, the transfer from aromatic products to aliphatic products can be observed in the sensitivity analysis. At 700 °C, Reactions 30 and 34 are enhancing the production of ethylene but amount of important consuming reactions diminishes and only Reaction 33 was identified by the sensitivity analysis. At even lower temperatures, there are no clearly influential reactions.

Comparison to hydrogen containing mixture it is interesting that as was the case with methane, the reactions effects can be inverted between the two mixtures. At 1000 °C, both Reaction 30 and 33 have opposite effects compared to hydrogen-free mixture. Reaction 33 enhances the formation and Reactions 24, 27 and 30 do the opposite. This is actually the opposite to the behaviour of methane. At 900 °C the situation is basically the same, only the numerical values are slightly lower and also Reaction 22 is important. At 800 °C only consuming reactions were found. These are Reactions 15, 20, 21, 22, 24, 25, 27, 30 and 33. 700 °C is similar, there is one more consuming reaction, Reaction 19, and the values are lower. At 600 °C, Reactions 15, 20, 21, 22, 27, 33 and 34 enhance the consumption of ethene. At 500 °C, the consuming reactions are 20, 22, 27 and 34.

3.7.2.1.4 Benzene

Benzene is one of the unwanted products of the thermal reactions. At 1000 °C, the strongest favouring effect on the formation comes from the Reactions 7 and 27. This corresponds to pathway via 1,3-butadiene. The strongest opposite effect comes from the Reactions 3 and 33. Reaction 33 is not wanted as it leads to heavier aromatic compounds. Reaction 3 is also the strongest inhibiting reaction at 900 °C. The strongest formation favouring Reactions are 1 and 33. At 800 °C, strongest formation favoring Reactions are 1, 2, and 33. The strongest reactions in favouring the consumption are 6 and 9. At 700 °C and below, it becomes harder and harder to find reactions which would favour the consumption of benzene. Other side is that the production rate of benzene becomes practically zero.

Results from the hydrogen containing mixture are quite similar at 1000 °C differing only slightly in magnitude. At 900 °C and below it is not possible to find reactions which would favour the consumption of benzene. It seems that hydrogen plays an important role in the formation of tar and soot.

3.7.3 A surface activity corrected model

The reaction mechanism presented in Eq 9-15 was fitted to experimental data[49]. As proposed by Cho et al [50], even though the reactions mostly occur in gas-phase, the formation of radical species takes largely place on the surfaces of the reactor walls. Therefore, the mechanism includes a component for carbonaceous deposit (CD) on the reactor wall. The surface properties of quartz glass and the formed carboneous deposits are different and assumptions was made that carbon coating is more active in forming hydrocarbon radicals. Another assumption is that the formation of the layer occurs so that the growth of an existing deposit is more likely than a formation of a new nucleiting centre. This assumption is in accordance with the visual inspection of the reactor as after experiments with short residence times, the reactor walls were covered with spots of deposits. With longer residence times, these spots grow in area.

The mechanism consists of six irreversible reactions and a sigmoidal growth curve for carbonaceous deposits (CD).

$$CH_4 + CD \rightarrow PSEUDO \tag{9}$$

$$C_2H_4 + C_2H_4 \rightarrow PSEUDO \tag{10}$$

$$C_2H_4 + CD \rightarrow PSEUDO \tag{11}$$

$$PSEUDO + CD \rightarrow PRODUCTS \tag{12}$$

$$PSEUDO + CD \rightarrow CH_4 \tag{13}$$

$$PSEUDO + CD \rightarrow C_2H_4 \tag{14}$$

$$CD(t) = \frac{A_1 - A_2}{1 + e^{\frac{t - x_0}{dx}}} + A_2 \tag{15}$$

The idea behind the surface activity corrected model is that the formation of carbonaceous deposit on the reactor walls has a different proficiency to form hydrocarbon radicals than the clean quartz glass surface. The activity is assumed to increase in a fashion of a sigmoidal curve. This assumption was made based on visual inspections made occasionally on the reactor after an experiment. If the residence time was short, there were only tiny black spots spread around the reactor walls. With prolonged residence times, the spots grew covered more and more of the surface.

The purpose of this model is to answer the question whether the reactor surfaces affect the outcome of gas-phase reaction scheme. That is why the model concentrates on the decomposition of methane and ethene.

The mechanism consists of five components: methane (CH_4), ethene (C_2H_4), pseudo intermediate (PSEUDO), stable products (PRODUCTS) and carbonaceous deposits (CD). Other components besides CD are stoichiometric but to depict a sigmoidal curve with elementary kinetics would have required several more reactions and therefore a Bolztmann curve was chosen to model the growth of the carbon layer on the reactor surface.

The Bolztmann curve is a sigmoidal curve which has four parameters. A_1 and A_2 are the initial and final value. Two other parameters, x_0 and dx correspond to point of inflection and time constant. For the parameter A_2, unity was chosen for value. The parameter values for A_1, x_0 and dx were estimated. The Bolztmann curve was chosen over other sigmoidal curves because of its combination of simplicity and easy adjustability.

Many sources suggest that a molecule-molecule reaction between two ethene molecules is a typical initiation reaction for thermal reactions of major hydrocarbon components in biomass gasification gas. Therefore, it was chosen as an initiation reaction to mechanism. But a mechanism consisting only of molecule-molecule reactions is unrealistic and five reactions, one for each hydrocarbon component and three for pseudo intermediate was taken into mechanism. These reactions represent molecule-radical reactions.

This approach is limited to mixtures containing large amounts of hydrogen. Based on the work of Li and Brenner[32] it was supposed that mainly hydrogen radicals affect reactivity.

3.8 Reactor model

Two reactor models were used in this study. The common thing for both is that the reactor is a tube reactor with plug flow. The plug flow conditions were confirmed by calculating the Reynolds number for the lowest used flows. In the first one, a temperature profile for the lower half of the reactor was measured. A pocket inside the reactor for the thermocouple does not allow measurements for the upper part of the reactor and therefore it was assumed that the temperature profile in the reactor was symmetric for the lower and the upper part of the reactor. The second model was an isothermal one. This type of model which takes into account only the isothermal part of the reactor is occasionally used in modeling thermal reactions. In a modern oven, the non-isothermal part is rather short compared to the iso-thermal one and it is assumed that it has a minor effect on the product distributions.

4 Experimental results, modeling and discussion

4.1 Experimental results

The experiments at the temperature interval of 500-1000ºC follow the pattern previously described by Zhil'tsova et al[51]. There is a short induction period followed by a phase of an exponential growth. The exponential growth then decelerates to a more slowly reacting phase, either a growing or decreasing one, depending on the species. Eventually, a steady-state operation is reached. Our experimental results follow the three first phases but a steady-state operation was not reached in all temperatures. The concentration profiles of individual components for the two mixtures are presented in Figures 7-18. The chosen components are: hydrogen, methane, ethyne, ethene, ethane and 1,3-butadiene.

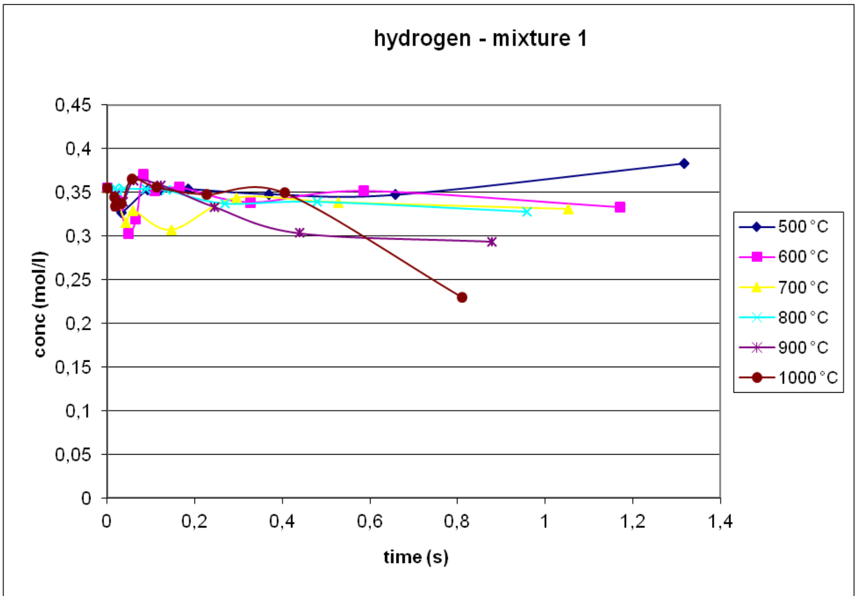

Figure 7. Hydrogen concentrations for mixture 1 as function of residence time.

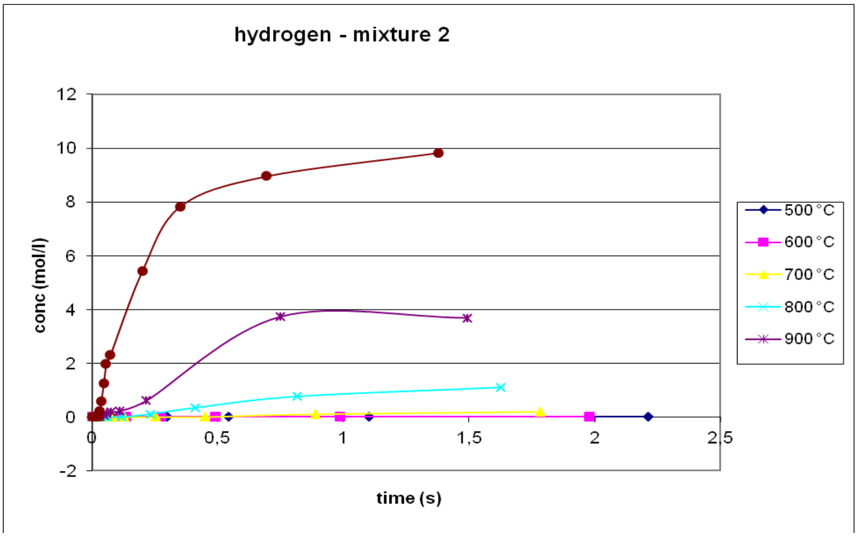

Figure 8. Hydrogen concentrations for mixture 2 as function of residence time.

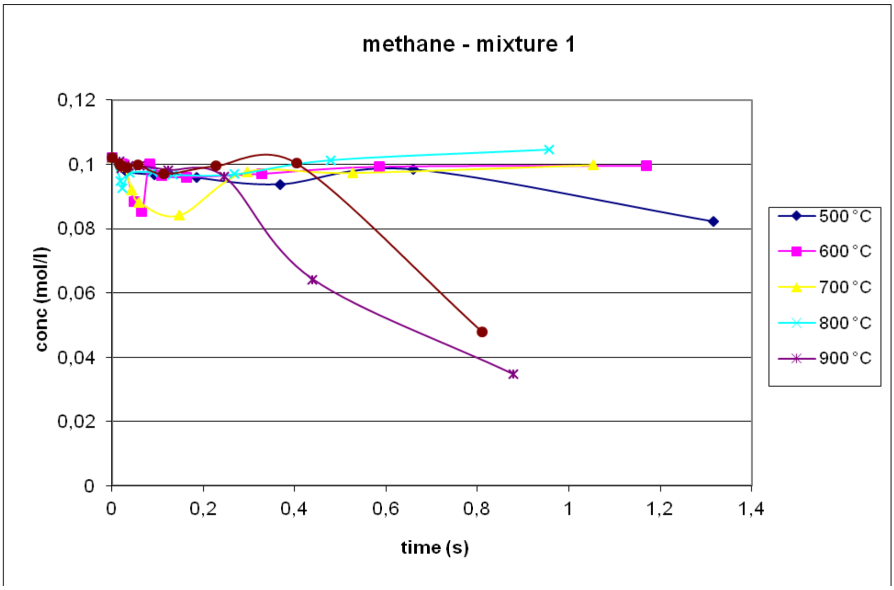

Figure 9. Methane concentrations for mixture 1 as function of residence time.

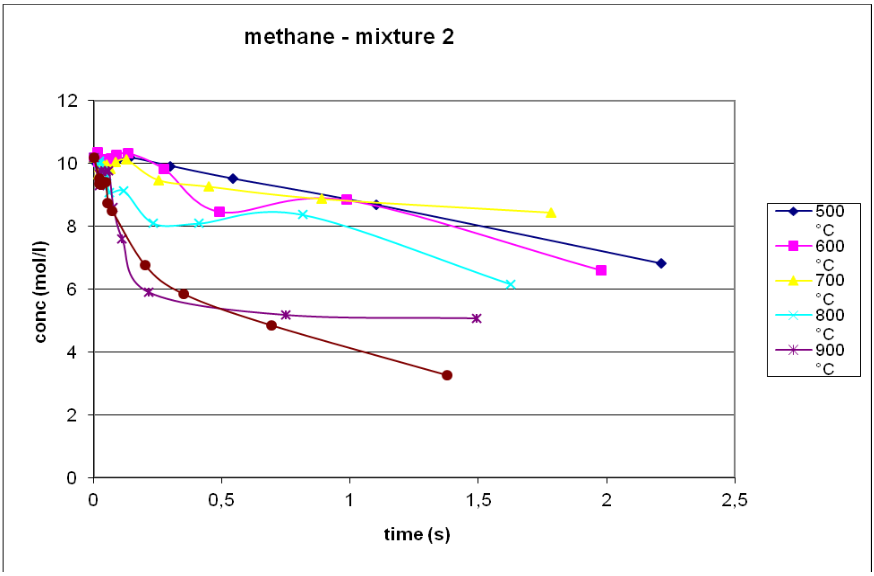

Figure 10. Methane concentrations for mixture 2 as function of residence time.

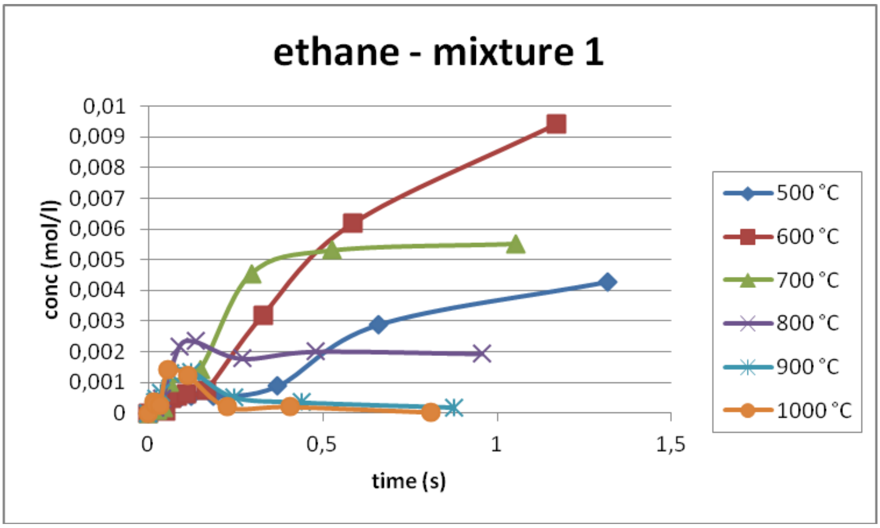

Figure 11. Ethane concentrations for mixture 1 as function of residence time.

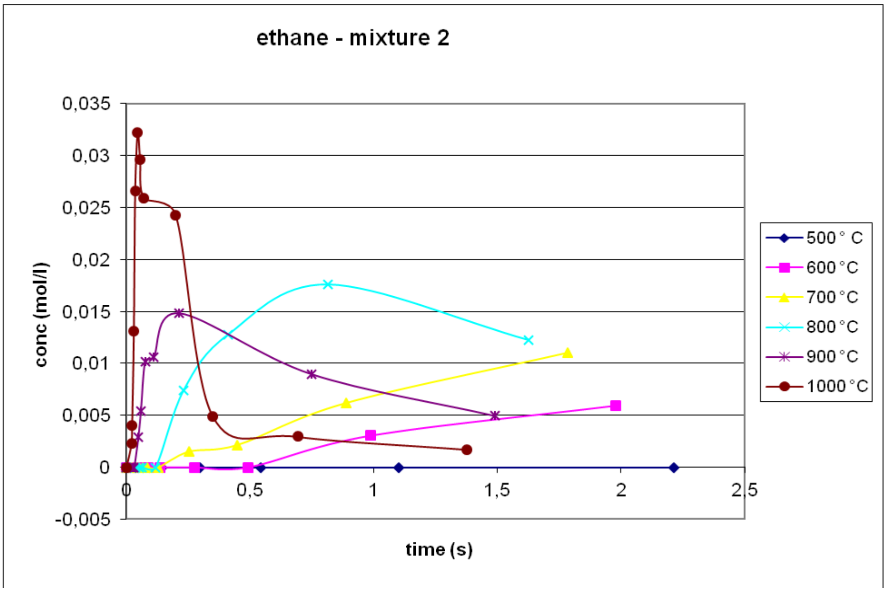

Figure 12 Ethane concentrations for mixture 2 as function of residence time

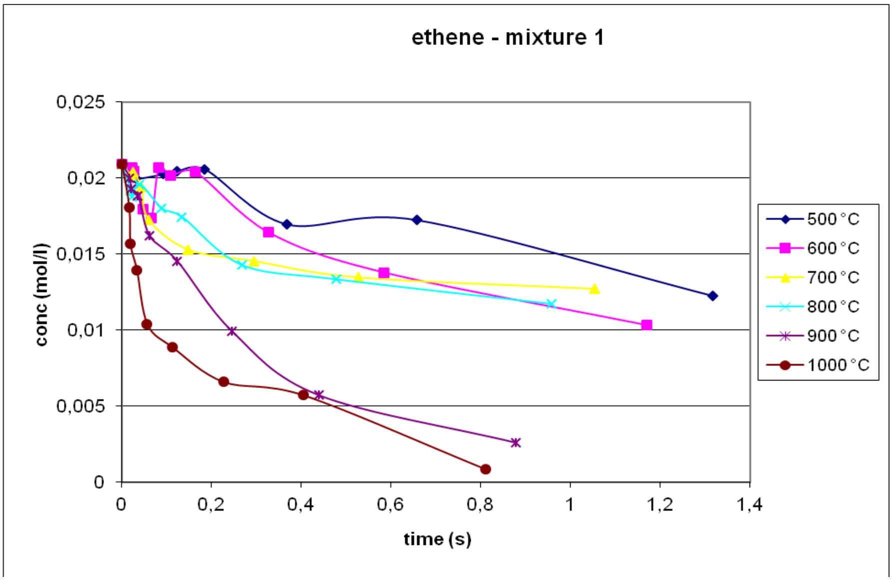

Figure 13. Ethene concentrations for mixture 1 as function of residence time.

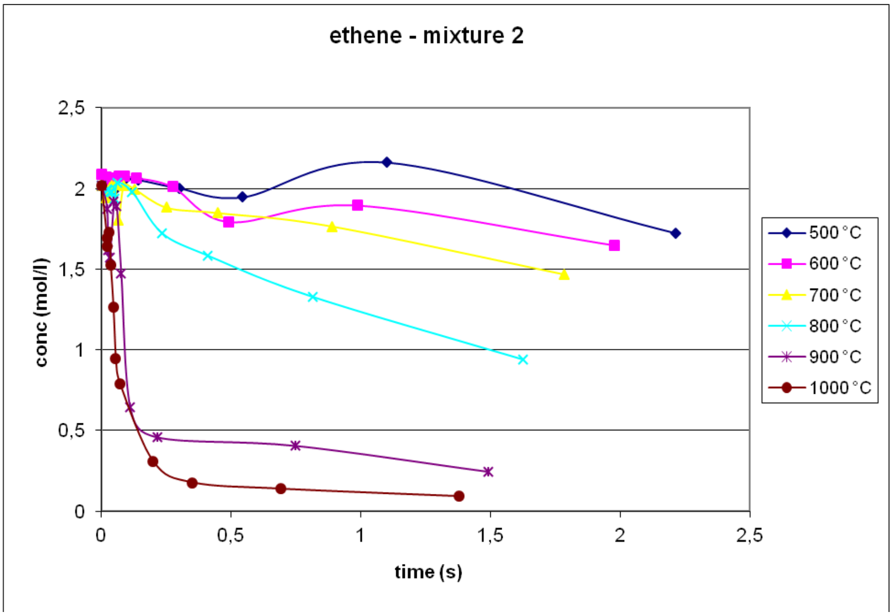

Figure 14. Ethene concentrations for mixture 2 as function of residence time.

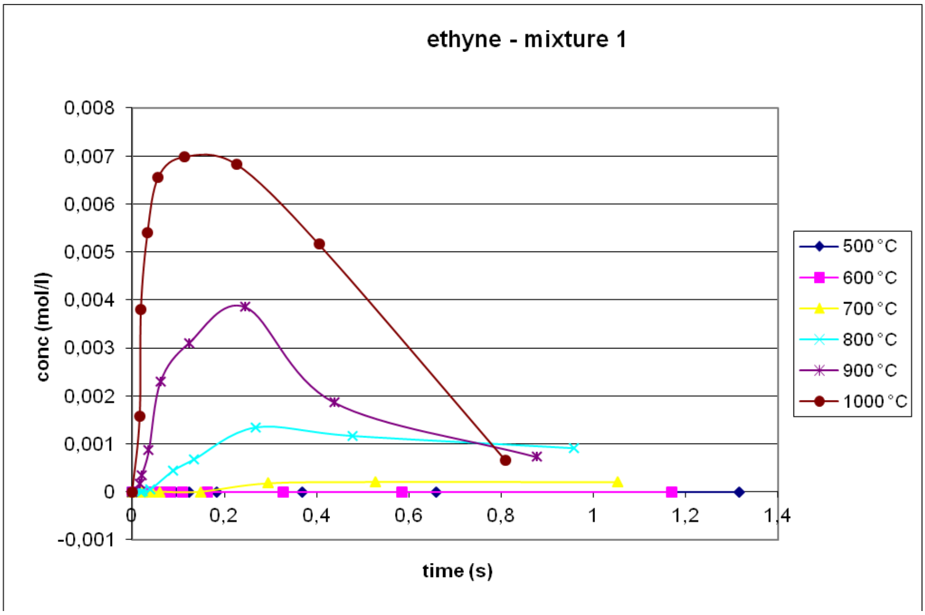

Figure 15. Ethyne concentrations for mixture 1 as function of residence time.

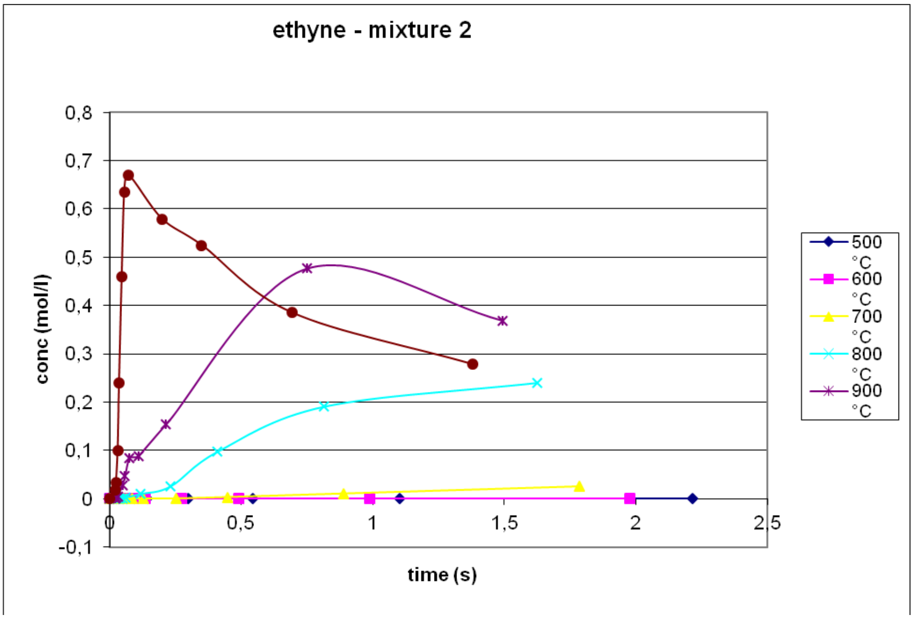

Figure 16. Ethyne concentrations for mixture 2 as function of residence time.

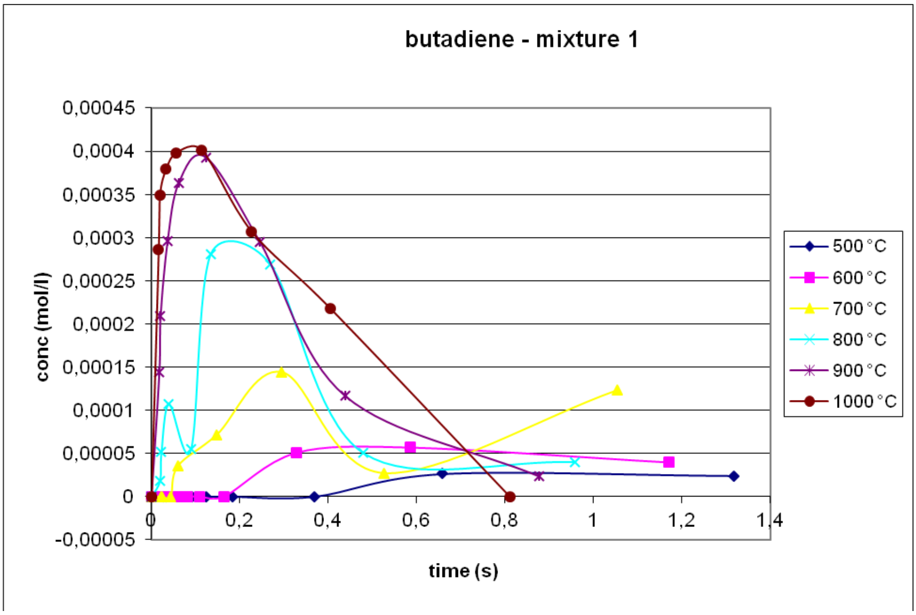

Figure 17. 1,3-butadiene concentrations for mixture 1 as function of residence time.

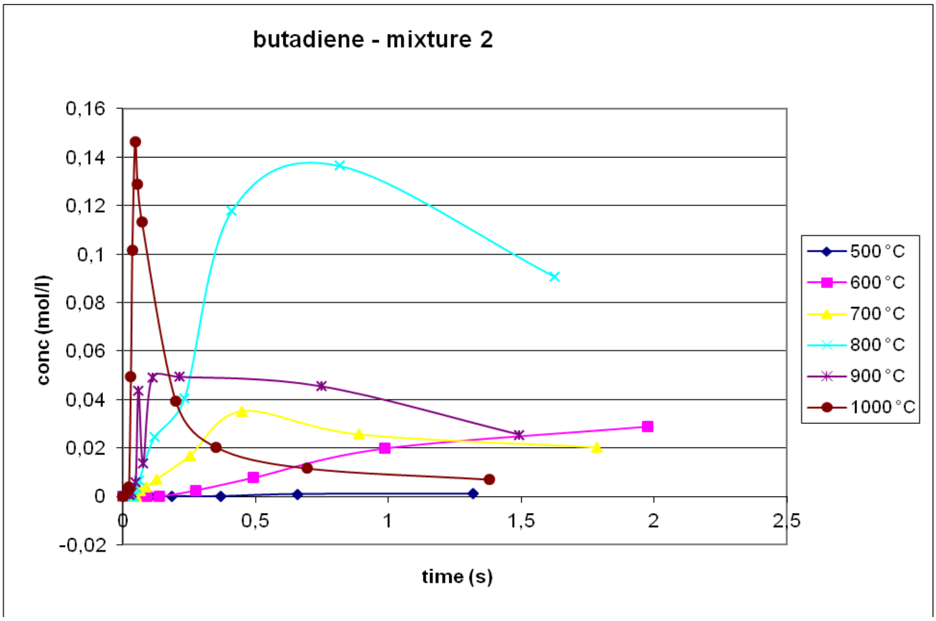

Figure 18. 1,3-butadiene concentrations for mixture 2 as function of residence time.

From Figures 7-8, the following observations can be made: in the experiments with hydrogen containing mixtures, the yield of hydrogen is more or less constant, while hydrogen is starting to form at 700 °C in the experiments without initial hydrogen in the initial mixture. This supports the reported behavior of the tar formation. Between 700 and 800 °C, there is a shift from the aliphatic tar to the aromatic one and therefore it can be expected that hydrogen is formed.

At 700 °C, the steady-state is obtained at approximately 900 ms and the yield of hydrogen exceeds slightly 0.1 mol-%. At 800 °C, these values are 900 ms and 1 mol-%. As the temperature is raised to 900 °C, the figures become 600 ms and 3 mol-%. At our highest temperature 1000 °C, the steady-state is obtained even faster, in 400 ms and the yield of hydrogen is 10 mol-%.

The hydrogen concentration profiles for the mixture without initial hydrogen show that the hydrogen starts to form from the hydrocarbons somewhere within the interval 700-800 °C. This is also the same interval where the tar composition turns from aliphatic waxes to aromatic compounds. This phenomenon was not observed in the mixture with initial hydrogen. Therefore, in practical applications, the formation of hydrogen cannot be used as an indication of the formation of aromatic species.

As a result of the large excess of hydrogen in mixture 2, more ethane is formed compared to mixture 1. This would indicate that ethene as presented in Figures 13-14, and at higher temperatures even acetylene are hydrogenated to ethane. At higher temperatures, ethane concentrations are significantly lower than those of acetylene. This is expected as acetylene is the most thermally stable C_2-species.

Below 800 °C, ethene behaves quite similarly for both mixtures. The hydrogen needed to convert ethene to ethane is formed mainly from methane if it is not present in the mixture initially. Above 800 °C, the ethane formation is reduced if no initial hydrogen is present.

Acetylene is formed at temperatures exceeding 700 °C. It seems that acetylene has an important role in the formation of aromatic tar compounds.

An interesting observation from the methane concentration profiles showns in Figures 9-10 is that hydrogen stabilizes methane. Unfortunately, this effect is only temporary and after a certain delay, similar concentrations are obtained. This is likely to be caused by a direct decomposition to elements. This phenomenon is becomes visible at 875 °C[52]. However, at higher temperatures the decomposition curves have very similar topologies, indicating that even relatively small amounts of hydrogen are sufficient to have an impact on the hydrocarbon reactivities.

The yields of ethane in Figures 11-12 show a different behavior from hydrogen. In the hydrogen-containing mixture, the yields have a maximum at 600 °C. The amounts change from 500 °C to 1000 °C as follows: 0.2, 0.8, 0.5, 0.2, 0.15, and 0.15 mol-%. The respective times to obtain these yields are 1000, 900, 400, 100, 100, and 100 ms. It is worth noticing that at temperatures 900 °C and 1000 °C, ethane has a maximum yield at approximately 100 ms, after which the yields start to decrease. In non-hydrogen mixtures, the behavior is different from the hydrogen containing mixtures. The times needed to obtain the steady-state or the maximum yields are higher up to 800 °C. The values listed in the same order as previously: not observed, 1000, 900, 400, 100, and 100 ms. The maximum yields are practically similar in the investigated temperature interval, namely 0.01 mol-%.

Figures 15-16 show how acetylene was formed at 700 °C and 800 °C faster in the hydrogen containing mixture. The maximum yields were approximately the same, 0.015 mol-% and 0.15 mol-% respectively. At 900 °C and 1000 °C, the acetylene formation took place faster and the maximal yields were higher, 0.5 mol-% and 1.0 mol-%, respectively.

C_3-species are also important intermediate products in the tar formation process. Interestingly, propene was never observed in significant amounts. Contrary to ethane, propane is formed only in hydrogen-free mixtures. Therefore, the hydrogenation of unsaturated C_3-species does not occur in significant amounts. This is especially interesting as the lighter C_2-species are readily hydrogenated. A possible explanation for this behavior could be that propyne is resonance-stabilized with two isomers, propyne and propadiene. Propyne and propene are formed at temperatures over 700 °C, as there is no initial hydrogen present in the system and at temperatures exceeding 900 °C for the hydrogen-containing mixtures. Propene is likely to be consumed in dimerization reactions, too.

The product distributions of these dimerization reactions are expectedly influenced by the temperature profile of the reactor. Allylic hydrogen is more reactive than vinylic hydrogen and therefore leading to non-conjugated C_6-species especially at low temperatures. These species can relatively easily undergo rearrangement and cyclization reactions to mono-unsaturated cyclic compounds, which were observed in small quantities by off-line GC-MS. At higher temperatures even vinylic hydrogen is likely to be radicalized forming higher molecular-weight compounds with conjugated double bonds. For instance, a reaction between two propene molecules with vinylic radicals can react to 2,4-hexadiene.

At high temperatures, propene is formed and consumed rapidly most likely indicating the formation of heavier hydrocarbons; for instance, formation of cyclopentadiene according to reaction 6. However, at lower temperatures, a steady-state of the propene yield is obtained. As propene is formed only in hydrogen-free mixtures at lower temperatures, this could be interpreted as an indication of balanced dimerization reactions and corresponding decomposition reactions.

Besides 1,3-butadiene in Figures 17-18, C_4-species were observed in few occasions. At 500 °C, n-butane was detected in small amounts, indicating the formation of aliphatic tar. On the contrary, at 900 and 1000 °C, minor amounts of butenes and butanes were formed. 1,3-butadiene, on the other hand, was observed at each temperature and mixture. As reaction 3 shows, this compound is formed easily from the ethene which is abundantly converted to other hydrocarbons. Therefore, it seems that this compound is one of the most important intermediate products in the formation both aliphatic and aromatic tars.

Many of the compounds found in the product mixture are known from previous works done on the pyrolysis of ethene [6,53]. However, the product distributions obtained in this study differ vastly from the values reported previously. According to Back et al[6]., propene, ethane and 1- butene are the main products of ethene pyrolysis at 500 °C. Practically no propene was observed in our experiments and 1,3-butadiene was one of the main components instead. Compared to Norinaga et al[14]., the biggest difference is the low amounts of the C_3-species in their work carried out at 900 °C. This can be explained, if the proposed decomposition reaction to ethenyl and methyl radicals is considered reversible and therefore balanced by the concentration of methyl radicals. The major reason for the lack of 1-butene in our experiments is probably the shorter residence times compared to those used by Bossard and Back[10].They proposed that 1-butene is formed mainly by decomposition reactions and these decomposition reactions are favored by low pressures[54]. Though methane conversions are low compared to ethylene conversions, it seems that even minute amounts methane-derived radicals affect the thermal chemistry of hydrocarbons.

The amount of carbon deposited in the reactor is higher than for the gasification gas when considering the mixture without hydrogen. When hydrogen is added to the reacting mixture, the amounts of tar compounds in the reactor correspond more accurately to those of real gasification gas. This is in accordance with hydrogen content inhibiting carbon deposition as proposed previously by Becker et al[55].

Considering the thermal stability of the hydrocarbons, it is easy to notice that most of the light molecular weight compounds are intermediates. The huge difference in magnitude of the ethyne and 1,3-butadiene concentrations in two mixtures, indicate that hydrogen has a major role in the reactivity of these compounds.

Perhaps the most striking feature of the experimental data is the clear peak in the profiles before 0.5 seconds. At first, this was thought to be caused by mistakes in the experimental work but the phenomenon is too consistent to be caused by an inadequate laboratory practice. There are probably few experimental points which are caused by larger experimental scattering but in large scale, the probable reason is the growth of carbonaceous deposits on the quartz surface. The exact mechanism is unknown but the curvature of the profiles suggests that the mechanism resembles the Kisliuk mechanism[56], i.e, the growth of existing deposits is more probable than the formation of new centra of growth.

4.2 Summary of modeling efforts

A purely homogeneous gas-phase reaction model is not suitable for a quantitative description of the system. Even the tested detailed model had difficulties in predicting the behavior of the system correctly.

A hypothesis was that this problem could be solved by parameter estimation. The uncertainties of the published kinetic parameter values[57] are high. The uncertainties range from 30 % up to a factor of 10. As Figures 19-20 demonstrate, this is not the case, even though a better fit to experimental data was obtained but still better results were needed. A CMA-ES algorithm[21] along with other schemes was tested and even though the evolutionary algorithms gave a better fit to the experimental data than iterative methods, probably due to the high dimensionality of the problem, the accuracy of the predictions remained inadequate.

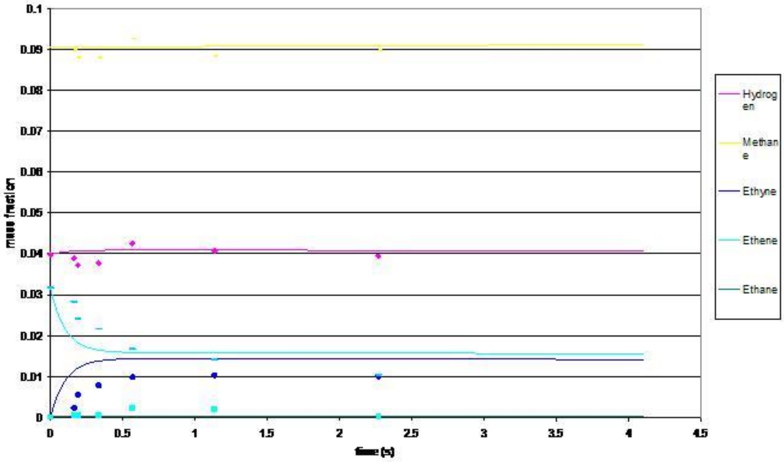

Figure 19 Our compact model at 1000°C

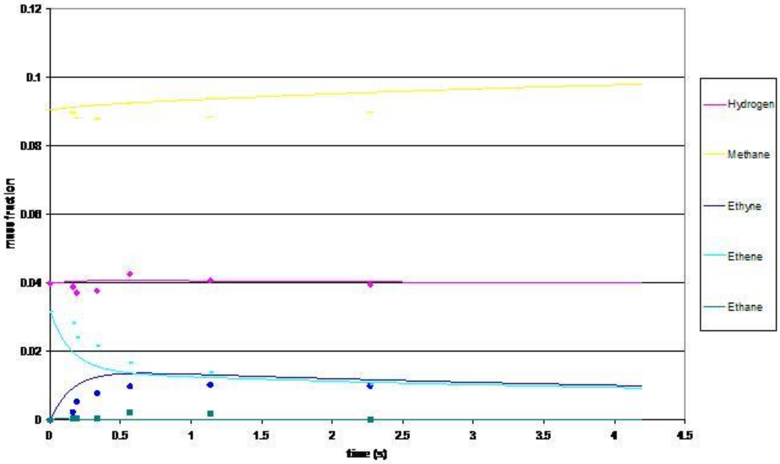

Figure 20 LLNL model at 1000°C

Similar results were obtained by estimating the parameters of the LLNL model[40] and our compact model. The simulation results by the LLNL have a slightly better accuracy than our compact model but the difference is not large. It is worth noticing that the LLNL with its approximately 600 reactions is much smaller than the detailed models which comprise of over ten thousand reactions.

Comparing the predictions of LLNL n-butane flame model and our model, it can be noticed that their predictions on the major species are very similar. The only observable difference is the fact that LLNL model performs better when the residence time exceeds approximately 1 s. This is due to fact that LLNL model includes the formation of carbonaceous deposits, whereas our model is limited to gas-phase reactions only. This indicates that the gas-phase pre-equilibrium is reached in approximately 1 s, but the formation of condensed phase continues to grow slowly.

Figures 19-20 show that, both the LLNL and the developed reduced, reaction mechanism are able to describe the behaviour of the system quantitatively. The developed model performs well with short residence times. At longer residence times, the lack of depositing carbon affects the model predictions slightly negatively. To compare the goodness of the fit for the developed model regression analysis was performed in Excel by data analysis tool pack. The R2 value of the model was 0.823 prior to the parameter estimation and 0.966 after the parameter estimation. The calculated sum of least square values was over 10 % lower for the parameter estimated model.

The major source of error in model are the minor compounds, such as ethyne and 1,3-butadiene, which are expected to participate in the formation of tar and soot. Therefore, a model which is limited to gas-phase reactions, cannot predict these compounds accurately. Another possible source of error, a minor one compared to the previous one, is the analysis of hydrogen. Hydrogen is analysed by a temperature conductivity detector, which does not have the same detection limits as the flame ion detector gives for the analysis of hydrocarbons.

The goodness of the fit was estimated by the sum of squares, which was calculated from experimental results of our own. Kinetic experiments were conducted at six temperatures from 500 °C to 1000 °C and for two different compositions. Both mixtures contained 2 mol-% ethene and 10 mol-% methane and the other one had 35 mol-% of hydrogen**.** Nitrogen was used as a balance gas. All in all, 120 experimental points were recorded for the calculation of sum of squares. The experimental setup is presented in detail in Suominen et al[49]. In case of a detailed kinetic model from LLNL, the sum of squares was lower, even though the magnitude was the same as with our reduced kinetic model prior to the parameter estimation.

A regression analysis of the model predictions and the experimental values was performed by the data analysis toolpack in Excel. It was observed that the R^2-value**,** the coefficient of determination, increased significantly by the parameter estimation and was 0.966 after the parameter estimation. The R^2-value is a measure of how likely the model predicts the future outcomes. The sum of square values in both cases were over 10 % lower after the parameter estimation compared to prior the parameter estimation. Graphical illustrations of the experimental values compared to model predictions prior to and after parameter estimation are presented in Figure 19-20.

In case of the LLNL model, the advantage of the adaptation of the mutation distribution could not be observed as the parameter values were not allowed to change more than 5 % and the best combination of parameter values was found at less than $30n$ function evaluations which is according to Hansen and Ostermeier[21] the limit for the adaptation to improve the strategy behaviour. In the case of our reduced model, more evaluations were required to obtain a solution with an acceptable accuracy. Therefore, the adaptation did have time to evolve. The same restriction of 5 % was applied even here. Even in this case, the full advantage of the adaptation as the limit of $100n^2$ function evaluations was not reached.

During the development of our model, we tried to perform the parameter estimation on preliminary models, too. In a case when the estimated parameters were not close to the literature findings, considerably more function evaluations were needed to reach a satisfactory accuracy for the model. In attempts like these, no restrictions were applied. This indicates that CMA-ES could be an interesting candidate for parameter estimation in such applications, where the magnitudes of the parameters are unknown and the amount of parameters is large. Possible applications are problems, in which diffusion and/or adsorption effects are added to complex chemical kinetics.

Hansen and Kern[58] have reported that increasing the population, in many cases, considerably increases the performance of the algorithm. In our applications, this kind of behaviour could not be observed in significant magnitude. As some test functions in their report did not either exhibit such behaviour, this cannot considered a surprising result. It is, though, possible that the population size should have been increased even more than we did to obtain an increase in algorithm performance.

Different parameter estimation approaches were tested. We tried to estimate all the parameters in the modified Arrhenius equation presented in Eq. 6 and different combinations of them. The most efficient way was to estimate only one parameter. Intuitively, this is clear as the size of covariance matrix increases but the amount of data from which it is estimated does not increase.

4.2.1 Amount of good solutions

The difficulties in the parameter estimation lead to a hypothesis that there are many possible reaction mechanisms which give a good fit to experimental data. This assumption was tested by Markov Chain Monte Carlo (MCMC) assisted parameter estimation technique, where all possible reactions were given two parameters: a numeric rate constant and a Boolean parameter which either includes or excludes the reaction from the model. The purpose was to test whether the MCMC could converge to a right mechanism and to determine the amount of mechanisms which yield a good fit to experimental data. In the scheme, a mechanism of eight species was used. The pseudo experimental data consisted of simulation results at eight time points. The scheme was not able to the converge to right solution and the amount of solutions with good fit to experimental data was estimated to be approximately 2.5 %.

4.2.2 Differential algebra

Differential algebra was tested to study the parameter estimability of the system. A similar approach as suggested in G. Margaria et al.[59], N. Meshkat et al.[60] and M. P. Saccomani et al.[61] was tested but even the compact model was too large that the Rosenfeld-Groebner algorithm could have utilized. This is a definitely interesting approach to evaluate the parameter estimability in the future but the extremely high computational cost is too high for applications such as ours for the time being.

4.2.3 Unconventional modelling solutions

If a sigmoidal function such as a Boltzmann function, which is given in Equation 16, was used to model the growth of the deposits, the fit on experimental data is excellent. Similar results can be obtained by a peak function correction to radical concentrations as suggested by Suominen and Salmi[62]. The sigmoidal function is presented below in Figure 21.

$$y(t) = \frac{A_1 - A_2}{1 + e^{\frac{t - x_o}{dx}}} + A_2 \qquad (16)$$

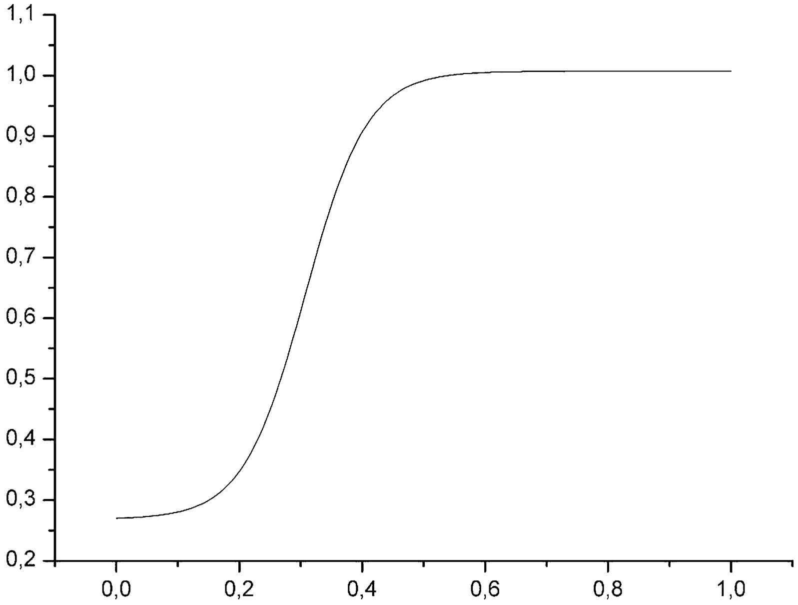

Figure 21 An example of Boltzmann function

Basically, the success behind this function is that even the clean quartz glass creates radicals, in much slower rate than the carbenous deposits, though. By adjusting parameter A_1, the initial level can be altered. Parameter dx affects the velocity by which the deposits grow and parameter A_2 gives the upper limit, in this case, the evident choice is unity which corresponds logically to the situation where the whole quartz surface is covered by carbenous deposits. Finally, the parameter x_0 affects the placement of the point of inflection, e.g. the point where the second derivative changes the sign.

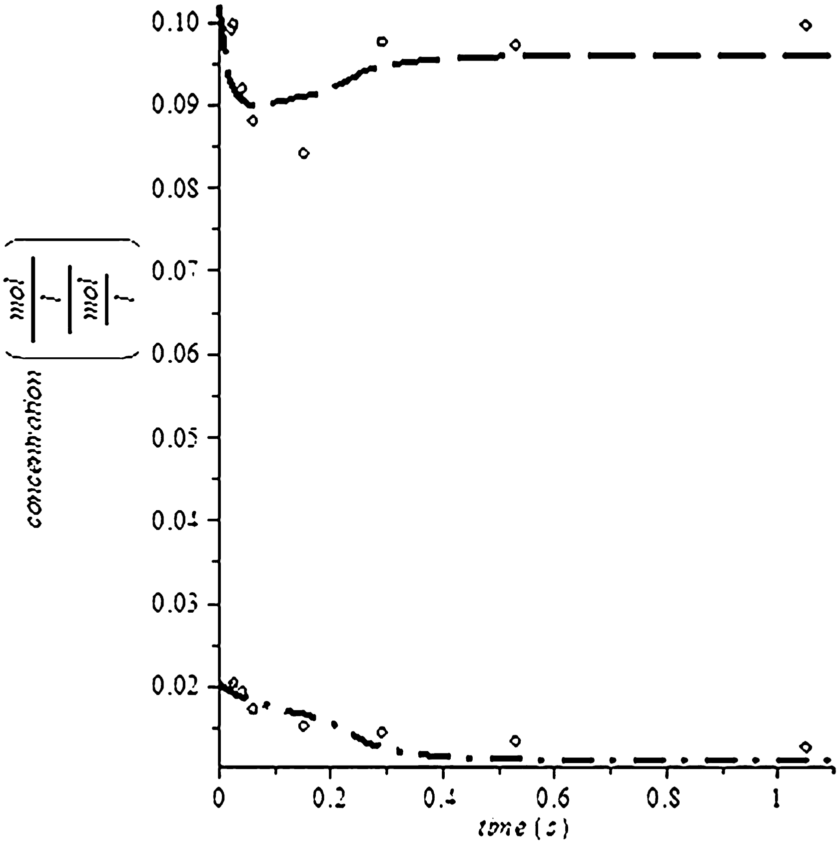

Figure 22 concentration profiles at 700 °C; methane dashed line, ethylene dot-dashed line

The modeling results fit very well the experimental data as Figure 22 demonstrates. For methane and ethene, the fit is excellent. The swag at the lower temperatures is caused by the formation of the carbenous deposits on the reactor walls. The side product of this process is methane. The lower the temperature, the later the swag appears on the methane concentration profile. At temperatures high enough, the concentration profile of methane is flat indicating that the formation of carboneous deposits is so fast that our experimental setup cannot observe it.

Figure 23 presents the same experimental results without the correction. If the concentration profiles corrected for surface activity are compared to simulations of the same system without the CD effect, it is clear that the surface coverage of carbonaceous deposits is an important variable in the system studied. Modeling the delay without the sigmoidal curve would require a much more complex mechanism than ours.

4.3 Discussion – gas-phase or surface reaction?

The experimental data are in accordance with the previous studies on thermal reactions of light hydrocarbons. The reactivity of the mixture increases with temperature and more unsaturated compunds are formed at elevated temperatures

The HACA-mechanism[63,64,65], hydrogen abstraction – C_2H_2 addition, is a classical theory for modelling the growth of aromatic species. There are several cases where the HACA-mechanism fails to explain the growth of aromatic molecules. Perhaps the main reason is that the HACA-mechanism is a slow mechanism[66,67]. Other proposed, more rapid, mechanisms include the PAC-mechanism, phenyl addition/cyclization, and MAC-mechanism, methyl addition/cyclization, ring-ring condensation, aryl-

aryl combination, particle filler model and condensation of an aromatic radical to a neutral species. A comparative study of the mechanisms was written by Shukla and Koshi.[68]

It is outside the scope for this thesis to analyze the soot formation in detail, but it is important that components which are a part of these mechanisms are observed in this study. These compounds include hydrogen, methane, ethyne and indirectly 1,3-butene as an intermediate to six-membered ring structures and ethane which is a stable product at lower temperatures. These compounds are chosen to be discussed in more detail.

A similar computational chemistry approach as Li and Brenner[32] performed for ethyne, ethene, ethane and methane would be interesting to be applied for three and four carbon atom molecules. In this way, a better understanding for the possibilities of controlling the soot formation could be obtained.

The carbenous deposits on the reactor surface affect the system to a great extent. Even though they can be used to control the amount of tar formed, they also affect the conversion of light hydrocarbons if the reactor material has different surface properties than the carbonaceous deposits.

To which extent the reactions occur in the gas phase is an important and interesting question for which our experimental apparatus could not produce necessary data. The literature concerning this issue is controversial. If the change in tar composition from aliphatic to aromatic compounds is taught to be caused by the kinetic entropy, then the proportion of high molecular weight aliphatic compounds to aromatic compounds could be used to estimate the relation of gas-phase and surface reactions. As the kinetic entropy is severely reduced during sorption, the reactions should be directed towards the aliphatic compounds even at elevated temperatures. Therefore, it seems that gas-phase reactions are the dominant ones at least at elevated temperatures.

The importance of the surfaces in forming radical ions is not as contradictory as the gas-phase versus surface reaction issue. A significant amount of radicals are formed on the surface. The formed carbenous deposits have different physical properties than the quartz glass used as the reactor material and the concentration profiles of the product mixture exhibit a behaviour which can be explained by a sigmoidal type of growth of the surface coverage by the carbonaceous deposits. An interesting question remains: to which extent the surface material affects the formation of radicals and how important is the specific surface area? Unfortunately we were unable to isolate enough carboneus deposits from the reactor to be able to measure its surface area. Nor were we able to make any measurements considering the possible time-dependent behaviour of the carbonaceous deposits.

Another problem related to the reactor material exists. This challenge is illustrated by Kopinke et al.[30] Their measurements of deposits reveal that the mass of deposits in a steel reactor does not follow neither a linear nor an exponential growth. The same phenomenon was observed even in their measurements of deposits in quartz glass reactor but a distinct growth pattern can still be observed. This is an unfortunate effect when considering the modelling of soot formation in industrial scale equipment. Fortunately, the surface area-volume ratio[31] for industrially applied reactors is more advantageous and the overall effect is likely to be less than in laboratory scale.

Figure 23 illustrates different reaction types. Reaction A is an Eley-Rideal type of reaction where one reactant is in the gas-phase while the other one is adsorbed on the surface. Reaction B illustrates a Langmuir-Hinshelwood type of reaction. The difference to the reaction A is that both reactants are adsorbed on the surface. In reaction C, a radical species is formed as a molecular species comes in contact with a surface. Finally, reaction D depicts a situation where a molecule forms radical species in the gas-phase. The letter M is used to mark an atom or molecule to which the reacting species collides.

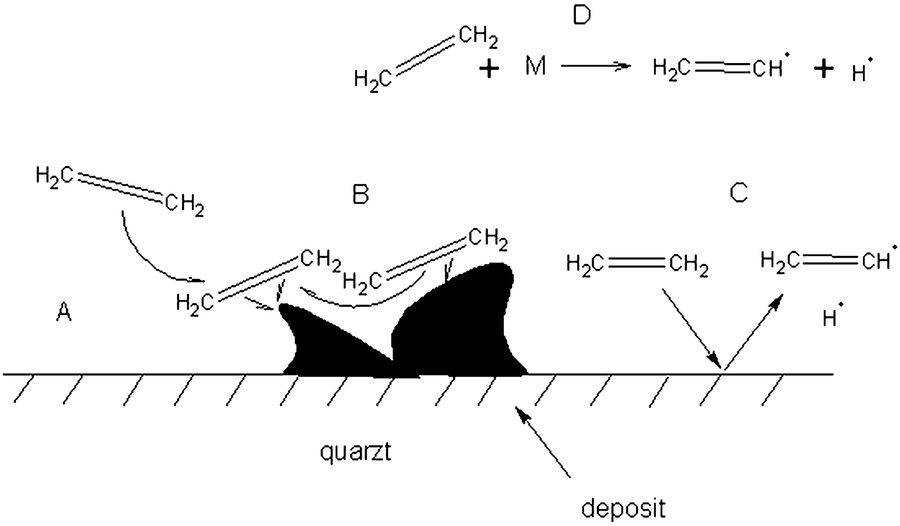

Figure 23. Different reaction types: A) Eley-Rideal B) Langmuir Hinshelwood C) Radical formation on surface D) Radical formation in gas-phase.

5 Conclusions

Description of the thermal decomposition kinetics of ethene-methane mixtures in the presence and absence of hydrogen was investigated by literature survey, kinetic experiments and modeling effort. Even though, the scope of the thesis was limited to the reactions of light hydrocarbon components present in gasification gas in the presence and absence of hydrogen, the system is very complicated.

The work on this thesis is illustrated in Figure 24. The work began from design of the experimental apparatus and planning of the kinetic experiments. Simultaneously with experimental work, first model was developed. The kinetic data was analyzed and need for better software to handle the huge model and large number of experimental data was recognized. With new software, a full kinetic model approach was tested. Then the efforts were concentrated on simplifying the model. By careful interpretation of findings from literature survey, a compact model with physical background was developed.

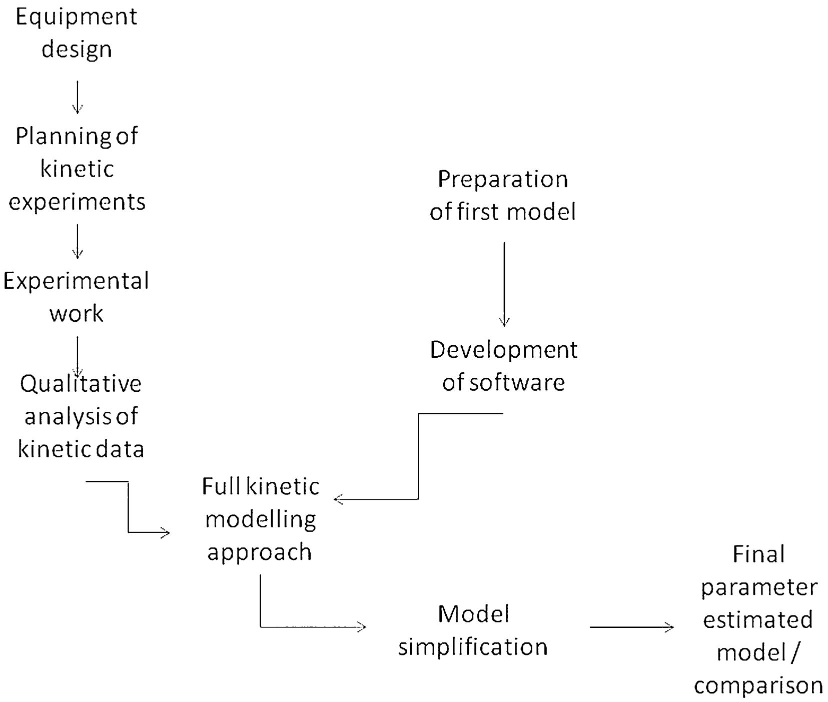

Figure 24. A flowsheet of the thesis work

The experimental work was carried out at a temperature interval of 500-1000 ºC. This temperature interval includes the transition temperature in product distributions from aliphatic tar to aromatic tar. The experimental data were obtained on a time interval seldomly used. There exist shock tube experiments from micro- to millisecond scale and there are experimental data from few hundred milliseconds up to several seconds but data from the intermediate area from 10-20 millisecond to few hundred milliseconds are scarce. All the experiments were carried out under atmospheric pressure. From industrial point of view, it would be interesting to obtain measurements from elevated pressures, but the modeling effort would become more difficult, if the pressure would have to be taken as an additional parameter.

The experimental results showed a similar behavior which is depicted by Zhil'tsova et al[51]. There is a short induction period followed by an exponential growth of product molecules, after which the system reaches a steady state

A parameter estimation software based on the Chemkin simulation software was developed. The estimation of parameters was performed by a CMA-ES algorithm. Even other algorithms were tested but the results were either comparable or inferior to the results obtained by CMA-ES. It is though necessary to remember that the full power of CMA-ES was not utilized as the algorithm converged to a result before the covariance matrix update scheme was initiated.

The Markov Chain Monte Carlo (MCMC) simulations on a simple reaction system showed that finding a correct reaction mechanism is a tedious task, if it is based solely on experimental data. It has been discussed that a viable method to reduce the amount of mechanisms which yield good fit to experimental data is in-situ measurement of radical species. Unfortunately, we did not have a such an analytical apparatus at our disposal.

Reliable numerical data on kinetic parameters would be invaluable in modeling efforts. At the current moment, published kinetic data must be reviewed critically. Typically, uncertainties for reaction rate parameters are from 30 % to a factor of 10 for this kind of systems. Some published models are based on the estimating simultaneously tens of parameters. The results of this kind of approach should be avoided.

The kinetic entropy seems to be among the reasons why the tar consists of aliphatic compounds at lower temperatures but more and more aromatic compounds are produced by thermal reactions at higher temperatures. This is affected by the reactor material and geometry.

The conversion of the light hydrocarbons to tar is affected by the forming carbonaceous deposits. The quartz glass reactor used in our experiments has a lower surface area than the carbonaceous deposits, and therefore, the amount of radicals formed at the surface is increased which leads to higher conversions of light hydrocarbons.

Notation

A	pre-exponential parameter in Arrhenius equation
b	exponential parameter in Arrhenius equation
CMA-ES	covariance matrix adaptation evolutionary strategy
Ea	activation energy
EA	evolutionary algorithm
MCMC	Markov Chain Monte Carlo

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Appendix I

The LLNL mechanism used in the work as a Chemkin input file:

```
! reference:
! Marinov, N. M., Pitz, W. J., Westbrook, C. K., Vincitore, A. M.,
! Castaldi, M. J., Senkan, S. M. "Aromatic and Polycyclic Aromatic
! Hydrocarbon Formation in a Laminar Premixed n-Butane Flame"
! Combustion and Flame 114 192-213 (1998).
! UCRL-WEB-204236
! Review and release date: May 19, 2004.
!
! Date: Tue, 19 Jan 1999 11:38:35 -0800 (PST)
! From: "Nick M. Marinov" <marinov1@llnl.gov>

elements h   o    c  ar n    end
species
h2 h
ch4 ch3 ch2 ch ch2o hco co2 co o2 o oh ho2 h2o2 h2o
c2h hcco c2h2 c2h3 c2h4 c2h5 c2h6 ch2oh ch3o hccoh h2ccch
c3h2 ch2(s) ch2co c4h2 c5h2 c5h3 c6h2 c2 c2o c hcoh
ch2chcch hcchcch h2cccch c6h5 c6h6 c6h5o
ch2chchch ch2chcch2
h2c4o ch2chchch2 ch3oh ch2hco
c-c5h5 c-c5h5o c-c5h6 c6h5oh c10h8 c-c5h4oh c-c5h4o
c4h10 pc4h9 sc4h9 c4h8-1 c4h8-2 c4h7
c3h6 ac3h5 pc3h5
sc3h5 ch2chcho pc3h4 ac3h4 ch3co c6h5ch2 c6h5ch3
ch2chco ch3chco ch3hco chocho
c3h8 ic3h7 nc3h7 ch3chcch2  ch3ccch2
c6h5c2h5 c10h10 c10h9 c10h7
c6h4c2h3 c6h4c2h c6h5c2h3 c6h5c2h c10h7o
c6h5cho c6h5co hoc6h4ch3 c6h5ch2oh oc6h4o
oc6h4ch3 c10h7ch2 c10h7ch3
ch3c6h4ch3 indene indenyl acenphthln phnthrn
ch3chcch ch3ch2cch ch3c6h4ch2
phnthryl-1 phnthryl-9 flrnthn
ch3c6h4c2h3 ch3c6h4c2h5
c-2*4c6h6o c-c5h7 l-c5h8 l-c5h7
c10h7c2h5 c10h7c2h3 c10h7oh c6h5cco
c6h5chch c6h5cch2 c10h7cch2 c10h7cch c10h6cch
anthracn ch3indene ch3indenyl ch3phnthrn pyrene
fluoryl fluorene h2cccch2 chchcho hcccho hccco
hc4-p(def)pthn hc4-p(def)pthyl phnthroxy-1 phnthroxy-9
bz(a)ndene bz(a)ndnyl phnthrol-1 phnthrol-9 biphenyl bz(a)phnthrn
bz(ghi)fln fulvene ch3cy24pd ch3cy24pd1 ch3dcy24pd cyc6h7
fulvenyl ar n2 end
thermo
end
reactions
   oh+h2=h+h2o             2.14E+08  1.52  3449.0 !Marinov 1995a
   o+oh=o2+h               2.02E+14  -0.4     0.0 !Marinov 1995a
   o+h2=oh+h               5.06E+04  2.67  6290.0 !Marinov 1995a
   h+o2(+m)=ho2(+m)        4.52E+13  0.0      0.0 !Marinov 1995a
```

```
   low /  1.05E+19  -1.257  0.0 /               !Marinov 1995a
!   h2o/0.0/ h2/0.0/ ch4/10.0/ co2/3.8/ co/1.9/
   h2o/0.0/ h2/0.0/ n2/0.0/ ch4/10.0/ co2/3.8/ co/1.9/
   h+o2(+n2)=ho2(+n2)      4.52E+13  0.0      0.0 !Marinov 1995a
   low / 2.03E+20  -1.59    0.0  /              !Marinov 1995a
   h+o2(+h2)=ho2(+h2)      4.52E+13  0.0      0.0 !Marinov 1995a
   low / 1.52E+19  -1.133   0.0 /              !Marinov 1995a
   h+o2(+h2o)=ho2(+h2o)    4.52E+13  0.0      0.0 !Marinov 1995a
   low / 2.10E+23  -2.437   0.0 /              !Marinov 1995a
   oh+ho2=h2o+o2           2.13E+28 -4.827 3500.0 !Hippler 1995
    dup
   oh+ho2=h2o+o2          9.10E+14  0.0  10964.0 !Hippler 1995
    dup
   h+ho2=oh+oh             1.50E+14  0.0  1000.0  !Marinov 1995a
   h+ho2=h2+o2             8.45E+11  0.65 1241.0  !Marinov 1995a
   h+ho2=o+h2o            3.01E+13  0.0  1721.0  !Marinov 1995a
   o+ho2=o2+oh                   3.25E+13  0.0     0.0  !Marinov 1995a
   oh+oh=o+h2o             3.57E+04  2.4 -2112.0  !Marinov 1995a
   h+h+m=h2+m              1.00E+18 -1.0     0.0  !Marinov 1995a
   h2o/0.0/ h2/0.0/
   h+h+h2=h2+h2            9.20E+16 -0.6     0.0  !Marinov 1995a
   h+h+h2o=h2+h2o          6.00E+19 -1.25    0.0  !Marinov 1995a
   h+oh+m=h2o+m            2.21E+22 -2.0     0.0  !Marinov 1995a
    h2o/6.4/
   h+o+m=oh+m              4.71E+18 -1.0     0.0  !Marinov 1995a
    h2o/6.4/
   o+o+m=o2+m              1.89E+13  0.0 -1788.0  !Marinov 1995a
   ho2+ho2=h2o2+o2         4.20E+14  0.0 11982.0  !Marinov 1995a
   dup
   ho2+ho2=h2o2+o2         1.30E+11  0.0 -1629.0  !Marinov 1995a
   dup
   oh+oh(+m)=h2o2(+m)      1.24E+14 -0.37    0.0  !Marinov 1995a
   low /  3.04E+30   -4.63   2049.0 /           !Marinov 1995a
    troe / 0.470   100.0   2000.0  1.0E+15/
   h2o2+h=ho2+h2           1.98E+06  2.0  2435.0  !Marinov 1995a
   h2o2+h=oh+h2o           3.07E+13  0.0  4217.0  !Marinov 1995a
   h2o2+o=oh+ho2           9.55E+06  2.0  3970.0  !Marinov 1995a
   h2o2+oh=h2o+ho2         2.40E+00 4.042 -2162.0 !Marinov 1995a
   ch3+ch3(+m)=c2h6(+m)    9.22E+16 -1.174 636.0  !Walter  1990
   low / 1.14E+36 -5.246 1705.0/               !Walter  1990
   troe/ 0.405  1120.0   69.6    1.0E+15/
    h2o/5.0/ h2/2.0/ co2/3.0/ co/2.0/
   ch3+h(+m)=ch4(+m)       2.14E+15 -0.4    0.0        !Tsang 1986
   low/  3.31E+30   -4.0  2108.0 /             ! (a)
   troe / 0.0   1.0E-15   1.0E-15   40.0/
   h2o/5.0/ h2/2.0/ co2/3.0/ co/2.0/
   ch4+h=ch3+h2            2.20E+04 3.0   8750.0  !Miller 1992
   ch4+oh=ch3+h2o         4.19E+06 2.0   2547.0  !Marinov 1995
   ch4+o=ch3+oh           6.92E+08 1.56  8485.0  !Marinov 1995
   ch4+ho2=ch3+h2o2        1.12E+13 0.0   24640.0 !Marinov 1995
   ch3+ho2=ch3o+oh         7.00E+12 0.0      0.0  !Troe  1993
   ch3+ho2=ch4+o2         3.00E+12 0.0      0.0  !Marinov 1995
   ch3+o=ch2o+h           8.00E+13 0.0      0.0  !Marinov 1995
   ch3+o2=ch3o+o          1.45E+13 0.0   29209.0 !Klatt 1991
   ch3+o2=ch2o+oh         2.51E+11 0.0   14640.0 !Marinov 1995
   ch3o+h=ch3+oh           1.00E+14 0.0      0.0  !Miller 1992
   ch3+oh=ch2(s)+h2o       2.65E+13 0.0   2186.0  !Humpfer 1994
```

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ch3+oh=ch2+h2o          3.00E+06 2.0   2500.0  !Marinov 1996
ch3+oh=hcoh+h2          5.48E+13 0.0   2981.0  !Humpfer 1994
ch3+oh=ch2o+h2          2.25E+13 0.0   4300.0  ! (b)
ch3+h=ch2+h2            9.00E+13 0.0   15100.0 !Miller 1992
ch3+m=ch+h2+m           6.90E+14 0.0   82469.0 !Markus 1992
ch3+m=ch2+h+m           1.90E+16 0.0   91411.0 !Markus 1992
ch3+oh(+m)=ch3oh(+m)    5.65E+13 0.1      0.0  !Fagerstrom 1993
low/ 5.75E+41   -7.4   626.0 /              ! (c)
troe /  0.025   1.0E-15   8000.0   3000.0/
h2o /16.0/  h2/2.0/ co2/3.0/ co/2.0/
ch3oh(+m)=hcoh+h2(+m)   4.15E+16 -0.15 92285.0 ! (d)
low /  4.23E+44   -7.65     92911.0 /
troe / 0.025  1.0E-15   8000.0   3000.0/
h2o/16.0/ h2/2.0/ co2/3.0/ co/2.0/
ch3oh+oh=ch2oh+h2o      2.61E+05 2.182 -1344.0   !Tsang  1987
ch3oh+oh=ch3o+h2o       2.62E+06 2.056   916.0   !Tsang  1987
ch3oh+o=ch2oh+oh        3.88E+05 2.5    3080.0   !Tsang  1987
ch3oh+h=ch2oh+h2        1.70E+07 2.1    4868.0   !Tsang  1987
ch3oh+h=ch3o+h2         4.24E+06 2.1    4868.0   !Tsang  1987
ch3oh+ho2=ch2oh+h2o2    9.64E+10 0.0    12578.0  !Tsang  1987
ch3o+m=ch2o+h+m         5.45E+13 0.0    13497.0  !Choudhury1990
ch2oh+m=ch2o+h+m        1.00E+14 0.0    25000.0  !Miller 1992
ch3o+h=ch2o+h2          2.00E+13 0.0       0.0   !Miller 1992
ch2oh+h=ch2o+h2         2.00E+13 0.0       0.0   !Miller 1992
ch3o+oh=ch2o+h2o        1.00E+13 0.0       0.0   !Miller 1992
ch2oh+oh=ch2o+h2o       1.00E+13 0.0       0.0   !Miller 1992
ch3o+o=ch2o+oh          1.00E+13 0.0       0.0   !Miller 1992
ch2oh+o=ch2o+oh         1.00E+13 0.0       0.0   !Miller 1992
ch3o+o2=ch2o+ho2        6.30E+10 0.0    2600.0   !Miller 1992
ch2oh+o2=ch2o+ho2       1.57E+15 -1.0      0.0   !Baulch 1992
 dup
ch2oh+o2=ch2o+ho2       7.23E+13  0.0   3577.0   !Baulch 1992
 dup
hcoh+oh=hco+h2o         2.00E+13  0.0      0.0   !Marinov 1996
hcoh+h=ch2o+h           2.00E+14  0.0      0.0   !Marinov 1996
hcoh+o=co2+h+h          5.00E+13  0.0      0.0   !Marinov 1996
hcoh+o=co+oh+h          3.00E+13  0.0      0.0   !Marinov 1996
hcoh+o2=co2+h+oh        5.00E+12  0.0      0.0   ! (e)
hcoh+o2=co2+h2o         3.00E+13  0.0      0.0   ! (e)
ch2+h=ch+h2             1.00E+18  -1.56    0.0   !Miller 1992
ch2+oh=ch+h2o           1.13E+07  2.0   3000.0   !Miller 1992
ch2+oh=ch2o+h           2.50E+13  0.0      0.0   !Miller 1992
ch2+co2=ch2o+co         1.10E+11  0.0   1000.0   !Miller 1992
ch2+o=co+h+h            5.00E+13  0.0      0.0   !Miller 1992
ch2+o=co+h2            3.00E+13  0.0      0.0   !Miller 1992
ch2+o2=ch2o+o           3.29E+21 -3.3   2868.0   ! (f)
ch2+o2=co2+h+h          3.29E+21 -3.3   2868.0   ! (f)
ch2+o2=co2+h2           1.01E+21 -3.3   1508.0   ! (f)
ch2+o2=co+h2o           7.28E+19 -2.54  1809.0   ! (f)
ch2+o2=hco+oh           1.29E+20 -3.3    284.0   ! (f)
ch2+ch3=c2h4+h          4.00E+13  0.0      0.0   ! Miller 1992
ch2+ch2=c2h2+h+h        4.00E+13  0.0      0.0   ! Miller 1992
ch2+hcco=c2h3+co        3.00E+13  0.0      0.0   ! Miller 1992
ch2+c2h2=h2ccch+h       1.20E+13  0.0   6600.0   ! Miller 1992
ch2(s)+m=ch2+m          1.00E+13  0.0      0.0   ! Miller 1992
h /12.0/ c2h2 /4.0/ h2o/3.0/
ch2(s)+ch4=ch3+ch3      4.00E+13  0.0      0.0   ! Miller 1992
```

```
ch2(s)+c2h6=ch3+c2h5    1.20E+14  0.0      0.0   ! Miller 1992
ch2(s)+o2=co+oh+h       7.00E+13  0.0      0.0   ! Miller 1992
ch2(s)+h2=ch3+h         7.00E+13  0.0      0.0   ! Miller 1992
ch2(s)+c2h2=h2ccch+h    1.50E+14  0.0      0.0   ! Canosa-Mas85
ch2(s)+c2h4=ac3h5+h     1.30E+14  0.0      0.0   ! Canosa-Mas85
ch2(s)+o=co+h+h         3.00E+13  0.0      0.0   ! Miller 1992
ch2(s)+oh=ch2o+h        3.00E+13  0.0      0.0   ! Miller 1992
ch2(s)+h=ch+h2          3.00E+13  0.0      0.0   ! Miller 1992
ch2(s)+co2=ch2o+co      3.00E+12  0.0      0.0   ! Miller 1992
ch2(s)+ch3=c2h4+h       2.00E+13  0.0      0.0   ! Miller 1992
ch2(s)+ch2co=c2h4+co    1.60E+14  0.0      0.0   ! Miller 1992
ch+o2=hco+o             3.30E+13  0.0      0.0   ! Miller 1992
ch+o=co+h              5.70E+13  0.0      0.0   ! Miller 1992
ch+oh=hco+h             3.00E+13  0.0      0.0   ! Miller 1992
ch+oh=c+h2o             4.00E+07  2.0   3000.0   ! Miller 1992
ch+co2=hco+co           3.40E+12  0.0    690.0   ! Miller 1992
ch+h=c+h2               1.50E+14  0.0      0.0   ! Miller 1992
ch+h2o=ch2o+h           1.17E+15  -0.75    0.0   ! Miller 1992
ch+ch2o=ch2co+h         9.46E+13  0.0   -515.0   ! Miller 1992
ch+c2h2=c3h2+h          1.00E+14  0.0      0.0   ! Miller 1992
ch+ch2=c2h2+h           4.00E+13  0.0      0.0   ! Miller 1992
ch+ch3=c2h3+h           3.00E+13  0.0      0.0   ! Miller 1992
ch+ch4=c2h4+h           6.00E+13  0.0      0.0   ! Miller 1992
c+o2=co+o               2.00E+13  0.0      0.0   ! Miller 1992
c+oh=co+h               5.00E+13  0.0      0.0   ! Miller 1992
c+ch3=c2h2+h            5.00E+13  0.0      0.0   ! Miller 1992
c+ch2=c2h+h             5.00E+13  0.0      0.0   ! Miller 1992
ch2o+oh=hco+h2o         3.43E+09  1.18  -447.0   ! Miller 1992
ch2o+h=hco+h2           2.19E+08  1.77  3000.0   ! Miller 1992
ch2o+m=hco+h+m          3.31E+16  0.0   81000.0  ! Miller 1992
ch2o+o=hco+oh           1.80E+13  0.0   3080.0   ! Miller 1992
hco+o2=ho2+co           7.58E+12  0.0    410.0   ! Timonen 1988
hco+m=h+co+m            1.86E+17  -1.0 17000.0   ! Timonen 1987
h2o/5.0/ h2/1.87/ co2/3.0/ co/1.87/ ch4/2.81/
hco+oh=h2o+co           1.00E+14  0.0     0.0    ! Miller 1992
hco+h=co+h2             1.19E+13  0.25    0.0    ! Miller 1992
hco+o=co+oh            3.00E+13  0.0     0.0    ! Miller 1992
hco+o=co2+h             3.00E+13  0.0     0.0    ! Miller 1992
co+oh=co2+h             9.42E+03  2.25 -2351.0   ! (g)
co+o+m=co2+m            6.17E+14  0.0   3000.0   ! Miller 1992
co+o2=co2+o             2.53E+12  0.0  47688.0   ! Miller 1992
co+ho2=co2+oh           5.80E+13  0.0  22934.0   ! Miller 1992
c2h6+ch3=c2h5+ch4       5.50E-01  4.0   8300.0   ! Miller 1992
c2h6+h=c2h5+h2          5.40E+02  3.5   5210.0   ! Miller 1992
c2h6+o=c2h5+oh          3.00E+07  2.0   5115.0   ! Miller 1992
c2h6+oh=c2h5+h2o        7.23E+06  2.0    864.0   ! Baulch 1992
c2h5+h=c2h4+h2          1.25E+14  0.0   8000.0   ! Marinov 1995
c2h5+h=ch3+ch3          3.00E+13  0.0      0.0   ! Warnatz 1984
c2h5+h=c2h6             1.00E+14  0.0      0.0   ! Marinov 1996
c2h5+oh=c2h4+h2o        4.00E+13  0.0      0.0   ! Marinov 1995
c2h5+o=ch3+ch2o         1.00E+14  0.0      0.0   ! Herron 1988
c2h5+ho2=ch3+ch2o+oh    3.00E+13  0.0      0.0   ! Marinov 1995
c2h5+o2=c2h4+ho2        3.00E+20 -2.86  6760.0   ! Marinov 1995
c2h4+h=c2h3+h2         3.36E-07  6.0   1692.0   ! Dagaut 1990
c2h4+oh=c2h3+h2o        2.02E+13  0.0   5936.0   ! Miller 1992
c2h4+o=ch3+hco         1.02E+07  1.88   179.0   ! Baulch 1994
c2h4+o=ch2hco+h         3.39E+06  1.88   179.0   ! Baulch 1994
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c2h4+ch3=c2h3+ch4       6.62E+00  3.7   9500.0   ! Marinov 1995
c2h4+h (+m)=c2h5(+m)    1.08E+12  0.454 1822.0   ! Feng  1993
low / 1.112E+34  -5.0    4448.0 /               !  (h)
troe / 1.0   1.0E-15   95.0  200.0 /
h2o /5.0/ h2/2.0/ co2/3.0/ co/2.0/
c2h4(+m)=c2h2+h2(+m)    1.8E+13   0.0    76000.  ! Towell 1961
low / 1.5E+15  0.0  55443. /                     ! Kiefer 1983
c2h4(+m)=c2h3+h(+m)     2.00E+16  0.0   110000.  ! Dean  1985
low / 1.4E+15  0.0  81833. /                     ! Kiefer 1983
c2h3+h=c2h2+h2          4.00E+13  0.0      0.0   ! Miller 1992
c2h3+o=ch2co+h          3.00E+13  0.0      0.0   ! Miller 1992
c2h3+o2=ch2o+hco        1.70E+29 -5.312  6500.   ! Marinov 1998
c2h3+o2=ch2hco+o        3.50E+14 -0.611  5260.   ! Marinov 1998
c2h3+o2=c2h2+ho2        2.12E-06  6.0   9484.0   ! cfm/nmm 1996
c2h3+oh=c2h2+h2o        2.00E+13  0.0      0.0   ! Miller 1992
c2h3+c2h=c2h2+c2h2      3.00E+13  0.0      0.0   ! Miller 1992
c2h3+ch=ch2+c2h2        5.00E+13  0.0      0.0   ! Miller 1992
c2h3+ch3=ac3h5+h        4.73E+02  3.7   5677.0   ! (i)
c2h3+ch3=c3h6           4.46E+56 -13.0 13865.0   ! (i)
c2h3+ch3=c2h2+ch4       2.00E+13  0.0      0.0   ! Fahr  1991
c2h3+c2h2=ch2chcch+h    2.00E+12  0.0   5000.0   ! Miller 1992
c2h3+c2h4=ch2chchch2+h  5.00E+11  0.0   7304.0   ! Tsang 1986
c2h3+c2h3=ch2chcch2+h   7.00E+13  0.0      0.0   ! Fahr  1991
c2h3+c2h3=c2h4+c2h2     1.45E+13  0.0      0.0   ! Fahr  1991
c2h2+oh=c2h+h2o         3.37E+07  2.0  14000.0   ! Miller 1992
c2h2+oh=hccoh+h         5.04E+05  2.3  13500.0   ! Miller 1992
c2h2+oh=ch2co+h         2.18E-04  4.5  -1000.0   ! Miller 1992
dup
c2h2+oh=ch2co+h         2.00E+11  0.0      0.0   ! Vandooren 1977
dup
c2h2+oh=ch3+co          4.83E-04  4.0  -2000.0   ! Miller 1992
hccoh+h=ch2co+h         1.00E+13  0.0      0.0   ! Miller 1992
c2h2+o=ch2+co           6.12E+06  2.0   1900.0   !   (j)
c2h2+o=hcco+h           1.43E+07  2.0   1900.0   !   (j)
c2h2+o=c2h+oh           3.16E+15 -0.6   15000.0  ! Miller 1992
c2h2+ch3=c2h+ch4        1.81E+11  0.0   17289.0  ! Tsang  1986
c2h2+o2=hcco+oh         4.00E+07  1.5   30100.   ! Marinov 1998
c2h2+m=c2h+h+m          4.20E+16  0.0  107000.0  ! Miller 1992
c2h2+h (+m)=c2h3(+m)    3.11E+11  0.58   2589.0  ! Knyazev 1995
low / 2.25E+40  -7.269   6577.0 /               !   (k)
troe /1.0 1.0E-15  675.0 1.0E+15 /
h2o /5.0/ h2/2.0/ co2/3.0/ co/2.0/
ch3hco+oh=ch3co+h2o     5.37E+10  0.73  -1110.0  ! Marinov 1995
ch3hco+h=ch3co+h2       4.09E+09  1.16   2400.0  ! Marinov 1995
ch3hco+o=ch3co+oh       5.89E+12  0.0    1810.0  ! Marinov 1995
ch3hco+ho2=ch3co+h2o2   1.70E+12  0.0   10700.0  ! Marinov 1995
ch3hco+o2=ch3co+ho2     2.00E+13  0.5   42200.0  ! Marinov 1995
ch3hco+ch3=ch3co+ch4    2.00E-06  5.64   2464.0  ! Marinov 1996
ch2hco+h=ch2co+h2       4.00E+13  0.0       0.0  ! Marinov 1996
ch2hco+o=ch2o+hco       1.00E+14  0.0       0.0  ! Marinov 1996
ch2hco+oh=ch2co+h2o     3.00E+13  0.0       0.0  ! Marinov 1996
ch2hco+o2=ch2o+co+oh    3.00E+10  0.0       0.0  ! Baulch  1992
ch2hco+ch3=>c2h5+co+h   4.90E+14 -0.50       0.0  !   (l)
ch2hco=ch2co+h          3.95E+38 -7.649 45115.0  ! Marinov 1995
chocho(+m)=ch2o+co(+m)  4.27E+12  0.0   50600.0  ! Marinov 1995
low /  8.91E+16    0.0    49200.0 /              ! Marinov 1995
chocho=co+co+h2         4.07E+42 -8.5   69278.0  !   (m)
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chocho+oh=hco+co+h2o     1.00E+13  0.0       0.0  ! Marinov 1995
chocho+o=hco+co+oh       7.24E+12  0.0    1970.0  ! Marinov 1995
chocho+h=ch2o+hco        1.00E+12  0.0       0.0  ! Marinov 1995
chocho+ho2=hco+co+h2o2   1.70E+12  0.0   10700.0  ! Marinov 1995
chocho+ch3=hco+co+ch4    1.74E+12  0.0    8440.0  ! Marinov 1995
chocho+o2=hco+co+ho2     1.00E+14  0.0   37000.0  ! Marinov 1995
ch3co(+m)=ch3+co(+m)     3.00E+12  0.0   16722.0  ! Warnatz 1984
low / 1.20E+15    0.0      12518.0 /              ! Warnatz 1984
ch2co+o=co2+ch2          1.75E+12  0.0    1350.0  ! Marinov 1995
ch2co+h=ch3+co           7.00E+12  0.0    3011.0  ! Warnatz 1984
ch2co+h=hcco+h2          2.00E+14  0.0    8000.0  !   (n)
ch2co+o=hcco+oh          1.00E+13  0.0    8000.0  ! Miller 1992
ch2co+oh=hcco+h2o        1.00E+13  0.0    2000.0  ! Miller 1992 (o)
ch2co+oh=ch2oh+co        3.73E+12  0.0   -1013.0  ! Brown 1989
ch2co(+m)=ch2+co(+m)     3.00E+14  0.0   70980.0  ! Miller 1992
low /  3.60E+15    0.0    59270.0 /               ! Miller 1992
c2h+h2=c2h2+h          4.09E+05  2.39    864.3  ! Miller 1992
c2h+o=ch+co              5.00E+13  0.0       0.0  ! Miller 1992
c2h+oh=hcco+h            2.00E+13  0.        0.0  ! Miller 1992
c2h+oh=c2+h2o            4.00E+07  2.0    8000.0  ! Miller 1992
c2h+o2=co+co+h           9.04E+12  0.0    -457.0  ! Opansky 1993
c2h+c2h2=c4h2+h          9.64E+13  0.0       0.0  ! Farhat 1993
c2h+c2h4=ch2chcch+h      1.20E+13  0.0       0.0  ! Tsang 1986
hcco+c2h2=h2ccch+co      1.00E+11  0.0    3000.0  ! Miller 1992
hcco+h=ch2(s)+co         1.00E+14  0.0       0.0  ! Miller 1992
hcco+o=h+co+co           8.00E+13  0.0       0.0  ! Peeters 1995
hcco+o=ch+co2            2.95E+13  0.0    1113.0  ! Peeters 1995
hcco+o2=hco+co+o         2.50E+08  1.0       0.0  ! Marinov 1998
hcco+o2=co2+hco          2.40E+11  0.0    -854.0  ! Marinov 1998
hcco+ch=c2h2+co          5.00E+13  0.0       0.0  ! Miller 1992
hcco+hcco=c2h2+co+co     1.00E+13  0.0       0.0  ! Miller 1992
hcco+oh=c2o+h2o          3.00E+13  0.0       0.0  ! Miller 1992
c2o+h=ch+co              1.00E+13  0.0       0.0  ! Miller 1992
c2o+o=co+co              5.00E+13  0.0       0.0  ! Miller 1992
c2o+oh=co+co+h           2.00E+13  0.0       0.0  ! Miller 1992
c2o+o2=co+co+o           2.00E+13  0.0       0.0  ! Miller 1992
c2+h2=c2h+h              4.00E+05  2.4    1000.0  ! Miller 1992
c2+o2=co+co            5.00E+13  0.0       0.0  ! Miller 1992
c2+oh=c2o+h              5.00E+13  0.0       0.0  ! Miller 1992
c3h8(+m)=c2h5+ch3(+m)    7.90E+22 -1.8   88629.0  ! Tsang 1988
low / 7.237E+27 -2.88 67448.0 /                   ! Al-Alami 1983
troe /1.0 1.0E-15 1500.0 1.0E+15/
h2o/5.0/ co2/3.0/ co/2.0/ h2/2.0/
c3h8+o2=ic3h7+ho2        4.00E+13  0.0   48610.0  ! Tsang 1988
c3h8+o2=nc3h7+ho2        4.00E+13  0.0   51360.0  ! Tsang 1988
c3h8+ho2=nc3h7+h2o2      4.76E+04  2.55  16492.0  ! Tsang 1988
c3h8+ho2=ic3h7+h2o2      9.64E+03  2.6   13909.0  ! Tsang 1988
c3h8+oh=nc3h7+h2o        3.16E+07  1.8     934.0  ! Cohen 1991
c3h8+oh=ic3h7+h2o        7.08E+06  1.9    -159.0  ! Cohen 1991
c3h8+o=nc3h7+oh          3.73E+06  2.4    5504.0  ! Cohen 1986
c3h8+o=ic3h7+oh          5.48E+05  2.5    3139.0  ! Cohen 1986
c3h8+h=ic3h7+h2          1.30E+06  2.4    4471.0  ! Tsang 1988
c3h8+h=nc3h7+h2          1.33E+06  2.54   6756.0  ! Tsang 1988
c3h8+ch3=nc3h7+ch4       9.04E-01  3.65   7153.0  ! Tsang 1988
c3h8+ch3=ic3h7+ch4       1.51E+00  3.46   5480.0  ! Tsang 1988
c3h8+c2h3=ic3h7+c2h4     1.00E+03  3.1    8830.0  ! Tsang 1988
c3h8+c2h3=nc3h7+c2h4     6.00E+02  3.3   10500.0  ! Tsang 1988
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c3h8+c2h5=ic3h7+c2h6    1.51E+00  3.46   7470.0  ! Tsang 1988
c3h8+c2h5=nc3h7+c2h6    9.03E-01  3.65   9140.0  ! Tsang 1988
c3h8+ac3h5=c3h6+nc3h7   2.35E+02  3.3   19842.0  ! Tsang 1988
c3h8+ac3h5=c3h6+ic3h7   7.83E+01  3.3   18169.0  ! Tsang 1988
nc3h7(+m)=c2h4+ch3(+m)  1.23E+13  -0.1  30202.0  ! Bencsura 1992
low / 5.485E+49  -10.0  35766.0 /                ! Bencsura 1992
troe / 2.17   1.0E-15   251.0   1185.0 /
h2o /5.0/ h2/2.0/ co2/3.0/ co/2.0/
nc3h7+o2=c3h6+ho2      3.58E+09   0.0   -3532.0  ! Dagaut 1992
ic3h7+o2=c3h6+ho2      6.10E+20   -2.86  7910.0  !   (p)
c3h6+h(+m)=ic3h7(+m)   5.70E+09   1.16    874.0  ! Seakins 1993
low / 1.64E+54   -11.1   9364.0 /                ! Marinov 1996
troe / 1.0   1.0E-15   260.0   3000.0 /
h2o /5.0/ h2/2.0/ co2/3.0/ co/2.0/
ic3h7+h=c2h5+ch3       5.00E+13   0.0       0.0  ! Tsang 1988
nc3h7+h=c2h5+ch3       1.00E+14   0.0       0.0  ! Tsang 1988
c3h6=pc3h5+h           7.58E+14   0.0  101300.0  ! Dagaut 1992
c3h6=sc3h5+h           1.45E+15   0.0   98060.0  ! Dagaut 1992
c3h6=c2h2+ch4          2.50E+12   0.0   70000.0  ! Hidaka 1992
c3h6=ac3h4+h2          3.00E+13   0.0   80000.0  ! Hidaka 1992
c3h6+ho2=ac3h5+h2o2    9.64E+03   2.6   13910.0  ! Tsang 1991
c3h6+oh+o2=ch3hco+ch2o+oh 3.00E+10  0.0 -8280.0  ! Dagaut 1992
c3h6+oh=ac3h5+h2o      3.12E+06   2.0    -298.0  ! Tsang 1991
c3h6+oh=sc3h5+h2o      1.11E+06   2.0    1451.0  ! Tsang 1991
c3h6+oh=pc3h5+h2o      2.11E+06   2.0    2778.0  ! Tsang 1991
c3h6+o=ch3chco+h+h     5.01E+07   1.76     76.0  ! Tsang 1991
c3h6+o=c2h5+hco        1.58E+07   1.76  -1216.0  ! Tsang 1991
c3h6+o=ac3h5+oh        5.24E+11   0.7    5884.0  ! Tsang 1991
c3h6+o=pc3h5+oh        1.20E+11   0.7    8959.0  ! Tsang 1991
c3h6+o=sc3h5+oh        6.03E+10   0.7    7632.0  ! Tsang 1991
c3h6+h=c2h4+ch3        7.23E+12   0.0    1302.0  ! Tsang 1991
c3h6+h=ac3h5+h2        1.73E+05   2.5    2492.0  ! Tsang 1991
c3h6+h=sc3h5+h2        4.09E+05   2.5    9794.0  ! Tsang 1991
c3h6+h=pc3h5+h2        8.04E+05   2.5   12284.0  ! Tsang 1991
c3h6+o2=pc3h5+ho2      2.00E+13   0.0   47600.0  ! Dagaut 1992
c3h6+o2=sc3h5+ho2      2.00E+13   0.0   44000.0  ! Dagaut 1992
c3h6+o2=ac3h5+ho2      2.29E+12   0.0   39200.0  ! Dagaut 1992
c3h6+ch3=ac3h5+ch4     2.22E+00   3.5    5675.0  ! Tsang 1991
c3h6+ch3=sc3h5+ch4     8.43E-01   3.5   11656.0  ! Tsang 1991
c3h6+ch3=pc3h5+ch4     1.35E+00   3.5   12848.0  ! Tsang 1991
c3h6+hco=ac3h5+ch2o    1.08E+07   1.9   17010.0  ! Tsang 1991
ch3chco+oh=ch2chco+h2o 4.00E+06   2.0       0.0   !   (q)
ch3chco+o=ch2chco+oh   7.60E+08   1.5    8500.0   !   (q)
ch3chco+h=ch2chco+h2   2.00E+05   2.5    2500.0   !   (q)
ch3chco+h=c2h5+co      2.00E+13   0.0    2000.0   !   (r)
ch3chco+o=ch3+hco+co   3.00E+07   2.0       0.0   !   (s)
ch2chcho+oh=ch2chco+h2o 1.00E+13  0.0       0.0   !   (t)
ch2chcho+o=ch2chco+oh  7.24E+12   0.0    1970.0   !   (t)
ch2chcho+o=ch2co+hco+h 5.01E+07   1.76     76.0   !   (s)
ch2chcho+h=ch2chco+h2  3.98E+13   0.0    4200.0   !   (t)
ch2chcho+h=c2h4+hco    2.00E+13   0.0    3500.0   !   (r)
ch2chcho+o2=ch2chco+ho2 3.00E+13  0.0   36000.0   !   (u)
ch2chco=c2h3+co        1.00E+14   0.0   34000.0   !   (v)
ch2chco+o=c2h3+co2     1.00E+14   0.0       0.0   !   (w)
ac3h5+o2=ch2chcho+oh   1.82E+13  -0.41 22859.0   ! Bozzelli 1993
ac3h5+o2=ac3h4+ho2     4.99E+15  -1.4  22428.0   ! Bozzelli 1993
ac3h5+o2=ch2hco+ch2o   1.06E+10  0.34  12838.0   ! Bozzelli 1993
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ac3h5+o2=c2h2+ch2o+oh  2.78E+25  -4.8  15468.0   ! Bozzelli 1993
ac3h5+ho2=ch2chcho+h+oh 1.00E+13 0.0        0.0   ! Tsang 1991
ac3h5+oh=ac3h4+h2o     1.00E+13  0.0        0.0   ! Tsang 1991
ac3h5+h=ac3h4+h2       5.00E+13  0.0        0.0   ! Tsang 1991 (x)
ac3h5+h=c3h6          1.88E+26  -3.6   5468.0   !   (y)
ac3h5+o=ch2chcho+h     1.81E+14  0.0        0.0   ! Slagle 1992
ac3h5+ch3=ac3h4+ch4    3.02E+12  -0.32  -131.0   ! Tsang 1991
ac3h5+c2h2=c-c5h6+h    2.95E+32  -5.83 25733.0   !   (y)
ac3h5+ch3=c4h8-1       1.76E+50  -11.0 18600.0   !   (y)
ac3h5+c2h3=c-c5h6+h+h  1.59E+65  -14.0 61265.0   !   (y)
pc3h5+o2=ch3hco+hco    1.09E+23  -3.29  3892.0   !   (z)
pc3h5+o2=ch3chco+h+o   1.60E+15  -0.78  3135.0   !   (z)
pc3h5+o=ch3chco+h      1.00E+14   0.0       0.0   !   (aa)
pc3h5+h=pc3h4+h2       2.00E+13   0.0       0.0   !   (aa)
pc3h5+oh=pc3h4+h2o     1.00E+13   0.0       0.0   !   (aa)
pc3h5+h=ac3h5+h        1.00E+14   0.0       0.0   ! Marinov 1996
sc3h5+h=ac3h5+h        1.00E+14   0.0       0.0   ! Marinov 1996
sc3h5+o2=ch3co+ch2o    1.09E+22  -3.29  3892.0   !   (z)
sc3h5+o=ch2co+ch3      1.00E+14   0.0       0.0   !   (aa)
sc3h5+h=pc3h4+h2       4.00E+13   0.0       0.0   !   (aa)
sc3h5+oh=pc3h4+h2o     2.00E+13   0.0       0.0   !   (aa)
ac3h4+h=h2ccch+h2      2.00E+07   2.0    5000.0   ! Marinov 1998
ac3h4+o=c2h4+co        1.34E+07   1.88    179.0   !   (bb)
ac3h4+oh=h2ccch+h2o    1.00E+07   2.0    1000.0   ! Marinov 1998
ac3h4+ch3=h2ccch+ch4   1.50E+00   3.5    5600.0   ! Marinov 1998
ac3h4=pc3h4            1.48E+13   0.0    60401.   ! Lifshitz 1975
pc3h4+h=h2ccch+h2      2.00E+07   2.0    5000.0   ! Marinov 1998
pc3h4+o=c2h4+co        1.50E+13   0.0    2102.0   ! Warnatz84 (cc)
pc3h4+oh=h2ccch+h2o    1.00E+07   2.0    1000.0   ! Marinov 1998
pc3h4+ch3=h2ccch+ch4   1.50E+00   3.5    5600.0   ! Marinov 1998
pc3h4+h=ch3+c2h2       5.12E+10   1.0    2060.0   ! Marinov 1998
pc3h4+h(+m)=sc3h5(+m)  6.50E+12   0.0    2000.0   ! Wagner 1972
low / 8.45E+39  -7.27    6577.0 /                !  (dd)
ac3h4+h(+m)=ac3h5(+m)  1.20E+11   0.69   3007.0   ! Tsang 1992
low / 5.56E+33   -5.0    4448.0 /              !  (ee)
ac3h4+h(+m)=sc3h5(+m)  8.49E+12   0.0    2000.0   ! Wagner 1972
low / 1.11E+34   -5.0    4448.0 /               !  (ee)
h2ccch+o2=ch2co+hco    3.00E+10 0.0      2868.0   ! Miller 1992
h2ccch+o=ch2o+c2h      2.00E+13 0.0         0.0   ! Miller 1992
h2ccch+h=c3h2+h2       5.00E+13 0.0      3000.0   ! Miller 1992
h2ccch+oh=c3h2+h2o     2.00E+13 0.0         0.0   ! Miller 1992
h2ccch+c2h3=c-c5h5+h   9.63E+40 -7.8    28820.0   ! Marinov 1996
h2ccch+ch3=ch3chcch2   5.00E+12 0.0         0.0   ! Wu 1987
h2ccch+ch3=ch3ch2cch   5.00E+12 0.0         0.0   ! Wu 1987
h2ccch+ch=hcchcch+h    7.00E+13 0.0         0.0   ! Miller 1992
h2ccch+ch=h2cccch+h    7.00E+13 0.0         0.0   ! Miller 1992
h2ccch+h(+m)=ac3h4(+m) 1.66E+15 -0.37       0.0   !  (ff)
low / 3.36E+45 -8.52  6293.0  /                 ! Kiefer 1995 (gg)
h2o/5.0/ h2/2.0/ co2/3.0/ co/2.0/ o2/2.0/ c2h2/2.0/
h2ccch+h(+m)=pc3h4(+m) 1.66E+15 -0.37       0.0   !  (ff)
low / 8.78E+45 -8.9   7974.0 /                  ! Kiefer 1995 (gg)
h2o /5.0/ h2/2.0/ co2/3.0/ co/2.0/ o2/2.0/ c2h2/2.0/
h2ccch+h2ccch=c6h6     5.562e20  -2.535  1692.0  ! Marinov 1998
h2ccch+ac3h5=fulvene+h+h 5.562e20 -2.535 1692.0  ! Marinov 1998
h2ccch+h2ccch=c6h5+h   2.00e12  0.0         0.0   ! Marinov 1998
c3h2+o2=hcco+co+h     5.00E+13  0.0         0.0   ! Miller 1992
c3h2+oh=c2h2+hco      5.00E+13  0.0         0.0   ! Miller 1992
```

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chchcho+o2=hco+chocho 3.00E+12  0.0        0.0   !  (hh)
chchcho=c2h2+hco      1.00E+14  0.0    33000.0   !  (ii)
chchcho+h=ch2chco+h   1.00E+14  0.0        0.0   ! Marinov 1996
chchcho+oh=hcccho+h2o 1.00E+13  0.0        0.0   !  (aa)
chchcho+h=hcccho+h2   2.00E+13  0.0        0.0   !  (aa)
hcccho+h=c2h2+hco     1.00E+14  0.0     3000.0   !  (jj)
hcccho+oh=hccco+h2o   1.00E+13  0.0        0.0   !  (t)
hcccho+h=hccco+h2     4.00E+13  0.0     4200.0   !  (t)
hccco+o2=hco+co+co    1.40E+09  1.0        0.0   !  (kk)
hccco+h=c2h2+co       1.00E+14  0.0        0.0   !  (kk)
c4h10=c2h5+c2h5       2.00E+16  0.0    81300.0   ! Pitz 1991
c4h10=nc3h7+ch3       1.74E+17  0.0    85700.0   ! Pitz 1991
c4h10=pc4h9+h         1.00E+14  0.0   100000.0   ! Pitz 1991
c4h10=sc4h9+h         1.00E+14  0.0   100000.0   ! Pitz 1991
c4h10+o2=pc4h9+ho2    2.50E+13  0.0    49000.0   ! Pitz 1991
c4h10+o2=sc4h9+ho2    4.00E+13  0.0    47600.0   ! Pitz 1991
c4h10+ac3h5=pc4h9+c3h6  7.94E+11 0.0   20500.0   ! Pitz 1991
c4h10+ac3h5=sc4h9+c3h6  3.16E+11 0.0   16400.0   ! Pitz 1991
c4h10+ch3=pc4h9+ch4   5.00E+11  0.0    13600.0   ! Marinov 1998
c4h10+ch3=sc4h9+ch4   4.30E+11  0.0    10500.0   ! Marinov 1998
c4h10+h=pc4h9+h2      2.84E+05  2.54    6050.0   ! Marinov 1998
c4h10+h=sc4h9+h2      5.68E+05  2.40    3765.0   ! Marinov 1998
c4h10+oh=pc4h9+h2o    4.13E+07  1.73    753.0    ! Pitz 1991
c4h10+oh=sc4h9+h2o    7.23E+07  1.64   -247.0    ! Pitz 1991
c4h10+o=pc4h9+oh      1.13E+14  0.0     7850.0   ! Pitz 1991
c4h10+o=sc4h9+oh      5.62E+13  0.0     5200.0   ! Pitz 1991
c4h10+ho2=pc4h9+h2o2  1.70E+13  0.0    20460.0   ! Pitz 1991
c4h10+ho2=sc4h9+h2o2  1.12E+13  0.0    17700.0   ! Pitz 1991
sc4h9(+m)=c3h6+ch3(+m) 2.14E+12 0.65   30856.0   ! Knyazev 1996
low /6.323e58 -12.85 35567./
h2o/5./ h2/2./ co2/3./ co/2./
sc4h9=c4h8-1+h        2.00E+13  0.0    40400.0   ! Pitz 1991
sc4h9=c4h8-2+h        5.01E+12  0.0    37900.0   ! Pitz 1991
pc4h9(+m)=c2h5+c2h4(+m) 1.06e13 0.0    27828.0   ! Knyazev 1996
low / 1.897e55 -11.91 32263./
h2o/5./ h2/2.0/ co2/3.0/ co/2.0/
pc4h9=c4h8-1+h        1.26E+13  0.0    38600.0   ! Pitz 1991
c4h8-1=c2h3+c2h5      1.00E+19  -1.0   96770.0   ! Pitz 1991
c4h8-1=h+c4h7         4.11E+18  -1.0   97350.0   ! Pitz 1991
c4h8-1+ch3=c4h7+ch4   1.00E+11  0.0     7300.0   ! Pitz 1991
c4h8-1+h=c4h7+h2      5.00E+13  0.0     3900.0   ! Pitz 1991
c4h8-1+o=nc3h7+hco    1.80E+05  2.5    -1029.0   ! Pitz 1991
c4h8-1+o=ch2chcho+ch3+h 9.67E+04 2.5   -1029.0   ! Pitz 1991
c4h8-1+oh=c4h7+h2o    2.25E+13  0.0     2217.0   ! Pitz 1991
c4h8-1+ac3h5=c4h7+c3h6 7.90E+10  0.0   12400.0   ! Pitz 1991
c4h8-1+o2=c4h7+ho2   4.00E+12   0.0    33200.0   ! Pitz 1991
c4h8-2=h+c4h7        4.11E+18  -1.0    97350.0   ! Pitz 1991
c4h8-2+ch3=c4h7+ch4  1.00E+11   0.0     8200.0   ! Pitz 1991
c4h8-2+h=c4h7+h2     5.00E+13   0.0     3800.0   ! Pitz 1991
c4h8-2+o=ic3h7+hco   2.79E+06   2.12   -1775.0   ! Pitz 1991
c4h8-2+oh=c4h7+h2o   3.90E+13   0.0     2217.0   ! Pitz 1991
c4h8-2+o=ch3co+c2h5  1.53E+07   1.87   -1476.0   ! Adusei 1994
c4h8-2+o=ch3+ch3chco+h 8.22E+06 1.87   -1476.0   ! Adusei 1994
c4h8-2+o2=c4h7+ho2   8.00E+13   0.0    37400.0   ! Pitz 1991
c4h7=ch2chchch2+h    1.00E+14   0.0    55000.0   ! Pitz 1991
c4h7+oh=ch2chchch2+h2o 1.00E+13 0.0        0.0   ! Pitz 1991
c4h7+ch3=ch2chchch2+ch4 8.00E+12 0.0       0.0   ! Pitz 1991
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c4h7+ac3h5=c3h6+ch2chchch2 6.31E+12 0.0    0.0   ! Pitz 1991
c4h7+o2=ch2chchch2+ho2 1.00E+09 0.0        0.0   ! Pitz 1991
c4h7+h=ch2chchch2+h2  3.16E+13  0.0        0.0   ! Pitz 1991
ch2chchch2+oh=ch2chchch+h2o  2.00E+07 2.0 5000.0 ! Miller 1992
ch2chchch2+oh=ch2chcch2+h2o  2.00E+07 2.0 2000.0 ! Miller 1992
ch2chchch2+o=hco+ac3h5     6.02E+08  1.45 -858.0 ! Adusei 1993
ch2chchch2+o=ch2hco+c2h3   1.00E+12  0.0     0.0 ! Pitz 1991
ch2chchch2+h=ch2chchch+h2  3.00E+07  2.0 13000.0 ! Miller 1992
ch2chchch2+h=ch2chcch2+h2  3.00E+07  2.0  6000.0 ! Miller 1992
ch3ch2cch+oh=ch3chcch+h2o  1.00E+07  2.0  2000.0 !  (q)
ch3ch2cch+h=c2h5+c2h2      1.00E+14  0.0  3000.0 !  (jj)
ch3chcch2+oh=ch2chcch2+h2o 2.00E+07  2.0  1000.0 !  (q)
ch3chcch2+oh=ch3ccch2+h2o  1.00E+07  2.0  2000.0 !  (ll)
ch3chcch2+oh=ch3chcch+h2o  2.00E+07  2.0  2500.0 !  (ll)
ch3chcch2+h=ch2chcch2+h2   5.00E+07  2.0  5000.0 !  (q)
ch3chcch2+h=ch3ccch2+h2    1.50E+07  2.0  6000.0 !  (ll)
ch3chcch2+h=ch3chcch+h2    3.00E+07  2.0  6500.0 !  (ll)
ch3chcch2+h=ch3+ac3h4      2.00E+13  0.0  2000.0 !  (r)
ch3chcch+h=ch3+h2ccch      1.00E+14  0.0     0.0 ! Marinov 1996
ch3chcch+o2=ch3chco+hco    4.16E+10  0.0  2510.0 ! Slagle 1992
ch3chcch+oh=ch2chcch+h2o   3.00E+13  0.0     0.0 !  (mm)
ch2chcch2+h=ch3+h2ccch     1.00E+14  0.0     0.0 !  (nn)
ch2chcch2+h=ch3ccch2+h     3.00E+13  0.0     0.0 !  (nn)
ch2chcch2+c2h2=c6h6+h      3.00E+11  0.0 14900.0 ! Marinov 1996
ch3ccch2+h=ch3+h2ccch      1.00E+14  0.0     0.0 ! Marinov 1996
ch3ccch2+o2=ch3co+ch2co    4.16E+10  0.0  2510.0 ! Marinov 1996
ch3ccch2+h=h2cccch2+h2     1.00E+14  0.0  8000.0 !  (mm)
ch3ccch2+oh=h2cccch2+h2o   1.00E+13  0.0     0.0 !  (mm)
ch2chchch+h=ch2chcch2+h    1.00E+14  0.0     0.0 ! Miller 1992
ch2chchch+oh=ch2chcch+h2o  2.00E+07  2.0  1000.0 ! Miller 1992
ch2chchch+h=ch2chcch+h2    3.00E+07  2.0  1000.0 ! Miller 1992
ch2chchch+c2h2=c6h6+h      1.60E+16 -1.33 5400.0 ! Wang 1994
ch3chcch(+m)=ch2chcch+h(+m) 1.00E+13 0.0 49000.0 !   (pp)
low / 2.00E+14    0.0    41000.0 /             !   (pp)
ch3ccch2(+m)=h2cccch2+h(+m)  1.00E+13 0.0 56000.0! Marinov 1996
 low / 2.00E14  0.0  48000.0/                    ! Marinov 1996
ch2chcch2(+m)=ch2chcch+h(+m) 1.00E+14 0.0 50000.0 ! Miller 1992
low / 2.00E+15    0.0    42000.0 /             ! Miller 1992
ch2chchch(+m)=ch2chcch+h(+m) 1.00E+14 0.0 37000.0 ! Miller 1992
low / 1.00E+14    0.0    30000.0 /               ! Miller 1992
ch2chchch+o2=chchcho+ch2o   1.00E+12 0.0     0.0 !   (qq)
ch2chchch+o2=ch2chcch+ho2   1.00E+07 2.0 10000.0 !   (rr)
ch3ccch2+h2ccch=c6h5ch2+h   3.00E+12 0.0     0.0 ! Marinov 1996
ch3chcch+h2ccch=c6h5ch2+h   3.00E+12 0.0     0.0 ! Marinov 1996
ch3ccch2+ch3ccch2=ch3c6h4ch2+h 3.00E+12 0.0  0.0 ! Marinov 1996
ch3chcch+ch3chcch=ch3c6h4ch2+h 3.00E+12 0.0  0.0 ! Marinov 1996
h2cccch2+oh=h2cccch+h2o     2.00E+07 2.0  2000.0 ! (ss)
h2cccch2+h=h2cccch+h2       3.00E+07 2.0  6000.0 ! (ss)
ch2chcch+oh=hcchcch+h2o     7.50E+06 2.0  5000.0 ! Miller 1992
ch2chcch+h=hcchcch+h2       2.00E+07 2.0 15000.0 ! Miller 1992
ch2chcch+oh=h2cccch+h2o     1.00E+07 2.0  2000.0 ! Miller 1992
ch2chcch+h=h2cccch+h2       3.00E+07 2.0  5000.0 ! Miller 1992
hcchcch+h=h2cccch+h         1.00E+14 0.0     0.0 ! Miller 1992
hcchcch+c2h2=c6h5           9.60E+70 -17.77 31300.! Wang   1994
hcchcch+o2=hccccho+hco      3.00E+12 0.0     0.0 !   (tt)
h2cccch+o2=ch2co+hcco       1.00E+12 0.0     0.0 ! Miller 1992
h2cccch+oh=c4h2+h2o         3.00E+13 0.0     0.0 ! Miller 1992
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h2cccch+o=ch2co+c2h         2.00E+13 0.0     0.0 ! Miller 1992
h2cccch+o=h2c4o+h           2.00E+13 0.0     0.0 ! Miller 1992
h2cccch+h=c4h2+h2           5.00E+13 0.0     0.0 ! Miller 1992
h2cccch+ch2=ac3h4+c2h       2.00E+13 0.0     0.0 ! Miller 1992
h2cccch+c2h2=c6h5           3.00E+11 0.0 14900.0 !   (uu)
h2cccch(+m)=c4h2+h(+m)      1.00E+14 0.0 47000.0 ! Marinov 1998
low / 2.0E+15 0.0 40000.0/                       ! Marinov 1998
hcchcch(+m)=c4h2+h(+m)      1.00E+14 0.0 36000.0 ! Miller 1992
low / 1.00E+14    0.0    30000.0  /            ! Miller 1992
c4h2+ch2=c5h3+h             1.30E+13 0.0  4326.0 ! Miller 1992
c4h2+ch=c5h2+h              1.00E+14 0.0     0.0 ! Miller 1992
c4h2+ch2(s)=c5h3+h          3.00E+13 0.0     0.0 ! Miller 1992
c4h2+c2h=c6h2+h             9.60E+13 0.0     0.0 ! Marinov 1996
c4h2+oh=h2c4o+h             6.66E+12 0.0  -410.0 ! Miller 1992
c4h2+o=c3h2+co              1.20E+12 0.0     0.0 ! Miller 1992
h2c4o+h=c2h2+hcco           5.00E+13 0.0  3000.0 ! Miller 1992
h2c4o+oh=ch2co+hcco         1.00E+07 2.0  2000.0 ! Miller 1992
l-c5h8+oh=l-c5h7+h2o        7.00E+06 2.0     0.0 !     (q)
l-c5h8+h=l-c5h7+h2          7.00E+06 2.0  5000.0 !     (q)
l-c5h8+h=ac3h5+c2h4         3.35E+08 1.5  2000.0 !     (r)
c-c5h7=c-c5h6+h             3.16E+15 0.0 36000.0 ! Arends 1993
c-c5h7=l-c5h7               3.16E+15 0.0 39500.0 ! Arends 1993
l-c5h7+o=ch2chcho+c2h3      2.00E+14 0.0     0.0 ! Marinov 1996
l-c5h7+h=l-c5h8             1.00E+14 0.0     0.0 ! Marinov 1996
c-c5h6+o2=c-c5h5+ho2        5.00E+13 0.0 35400.0 !    (vv)
c-c5h6+ho2=c-c5h5+h2o2      1.99E+12 0.0 11660.0 ! Emdee 1992
c-c5h6+oh=c-c5h5+h2o        3.43E+09 1.18 -447.0 ! Emdee 1992
c-c5h6+o=c-c5h5+oh          1.81E+13 0.0  3080.0 ! Emdee 1992
c-c5h6+h=c-c5h5+h2          2.19E+08 1.77 3000.0 ! Emdee 1992
c-c5h6+ch3=c-c5h5+ch4       3.11E+11 0.0  5500.0 !   (ww)
c-c5h6+c2h3=c-c5h5+c2h4     6.00E+12 0.0     0.0 ! Emdee 1992
c-c5h6+ch2chchch=c-c5h5+ch2chchch2  6.00E+12 0.0   0.0 ! Emdee 1992
c-c5h6+c6h5o=c-c5h5+c6h5oh  3.16E+11 0.0  8000.0 ! Emdee 1992
c-c5h5+h=c-c5h6             2.00E+14 0.0     0.0 ! Marinov 1996
c-c5h5+o=c-c5h4o+h          1.00E+14 0.0     0.0 ! Marinov 1996
c-c5h5+ho2=c-c5h5o+oh       3.00E+13 0.0     0.0 ! Emdee 1992
c-c5h5+oh=c-c5h4oh+h        3.00E+13 0.0     0.0 ! Emdee 1992
c-c5h5+c-c5h5=c10h8+h+h     2.00E+13 0.0  8000.0 ! Marinov 1998
c-c5h5o=ch2chchch+co        2.51E+11 0.0 43900.0 ! Emdee 1992
c-c5h4oh=c-c5h4o+h          2.10E+13 0.0 48000.0 ! Emdee 1992
c-c5h4o=co+c2h2+c2h2        1.00E+15 0.0 78000.0 ! Emdee 1992
c6h6+o2=c6h5+ho2            6.30E+13 0.0 60000.0 ! Emdee 1992
c6h6+oh=c6h5+h2o            1.63E+08 1.42 1454.0 ! Baulch 1992
c6h6+oh=c6h5oh+h            6.70E+12 0.0 10592.0 ! He 1988 (xx)
c6h6+o=c6h5o+h              2.40E+13 0.0  4670.0 ! Leidreiter 1989
c6h6+h=c6h5+h2              3.03E+02 3.3  5690.0 !   (yy)
c6h5+h=c6h6                 8.00E+13 0.0     0.0 ! Baulch 1992
c6h5+c2h4=c6h5c2h3+h        7.23E+01 3.5  8345.0 ! Yu  1994
c6h5+c2h2=c6h5c2h+h         3.98E+13 0.0 10099.0 ! Stein 1989
c6h5+oh=c6h5o+h             5.00E+13 0.0     0.0 ! Miller 1992
c6h5+o=c-c5h5+co            1.00E+14 0.0     0.0 ! Frank 1994
c6h5+o2=c6h5o+o             2.60E+13 0.0  6120.0 ! Frank 1994
c6h5+o2=oc6h4o+h            3.00E+13 0.0  8981.0 ! Frank 1994
c6h5+c6h5=biphenyl          5.00E+12 0.0     0.0 ! Fahr 1989
c6h5+c6h6=biphenyl+h        4.00E+11 0.0  4000.0 ! Fahr 1989
oc6h4o=c-c5h4o+co           1.00E+15 0.0 78000.0 ! Marinov 1996
c6h5o=co+c-c5h5             7.40E+11 0.0 43850.0 ! Frank 1994
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c6h5o+h=c6h5oh              1.00E+14 0.0      0.0 ! Arends 1993
c6h5o+h=c-2*4c6h6o          1.00E+14 0.0      0.0 ! Arends 1993
c6h5oh+oh=c6h5o+h2o         2.95E+06 2.0 -1310.0 ! Knispel 1990
c6h5oh+ch3=c6h5o+ch4        1.81E+11 0.0  7716.0 ! Mulcahy 1965
c6h5oh+h=c6h5o+h2           1.58E+13 0.0  6100.0 ! Arends 1993
c6h5oh+o=c6h5o+oh           2.81E+13 0.0  7352.0 ! Emdee 1992
c6h5oh+c2h3=c2h4+c6h5o      6.00E+12 0.0      0.0 ! Emdee 1992
c6h5oh+c6h5=c6h6+c6h5o      4.91E+12 0.0  4400.0 ! Emdee 1992
c-2*4c6h6o+h=c-c5h7+co      2.51E+13 0.0  4700.0 ! Arends 1993
c6h5ch3=c6h5+ch3            1.40E+16 0.0 99800.0 ! Emdee 1992
c6h5ch3+o2=c6h5ch2+ho2      2.00E+12 0.0 39080.0 ! Ingram 1994
c6h5ch3+oh=c6h5ch2+h2o      1.26E+13 0.0 2583.0  ! Emdee 1992
c6h5ch3+o=c6h5ch2+oh        5.00E+08 1.5 8000.0  ! Emdee 1992
c6h5ch3+h=c6h5ch2+h2        3.98E+02 3.44 3120.0 ! Emdee 1992
c6h5ch3+h=c6h6+ch3          1.20E+13 0.0 5148.0  ! Emdee 1992
c6h5ch3+o=oc6h4ch3+h        1.63E+13 0.0 3418.0  ! Emdee 1992
c6h5ch3+ch3=ch4+c6h5ch2     3.16E+11 0.0 9500.0  ! Emdee 1992
c6h5ch3+c6h5=c6h6+c6h5ch2   2.10E+12 0.0 4400.0  ! Emdee 1992
c6h5ch2+h=c6h5ch3           1.80E+14 0.0    0.0  ! Emdee 1992
c6h5ch2+c6h5oh=c6h5o+c6h5ch3 1.05E+11 0.0 9500.0 ! Emdee 1992
c6h5ch2+hoc6h4ch3=oc6h4ch3+c6h5ch3 1.05E+11 0.0 9500.0 ! Emdee 1992
c6h5ch2+o=c6h5cho+h         2.50E+14 0.0    0.0  ! Emdee 1992
c6h5ch2+o=c6h5+ch2o         8.00E+13 0.0    0.0  ! Emdee 1992
c6h5ch2+ho2=c6h5cho+h+oh    2.50E+14 0.0    0.0  ! Emdee 1992
c6h5ch2+ho2=c6h5+ch2o+oh    8.00E+13 0.0    0.0  ! Emdee 1992
c6h5ch2+ch3=c6h5c2h5        1.19E+13 0.0  221.0  ! Brand  1990
c6h5ch2+h2ccch=c10h10       1.00E+10 0.0    0.0  !  (zz)
c6h5ch2+c2h2=indene+h       3.20E+11 0.0 7000.0  !  (aaa)
c6h5ch2+c6h5cho=c6h5ch3+c6h5co 2.77E+03 2.81 5773.0 ! Emdee 1992
c6h5ch2+oh=c6h5ch2oh        6.00E+13 0.0    0.0  ! Emdee 1992
c6h5ch2oh+oh=c6h5cho+h2o+h  8.43E+12 0.0 2583.0  ! Emdee 1992
c6h5ch2oh+h=c6h5cho+h2+h    8.00E+13 0.0 8235.0  ! Emdee 1992
c6h5ch2oh+h=c6h6+ch2oh      1.20E+13 0.0 5148.0  ! Emdee 1992
c6h5ch2oh+c6h5ch2=c6h5cho+c6h5ch3+h 2.11E+11 0.0  9500. ! Emdee92
c6h5ch2oh+c6h5=c6h5cho+c6h6+h 1.40E+12 0.0 4400.0 ! Emdee 1992
c6h5cho+o2=c6h5co+ho2       1.02E+13 0.0 38950.0 ! Emdee 1992
c6h5cho+oh=c6h5co+h2o       1.71E+09 1.18 -447.0 ! Emdee 1992
c6h5cho+h=c6h5co+h2         5.00E+13 0.0  4928.0 ! Emdee 1992
c6h5cho+h=c6h5+ch2o         2.00E+13 0.0  2000.0 !  (r)
c6h5cho+h=c6h6+hco          1.20E+13 0.0  5148.0 ! Emdee 1992
c6h5cho+o=c6h5co+oh         9.04E+12 0.0  3080.0 ! Emdee 1992
c6h5cho+ch3=ch4+c6h5co      2.77E+03 2.81 5773.0 ! Emdee 1992
c6h5cho+c6h5=c6h6+c6h5co    7.01E+11 0.0  4400.0 ! Emdee 1992
c6h5co=c6h5+co              3.98E+14 0.0 29400.0 ! Emdee 1992
oc6h4ch3+h=hoc6h4ch3        2.50E+14 0.0      0.0 ! Emdee 1992
oc6h4ch3=c6h6+h+co          2.51E+11 0.0 43900.0 ! Emdee 1992
hoc6h4ch3+oh=oc6h4ch3+h2o   6.00E+12 0.0      0.0 ! Emdee 1992
hoc6h4ch3+h=oc6h4ch3+h2     1.15E+14 0.0 12400.0 ! Emdee 1992
hoc6h4ch3+h=c6h5ch3+oh      2.21E+13 0.0  7910.0 ! Emdee 1992
hoc6h4ch3+h=c6h5oh+ch3      1.20E+13 0.0  5148.0 ! Emdee 1992
c6h5c2h5+oh=c6h5c2h3+h2o+h  8.43E+12 0.0  2583.  ! Emdee 1992
c6h5c2h5+h=c6h5c2h3+h2+h    8.00E+13 0.0  8235.0 ! Emdee 1992
c6h5c2h3+oh=c6h4c2h3+h2o    1.63E+08 1.42 1454.0 ! Marinov 1996
c6h5c2h3+h=c6h4c2h3+h2      3.03E+02 3.3  5690.0 ! Marinov 1996
c6h5c2h3+oh=c6h5cch2+h2o    1.00E+07 2.0  2000.0 ! Marinov 1996
c6h5c2h3+h=c6h5cch2+h2      2.00E+07 2.0  6000.0 ! Marinov 1996
c6h5chch+h=c6h5cch2+h       1.00E+14 0.0      0.0 ! Marinov 1996
```

```
c6h5cch2+oh=c6h5c2h+h2o     2.00E+13 0.0     0.0 ! Marinov 1996
c6h5cch2+h=c6h5c2h+h2       5.00E+13 0.0     0.0 ! Marinov 1996
c6h5c2h+o=c6h5cco+h         4.80E+09 1.0     0.0 !  (bbb)
c6h5cco+o2=c6h5co+co2       1.00E+12 0.0     0.0 !  (ccc)
c6h5c2h+oh=c6h4c2h+h2o      1.63E+08 1.42 1454.0 ! Marinov 1996
c6h5c2h+h=c6h4c2h+h2        3.03E+02 3.3  5690.0 ! Marinov 1996
c6h5c2h+ch3=c6h4c2h+ch4     1.67E+12 0.0 15057.0 ! Marinov 1996
c6h4c2h+c2h2=c10h7          1.068E+04 2.324 -657.3 !Total Wang 94
c6h4c2h3+ch3=indene+h+h     2.00E+13 0.0     0.0 !   (eee)
ch3c6h4ch3+oh=ch3c6h4ch2+h2o 2.95E+13 0.0 2623.0 ! Marinov 1996
ch3c6h4ch3+o=ch3c6h4ch2+oh  5.00E+08 1.5  8000.0 ! Marinov 1996
ch3c6h4ch3+h=ch3c6h4ch2+h2  3.98E+02 3.44 3120.0 ! Marinov 1996
ch3c6h4ch2+c2h2=c10h10+h    3.20E+11 0.0  7000.0 ! Marinov 1996
ch3c6h4ch2+c2h2=ch3indene+h 3.20E+11 0.0  7000.0 ! Marinov 1996
ch3c6h4ch2+h=ch3c6h4ch3     7.46E+13 0.0    78.0 ! Brand   1990
ch3c6h4ch2+ch3=ch3c6h4c2h5  6.00E+12 0.0   221.0 ! Marinov 1996
indene+oh=indenyl+h2o       3.43E+09 1.18 -447.0 ! Marinov 1996
indene+o=indenyl+oh         1.81E+13 0.0  3080.0 ! Marinov 1996
indene+h=indenyl+h2         2.19E+08 1.77 3000.0 ! Marinov 1996
indenyl+h=indene            2.00E+14 0.0     0.0 ! Marinov 1996
indenyl+o=c6h5chch+co       1.00E+14 0.0     0.0 ! Marinov 1996
indenyl+ho2=c6h5chch+co+oh  1.00E+13 0.0     0.0 ! Marinov 1996
indenyl+c-c5h5=phnthrn+h+h  1.00E+13 0.0   8000.0 ! Marinov 1998
ch3c6h4c2h5+oh=ch3c6h4c2h3+h2o+h 8.43E+12  0.0  2583.0 ! Marinov 1996
ch3c6h4c2h5+h=ch3c6h4c2h3+h2+h   8.00E+13  0.0  8235.0 ! Marinov 1996
ch3c6h4c2h3+oh=indene+h+h2o      1.26E+13  0.0  2583.0 ! Marinov 1996
ch3c6h4c2h3+h=indene+h+h2        3.98E+02  3.44 3120.0 ! Marinov 1996
ch3indene+oh=ch3indenyl+h2o      3.43E+09  1.18 -447.0 ! Marinov 1996
ch3indene+o=ch3indenyl+oh        1.81E+13  0.0  3080.0 ! Marinov 1996
ch3indene+h=ch3indenyl+h2        2.19E+08  1.77 3000.0 ! Marinov 1996
ch3indene+h=indene+ch3           1.20E+13  0.0  5200.0 ! Marinov 1996
ch3indenyl+h=ch3indene           2.00E+14  0.0     0.0 ! Marinov 1996
ch3indenyl+c-c5h5=ch3phnthrn+h+h 1.00E+13  0.0  8000.0 ! Marinov 1998
c10h10+oh=c10h9+h2o              5.00E+06  2.0     0.0 ! Marinov 1996
c10h10+o=c10h9+oh                7.00E+11  0.7  6000.0 ! Marinov 1996
c10h10+h=c10h9+h2                2.00E+05  2.5  2500.0 ! Marinov 1996
c10h9+h=c10h10                   1.00E+14  0.0     0.0 ! Marinov 1996
c10h8+h=c10h9                    5.00E+14  0.0  5000.0 ! Sauer 1970
c10h8+oh=c10h7+h2o               2.44E+08  1.42 1454.0 ! Marinov 1996
c10h8+oh=c10h7oh+h               9.00E+12  0.0 10592.0 ! Marinov 1996
c10h8+o=c10h7o+h                 1.40E+13  0.0  1792.0 ! Frerichs 1990
c10h8+h=c10h7+h2                 4.55E+02  3.3  5690.0 ! Marinov 1996
c10h7+h=c10h8                    1.00E+14  0.0     0.0 ! Marinov 1996
c10h7+o2=c10h7o+o                1.00E+13  0.0     0.0 !  (fff)
c10h7+oh=c10h7o+h                5.00E+13  0.0     0.0 ! Marinov 1996
c10h7+ch3=c10h7ch2+h             2.00E+13  0.0     0.0 !  (eee)
c10h7+c2h2=acenphthln+h          1.00E+20 -2.08 12000.0 ! Wang 1994
c10h7+c2h2=c10h7cch+h            1.17E-7  5.248 -9482.0 ! Total Wang 1994
c10h7+c6h5=flrnthn+h+h           5.00E+12  0.0     0.0 !  (ggg)
c10h7+c6h6=flrnthn+h+h2          4.00E+11  0.0  4000.0 !  (hhh)
c10h7o+h=c10h7oh                 1.00E+14  0.0     0.0 ! Marinov 1996
c10h7oh+oh=c10h7o+h2o            2.95E+06  2.0 -1312.0 ! Marinov 1996
c10h7oh+h=c10h7o+h2              1.58E+13  0.0  6100.0 ! Marinov 1996
c10h7o=indenyl+co                7.40E+11  0.0 43850.0 ! Marinov 1996
c10h7ch3+oh=c10h7ch2+h2o         1.27E+13  0.0  2583.0 ! Marinov 1996
c10h7ch3+o=c10h7ch2+oh           5.00E+08  1.5  8000.0 ! Marinov 1996
c10h7ch3+h=c10h7ch2+h2           3.98E+02  3.44 3120.0 ! Marinov 1996
```

```
c10h7ch3+h=c10h8+ch3             1.20E+13  0.0  5148.0 ! Marinov 1996
c10h7ch2+h=c10h7ch3              1.00E+14  0.0     0.0 ! Marinov 1996
c10h7ch2+o=c10h7+ch2o            1.00E+14  0.0     0.0 ! Marinov 1996
c10h7ch2+ho2=>c10h7+ch2o+oh      1.00E+13  0.0     0.0 ! Marinov 1996
c10h7ch2+c2h2=bz(a)ndene+h       3.20E+11  0.0  7000.0 ! Marinov 1996
c10h7ch2+ch3=c10h7c2h5           1.19E+13  0.0   221.0 ! Marinov 1996
c10h7c2h5+oh=c10h7c2h3+h2o+h     8.44E+12  0.0  2583.0 ! Marinov 1996
c10h7c2h5+h=c10h7c2h3+h2+h       8.00E+13  0.0  8235.0 ! Marinov 1996
c10h7c2h3+oh=c10h7cch2+h2o       1.00E+07  2.0  2000.0 ! Marinov 1996
c10h7c2h3+h=c10h7cch2+h2         2.00E+07  2.0  6000.0 ! Marinov 1996
c10h7cch2+oh=c10h7cch+h2o        2.00E+13  0.0     0.0 ! Marinov 1996
c10h7cch2+h=c10h7cch+h2          5.00E+13  0.0     0.0 ! Marinov 1996
c10h7cch+oh=c10h6cch+h2o         1.63E+08  1.42 1454.0 ! Marinov 1996
c10h7cch+h=c10h6cch+h2           3.03E+02  3.3  5690.0 ! Marinov 1996
c10h7cch+h=acenphthln+h          8.459E+21  -2.614 7062.6 !Total Wang 1994
c10h6cch+c2h2=phnthryl-1         1.068E+04 2.324 -657.3 ! Total Wang 1994
fluorene+oh=fluoryl+h2o          3.43E+09  1.18   -447.0 ! Marinov 1996
fluorene+o=fluoryl+oh            1.81E+13  0.0    3080.0 ! Marinov 1996
fluorene+h=fluoryl+h2            2.19E+08  1.77   3000.0 ! Marinov 1996
fluoryl+h=fluorene               2.00E+14  0.0       0.0 ! Marinov 1996
bz(a)ndnyl+h=bz(a)ndene          2.00E+14  0.0       0.0 ! Marinov 1996
bz(a)ndene+oh=bz(a)ndnyl+h2o     3.43E+09  1.18   -447.0 ! Marinov 1996
bz(a)ndene+o=bz(a)ndnyl+oh       1.81E+13  0.0    3080.0 ! Marinov 1996
bz(a)ndene+h=bz(a)ndnyl+h2       2.19E+08  1.77   3000.0 ! Marinov 1996
bz(a)ndnyl+c-c5h5=bz(a)phnthrn+h+h 1.00E+13 0.0   8000.0 ! nmm 1996
phnthrn+oh=phnthryl-1+h2o        2.17E+08  1.42   1454.0 ! Marinov 1996
phnthrn+oh=phnthryl-9+h2o        5.43E+07  1.42   1454.0 ! Marinov 1996
phnthrn+oh=phnthrol-1+h          9.00E+12  0.0   10592.0 ! Marinov 1996
phnthrn+oh=phnthrol-9+h          9.00E+12  0.0   10592.0 ! Marinov 1996
phnthrn+h=phnthryl-1+h2          4.04E+02  3.3    5690.0 ! Marinov 1996
phnthrn+h=phnthryl-9+h2          1.01E+02  3.3    5690.0 ! Marinov 1996
anthracn=phnthrn                 8.00E+12  0.0   65000.0 ! Colket 1994
phnthryl-1+h=phnthrn             8.00E+13  0.0       0.0 ! Marinov 1996
phnthryl-9+h=phnthrn             8.00E+13  0.0       0.0 ! Marinov 1996
phnthryl-1+o2= phnthroxy-1+o     1.00E+13  0.0       0.0 !    (fff)
phnthryl-9+o2= phnthroxy-9+o     1.00E+13  0.0       0.0 !    (fff)
phnthrol-1+oh=phnthroxy-1+h2o    2.95E+06  2.0   -1310.0 ! Marinov 1996
phnthrol-1+h=phnthroxy-1+h2      1.59E+13  0.0    6100.0 ! Marinov 1996
phnthroxy-1+h=phnthrol-1         1.00E+14  0.0       0.0 ! Marinov 1996
phnthrol-9+oh=phnthroxy-9+h2o    2.95E+06  2.0   -1310.0 ! Marinov 1996
phnthrol-9+h=phnthroxy-9+h2      1.59E+13  0.0    6100.0 ! Marinov 1996
phnthroxy-9+h=phnthrol-9         1.00E+14  0.0       0.0 ! Marinov 1996
phnthroxy-1=bz(a)ndnyl+co        7.40E+11  0.0   43850.0 ! Marinov 1996
phnthroxy-9=fluoryl+co           7.40E+11  0.0   43850.0 ! Marinov 1996
phnthryl-1+c2h2=pyrene+h         3.492E+10 0.557  5658.0 ! Total Wang 1996
phnthryl-1+ch3=hc4-p(def)pthn+h+h       2.00E+13 0.0      0.0 !  (eee)
ch3phnthrn+oh=hc4-p(def)pthn+h2o+h      1.27E+13 0.0   2583.0 ! nmm 1996
ch3phnthrn+h=hc4-p(def)pthn+h2+h        3.98E+02 3.44  3120.0 ! nmm 1996
ch3phnthrn+h=phnthrn+ch3                1.20E+13 0.0   5148.0 !Marinov1996
hc4-p(def)pthn+oh=hc4-p(def)pthyl+h2o   3.43E+09   1.18 -447.0 !nmm96
hc4-p(def)pthn+o=hc4-p(def)pthyl+oh     1.81E+13   0.0  3080.0 !nmm96
hc4-p(def)pthn+h=hc4-p(def)pthyl+h2     2.19E+08   1.77 3000.0 !nmm96
hc4-p(def)pthyl+h=hc4-p(def)pthn        2.00E+14   0.0     0.0 !Marinov 1996
bz(a)phnthrn+h=bz(ghi)fln+h2+h          3.03E+02   3.3  5690.0 !Marinov 1996
bz(a)phnthrn+oh=bz(ghi)fln+h2o+h        1.63E+08   1.42 1454.0 !Marinov 1996
h2ccch+ch2=ch2chcch+h                   4.00E+13   0.0     0.0 !Miller 1992
c-c5h5+ch3=ch3cy24pd                    1.76E+50 -11.0  18600. !Ritter 1990
```

```
ch3cy24pd+h=c-c5h6+ch3                  1.00E+13   0.0  1300.0 !Ritter 1990
c6h6+h=ch3cy24pd1                       2.39E+27 -3.92  29200. !Ritter 1990
cyc6h7=ch3cy24pd1                       5.00E+12   0.0  38100. !Ritter 1990
ch3cy24pd1+h=ch3cy24pd                  1.00E+14   0.0     0.0 !Marinov 1998
ch3cy24pd1+h=c-c5h5+ch3                 1.00E+14   0.0     0.0 !Marinov 1998
cyc6h7=ch3dcy24pd                       5.50E+10   0.0  23500. !Ritter 1990
c6h6+h=cyc6h7                           4.87E+56 -12.73 26800. !Ritter 1990
ch3dcy24pd+h2=ch3cy24pd+h               4.00E+12   0.0  15000. !Ritter 1990
fulvene=c6h6                            9.84E+37  -7.4  76979. !Shandross1996
fulvene+h=c6h6+h                        3.00E+12   0.5  2000.0 !Marinov 1998
fulvene+h=fulvenyl+h2                   3.03E+2    3.3   5690. !Marinov 1998
fulvene+oh=fulvenyl+h2o                 1.63E+8   1.42   1454. !Marinov 1998
fulvenyl+h=c6h5+h                       1.00E+14   0.0   0.0   !Marinov 1998
fulvenyl+o2=c-c5h4o+hco                 1.00E+12   0.0   0.0   !Marinov 1998
end
```

Appendix II

The driver routine used in the parameter estimation software.

```
    PROGRAM LEAST

   IMPLICIT DOUBLE PRECISION (A-H, O-Z), INTEGER (I-N)

         CHARACTER KEYWRD*4, LINE*80, BBB*2, CCC*1, DDD*2
         CHARACTER REAC*26, REST*80, REST2*30, CHECK*1, FEND*3
         LOGICAL OK, OK2

         OK = .FALSE.
         OK2 = .FALSE.

         LLIN = 2
         LLOUT = 6
         LLNEW = 3
         LSQCHA = 4
         LRES = 7
         LCHEM = 8
         LINP = 9
         LPARS = 10
         LLSQS = 11
         LBEST = 12
         LTEST = 13
         LEVO = 14
         LTEST2 = 15
         LCHECK = 16
         I = 1
         ILSQ = 1
         J = 1
         K = 1
         BEST = 1000000
         FEND = 'END'

         OPEN (LTEST, FORM='FORMATTED', STATUS='OLD',
        1     FILE='pars.txt')
         OPEN (LTEST2, FORM='FORMATTED', STATUS='SCRATCH')
         OPEN (LCHEM, FORM='FORMATTED', STATUS='SCRATCH')
         OPEN (LINP, FORM='FORMATTED', STATUS='OLD',
        1       FILE='chem.inp')
         OPEN (LPARS, FORM='FORMATTED', STATUS='OLD',
        1    FILE='chem.tmp')

C   Opens needed files.

         DO I = 1,1500
           READ (LTEST, '(A1)',END=100),CHECK


C    Check that proposed constants are not negative

           IF (CHECK.EQ.'-') THEN
             TOTLSQ = 100000.0
             CLOSE(LTEST)
                        CLOSE(LTEST2)
```

```
                                    CLOSE(LCHEM)
                                    CLOSE(LINP)
                                    CLOSE(LPARS)
                        GOTO 900
                            END IF
                     END DO

C     If some constant is negative then give very large
C     fit value and skip the simulation to save time

100          REWIND(LTEST)
       OK = .TRUE.
             I = 1
             DO I = 1,1500
        IF (I.LT.7) THEN
                READ (LPARS,'(A68)',END=120),REST
                      WRITE (LCHEM,'(A)'),REST
        ELSE
                      IF (OK.EQV..TRUE.) THEN
                      READ (LPARS,'(A1)',END=120),CHECK
                              IF (CHECK.EQ.'!') THEN
                                OK = .FALSE.
                                BACKSPACE(LPARS)
                  READ (LPARS,'(A80)',END=120),REST
                                WRITE (LCHEM,'(A)'),REST
                              ELSE
                                BACKSPACE (LPARS)
                                      READ (LPARS,'(A26,X,1PE11.5,A30)',
            1         END=120),REAC,A,REST2
             READ (LTEST,'(F7.5,A2,A1,A2)',END=120),
            1         AAA,BBB,CCC,DDD
             WRITE (LTEST2,'(F7.5,A,A)'),AAA,BBB,DDD
             BACKSPACE (LTEST2)
             READ (LTEST2,'(1PE11.5)'),AAAA
             AAAA = AAAA/100
             A = A*AAAA
             WRITE (LCHEM,'(A,1PE11.5,X,A)'),REAC,A,REST2
                              ENDIF
                            ELSE
                              READ (LPARS,'(A80)',END=120),REST
                              WRITE (LCHEM,'(A)'),REST
                              OK = .TRUE.
                            ENDIF
                   ENDIF
             ENDDO


C      Read the proposed values and change the windows exp format
C      to unix exp format aka E+023 to E+23. Update chem.inp

120          I = 1
       REWIND(LCHEM)
       DO I = 1,5000
         READ (LCHEM,'(A80)',END=150),REST
         WRITE (LINP,'(A)'),REST
             END DO
150          WRITE (LINP,'(A)'),FEND
       CLOSE (LCHEM)
       CLOSE (LINP)
             CLOSE (LTEST)
             CLOSE (LTEST2)
             CLOSE (LPARS)
```

```
C     Updating chem.inp ends here

C    Ckinterp -> reads the reaction system and thermodynamic data
C    Then it is ready for senkin. This has to be edited later to
C    a subroutine... Much faster.

          DO J = 1,96

C     TESTING WITH ONE TEMPERATURE AND TIME

            OPEN (LLIN, FORM='FORMATTED', STATUS='OLD',
         1          FILE='senk.txt')
            OPEN (LLNEW, FORM='FORMATTED', STATUS='REPLACE',
         1          FILE='senk.inp')


            DO I = 1,15
        READ  (LLIN,  '(A4,A80)',END=101) KEYWRD, LINE
                            WRITE (LLNEW, '(A4,A)') KEYWRD, LINE
                     IF (KEYWRD .EQ. 'END') GOTO 200
            END DO

101      PRINT *,'error'
      REWIND (LLIN)
      I = 1

      DO I = 1,15
        READ (LLNEW, '(A4,A80)',END=200) KEYWRD, LINE
                     WRITE (LLIN, '(A4,A80)')KEYWRD, LINE
     END DO

200             CLOSE (LLNEW)

C    Updated senk.inp. Senk.txt

            CALL SYSTEM('senk.exe')

      CALL SYSTEM('post.exe')

                  CALL SYSTEM('del savesenk.bin')

C   Call senkin and post-processor. Like before, has to be revised
C   to subroutines...

          OPEN (LLSQS, FORM='FORMATTED', STATUS='OLD',
         1          FILE='lsqsums.txt')
          I = 1
          ILSQ = 12
          TOTLSQ = 0
   DO I=1,50000
      READ (LLSQS,'(2PD22.15)',END=320,ERR=315),SQSUM
        IF (SQSUM.EQ.5000000) THEN
           ILSQ = ILSQ - 1
           ELSE
                              TOTLSQ = TOTLSQ+SQSUM
                     ENDIF
   END DO
315   PRINT *,'ERROR'
320    CLOSE (LLSQS)
   IF (ILSQ.EQ.0) THEN
             TOTLSQ = 5000000
```

```
                              ELSE
                              TOTLSQ = TOTLSQ/ILSQ
               ENDIF

     END DO

     CALL SYSTEM('del lsqsums.txt')
               OPEN (LBEST, FORM='FORMATTED', STATUS='UNKNOWN',
             1             FILE='best.txt')

               OPEN (LINP, FORM='FORMATTED', STATUS='OLD',
             1             FILE='chem.inp')

321            I = 1
               READ (LBEST,'(2PD22.15)'),BEST
               REWIND(LBEST)
               IF (TOTLSQ.LT.BEST) THEN
                 BEST = TOTLSQ
                 WRITE (LBEST,'(2PD22.15)'),BEST
        DO I = 1, 5000
         READ (LINP,'(A80)',END=330), REST
         WRITE (LBEST,'(A)'),REST
         END DO
       END IF

330   CLOSE(LBEST)
     CLOSE(LINP)


900    OPEN (LEVO, FORM='FORMATTED', STATUS='REPLACE',
             1  FILE='toevo.txt')
     WRITE (LEVO,'(1PE20.14)'),TOTLSQ
     CLOSE (LEVO)

               END
```

The post processor routine used in the parameter estimation software.

```
PROGRAM post

       DOUBLE PRECISION equi,p,tau,flrt,v,q,tempin,temp,x0(100),y(100)
          DOUBLE PRECISION ynew(100),lsqsum,coff
       integer nn,k,nsys,kk,ii, loop
       logical lsens, htwo
          character word*7

          htwo = .FALSE.
        open(unit=20,file='savesenk.bin',status='unknown',
     #       form='unformatted')
        open(unit=52,file='lsqsums.txt',status='unknown',
      1           form='formatted', access='append')


        read(20) lsens
        read(20) nsys,kk,ii

 50     read(20,end=100, err=200) tau,p,temp,(y(k), k=1,kk)

       goto 50
```

```
100       close(20)

          LSQSUM = 500

          OPEN (UNIT=77,FILE='senk.inp',STATUS='OLD',
       1        FORM='FORMATTED')

          DO LOOP = 1,500
             READ(77,'(A7)',END=120),WORD
             IF (WORD .EQ. 'REAC H2') THEN
             HTWO = .TRUE.
             END IF
       END DO

120       CALL LSQ(Y,TEMP,TAU,LSQSUM,HTWO)


          WRITE(52,'(2PE22.15)'),LSQSUM

          CLOSE(52)




200       continue

        end

              SUBROUTINE LSQ(YPRIME,TEM,TIM,LSQSUM,HTWO)

              DOUBLE PRECISION YEXP1(20),YEXP2(20),TIME,TEMP
              DOUBLE PRECISION YPRIME(100),TEM,TIM,LSQSUM
              INTEGER LOOP1, LOOP2, LOOP3
              LOGICAL HTWO

C             PRINT *,TEM,TIM
              IF (HTWO .EQV. .TRUE.) THEN

                   IF (TEM .GT. 799 .AND. TEM .LT. 801) THEN
                         IF (TIM .GT. 13.0 .AND. TIM .LT. 13.2) THEN
                      YEXP1(1)=0
                      YEXP1(2)=0.045286
                      YEXP1(3)=0.077211
                      YEXP1(4)=0
                      YEXP1(5)=0
                      YEXP1(6)=0
                 YEXP1(7)=0.020113
                      YEXP1(8)=0
                      YEXP1(9)=0.007517
                      YEXP1(10)=0
                      YEXP1(11)=0
                      YEXP1(12)=0
                      YEXP1(13)=0
                      YEXP1(14)=0
                      YEXP1(15)=0.0000764
                      YEXP1(16)=0
                      YEXP1(17)=0
                      YEXP1(18)=0
                      YEXP1(19)=0.0000641
                      YEXP1(20)=0

                           ELSE IF (TIM .GT. 6.4 .AND. TIM .LT. 6.6) THEN
                           YEXP1(1)=0
```

```
     YEXP1(2)=0.039292
     YEXP1(3)=0.088571
     YEXP1(4)=0
     YEXP1(5)=0
     YEXP1(6)=0
YEXP1(7)=0.027141
     YEXP1(8)=0
     YEXP1(9)=0.004839
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0.00008
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0.0000318
     YEXP1(19)=0
     YEXP1(20)=0

          ELSE IF (TIM .GT. 3.5 .AND. TIM .LT. 3.7) THEN
          YEXP1(1)=0
     YEXP1(2)=0.039309
     YEXP1(3)=0.084259
     YEXP1(4)=0
     YEXP1(5)=0
     YEXP1(6)=0
YEXP1(7)=0.026631
     YEXP1(8)=0
     YEXP1(9)=0.001467
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0

          ELSE IF (TIM .GT. 1.7 .AND. TIM .LT. 1.9) THEN
          YEXP1(1)=0
     YEXP1(2)=0.040357
     YEXP1(3)=0.086976
     YEXP1(4)=0
     YEXP1(5)=0
     YEXP1(6)=0
YEXP1(7)=0.032695
     YEXP1(8)=0
     YEXP1(9)=0.00092
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0
```

```
          ELSE IF (TIM .GT. 1.1 .AND. TIM .LT. 1.3) THEN
          YEXP1(1)=0
     YEXP1(2)=0.040226
     YEXP1(3)=0.088297
     YEXP1(4)=0
     YEXP1(5)=0
     YEXP1(6)=0
YEXP1(7)=0.032454
     YEXP1(8)=0
     YEXP1(9)=0.000911
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0

          ELSE IF (TIM .GT. 0.8 .AND. TIM .LT. 1.0) THEN
          YEXP1(1)=0
     YEXP1(2)=0.040311
     YEXP1(3)=0.087871
     YEXP1(4)=0
     YEXP1(5)=0
     YEXP1(6)=0
YEXP1(7)=0.032179
     YEXP1(8)=0
     YEXP1(9)=0.000856
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0

          ELSE IF (TIM .GT. 0.6 .AND. TIM .LT. 0.8) THEN
          YEXP1(1)=0
     YEXP1(2)=0.034868
     YEXP1(3)=0.057104
     YEXP1(4)=0
     YEXP1(5)=0
     YEXP1(6)=0
YEXP1(7)=0.017192
     YEXP1(8)=0
     YEXP1(9)=0.000629
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0
     YEXP1(16)=0
     YEXP1(17)=0
```

```
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.4 .AND. TIM .LT. 0.6) THEN
           YEXP1(1)=0
      YEXP1(2)=0.038147
      YEXP1(3)=0.068358
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.025259
      YEXP1(8)=0
      YEXP1(9)=0.0000988
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.3 .AND. TIM .LT. 0.4) THEN
           YEXP1(1)=0
      YEXP1(2)=0.035859
      YEXP1(3)=0.085206
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.030514
      YEXP1(8)=0
      YEXP1(9)=0.000154
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.1 .AND. TIM .LT. 0.3) THEN
           YEXP1(1)=0
      YEXP1(2)=0.040739
      YEXP1(3)=0.087231
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.031537
      YEXP1(8)=0
      YEXP1(9)=0.00017
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
```

```
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE
           GO TO 500

           END IF

     ELSE IF (TEM .GT. 899 .AND. TEM .LT. 901 ) THEN
         IF (TIM .GT. 11.0 .AND. TIM .LT. 12.0) THEN
      YEXP1(1)=0
      YEXP1(2)=0.036939
      YEXP1(3)=0.087853
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.015934
      YEXP1(8)=0
      YEXP1(9)=0.01559
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000118
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 5.0 .AND. TIM .LT. 6.0) THEN
           YEXP1(1)=0
      YEXP1(2)=0.040084
      YEXP1(3)=0.089972
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.021861
      YEXP1(8)=0
      YEXP1(9)=0.010505
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000174
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 3.0 .AND. TIM .LT. 3.7) THEN
           YEXP1(1)=0
      YEXP1(2)=0.037811
      YEXP1(3)=0.086237
      YEXP1(4)=0
      YEXP1(5)=0
```

```
      YEXP1(6)=0
YEXP1(7)=0.025502
      YEXP1(8)=0
      YEXP1(9)=0.005311
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000152
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

            ELSE IF (TIM .GT. 1.5 .AND. TIM .LT. 1.9) THEN
            YEXP1(1)=0
      YEXP1(2)=0.040774
      YEXP1(3)=0.087478
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.032495
      YEXP1(8)=0
      YEXP1(9)=0.001254
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

            ELSE IF (TIM .GT. 1.0 .AND. TIM .LT. 1.2) THEN
            YEXP1(1)=0
      YEXP1(2)=0.039994
      YEXP1(3)=0.087333
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.031907
      YEXP1(8)=0
      YEXP1(9)=0.001092
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

            ELSE IF (TIM .GT. 0.8 .AND. TIM .LT. 0.9) THEN
            YEXP1(1)=0
      YEXP1(2)=0.043559
```

```
     YEXP1(3)=0.093641
     YEXP1(4)=0
     YEXP1(5)=0
     YEXP1(6)=0
YEXP1(7)=0.033773
     YEXP1(8)=0
     YEXP1(9)=0.000965
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0

          ELSE IF (TIM .GT. 0.6 .AND. TIM .LT. 0.7) THEN
          YEXP1(1)=0
     YEXP1(2)=0.03449
     YEXP1(3)=0.073317
     YEXP1(4)=0
     YEXP1(5)=0
     YEXP1(6)=0
YEXP1(7)=0.026069
     YEXP1(8)=0
     YEXP1(9)=0.000788
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0

          ELSE IF (TIM .GT. 0.4 .AND. TIM .LT. 0.5) THEN
          YEXP1(1)=0
     YEXP1(2)=0.031946
     YEXP1(3)=0.074296
     YEXP1(4)=0
     YEXP1(5)=0
     YEXP1(6)=0
YEXP1(7)=0.026403
     YEXP1(8)=0
     YEXP1(9)=0.0000104
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0
```

```
          ELSE IF (TIM .GT. 0.25 .AND. TIM .LT. 0.3) THEN
          YEXP1(1)=0
     YEXP1(2)=0.037396
     YEXP1(3)=0.088594
     YEXP1(4)=0
     YEXP1(5)=0
     YEXP1(6)=0
YEXP1(7)=0.031755
     YEXP1(8)=0
     YEXP1(9)=0.000135
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0

          ELSE IF (TIM .GT. 0.1 .AND. TIM .LT. 0.25) THEN
          YEXP1(1)=0
     YEXP1(2)=0.038183
     YEXP1(3)=0.089412
     YEXP1(4)=0
     YEXP1(5)=0
     YEXP1(6)=0
YEXP1(7)=0.0323336
     YEXP1(8)=0
     YEXP1(9)=0.000151
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0

          ELSE
          GO TO 500

          END IF


          ELSE IF (TEM .GT. 999 .AND. TEM .LT. 1001 ) THEN
        IF (TIM .GT. 10.0 .AND. TIM .LT. 11.0) THEN
     YEXP1(1)=0
     YEXP1(2)=0.036574
     YEXP1(3)=0.087705
     YEXP1(4)=0
     YEXP1(5)=0.000297
     YEXP1(6)=0
YEXP1(7)=0.019578
     YEXP1(8)=0
     YEXP1(9)=0.009099
     YEXP1(10)=0
     YEXP1(11)=0
```

```
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000365
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 5.0 .AND. TIM .LT. 6.0) THEN
           YEXP1(1)=0
      YEXP1(2)=0.037811
      YEXP1(3)=0.086418
      YEXP1(4)=0
      YEXP1(5)=0.000304
      YEXP1(6)=0
YEXP1(7)=0.020944
      YEXP1(8)=0
      YEXP1(9)=0.008848
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.0000821
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 2.5 .AND. TIM .LT. 3.7) THEN
           YEXP1(1)=0
      YEXP1(2)=0.038674
      YEXP1(3)=0.087424
      YEXP1(4)=0
      YEXP1(5)=0.000264
      YEXP1(6)=0
YEXP1(7)=0.022769
      YEXP1(8)=0
      YEXP1(9)=0.007635
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000434
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 1.4 .AND. TIM .LT. 1.9) THEN
           YEXP1(1)=0
      YEXP1(2)=0.032502
      YEXP1(3)=0.070963
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.022548
      YEXP1(8)=0
```

```
      YEXP1(9)=0.002242
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000204
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.85 .AND. TIM .LT. 0.99) THEN
           YEXP1(1)=0
      YEXP1(2)=0.039816
      YEXP1(3)=0.086759
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.030522
      YEXP1(8)=0
      YEXP1(9)=0.002183
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.0000468
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.7 .AND. TIM .LT. 0.8) THEN
           YEXP1(1)=0
      YEXP1(2)=0.041009
      YEXP1(3)=0.088882
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.031449
      YEXP1(8)=0
      YEXP1(9)=0.001847
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.0000309
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.55 .AND. TIM .LT. 0.6) THEN
           YEXP1(1)=0
      YEXP1(2)=0.036012
      YEXP1(3)=0.076826
      YEXP1(4)=0
      YEXP1(5)=0
```

```
      YEXP1(6)=0
YEXP1(7)=0.02632
      YEXP1(8)=0
      YEXP1(9)=0.001647
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000104
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.4 .AND. TIM .LT. 0.5) THEN
           YEXP1(1)=0
      YEXP1(2)=0.03404
      YEXP1(3)=0.078938
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.029074
      YEXP1(8)=0
      YEXP1(9)=0.000255
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.23 .AND. TIM .LT. 0.27) THEN
           YEXP1(1)=0
      YEXP1(2)=0.037721
      YEXP1(3)=0.088671
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.031699
      YEXP1(8)=0
      YEXP1(9)=0.000157
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.1 .AND. TIM .LT. 0.22) THEN
           YEXP1(1)=0
      YEXP1(2)=0.038354
```

```
     YEXP1(3)=0.088601
     YEXP1(4)=0
     YEXP1(5)=0
     YEXP1(6)=0
YEXP1(7)=0.031469
     YEXP1(8)=0
     YEXP1(9)=0.000145
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0

          ELSE
          GO TO 500

          END IF


    ELSE IF (TEM .GT. 1099 .AND. TEM .LT. 1101 ) THEN
        IF (TIM .GT. 9.0 .AND. TIM .LT. 11.0) THEN
     YEXP1(1)=0
     YEXP1(2)=0.036262
     YEXP1(3)=0.092035
     YEXP1(4)=0
     YEXP1(5)=0.001306
     YEXP1(6)=0
YEXP1(7)=0.018047
     YEXP1(8)=0
     YEXP1(9)=0.003201
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0.000119
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0

          ELSE IF (TIM .GT. 4.5 .AND. TIM .LT. 6.0) THEN
          YEXP1(1)=0
     YEXP1(2)=0.038038
     YEXP1(3)=0.09038
     YEXP1(4)=0
     YEXP1(5)=0.0017
     YEXP1(6)=0
YEXP1(7)=0.020808
     YEXP1(8)=0
     YEXP1(9)=0.003355
     YEXP1(10)=0.0000264
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
```

```
      YEXP1(15)=0.000152
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 2.3 .AND. TIM .LT. 3.0) THEN
           YEXP1(1)=0
      YEXP1(2)=0.037601
      YEXP1(3)=0.085925
      YEXP1(4)=0
      YEXP1(5)=0.001945
      YEXP1(6)=0
YEXP1(7)=0.022122
      YEXP1(8)=0
      YEXP1(9)=0.002956
      YEXP1(10)=0.0000273
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000805
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 1.2 .AND. TIM .LT. 1.5) THEN
           YEXP1(1)=0
      YEXP1(2)=0.040181
      YEXP1(3)=0.087734
      YEXP1(4)=0
      YEXP1(5)=0.001
      YEXP1(6)=0
YEXP1(7)=0.027645
      YEXP1(8)=0
      YEXP1(9)=0.003971
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000859
      YEXP1(16)=0
      YEXP1(17)=0.0000138
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.85 .AND. TIM .LT. 0.99) THEN
           YEXP1(1)=0
      YEXP1(2)=0.040467
      YEXP1(3)=0.088763
      YEXP1(4)=0
      YEXP1(5)=0.00066
      YEXP1(6)=0
YEXP1(7)=0.028601
      YEXP1(8)=0
      YEXP1(9)=0.003721
      YEXP1(10)=0
      YEXP1(11)=0
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```
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000169
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.65 .AND. TIM .LT. 0.7) THEN
           YEXP1(1)=0
      YEXP1(2)=0.023386
      YEXP1(3)=0.053538
      YEXP1(4)=0
      YEXP1(5)=0.000302
      YEXP1(6)=0
YEXP1(7)=0.017699
      YEXP1(8)=0
      YEXP1(9)=0.00217
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000476
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.50 .AND. TIM .LT. 0.55) THEN
           YEXP1(1)=0
      YEXP1(2)=0.025334
      YEXP1(3)=0.046024
      YEXP1(4)=0
      YEXP1(5)=0.00019
      YEXP1(6)=0
YEXP1(7)=0.01398
      YEXP1(8)=0
      YEXP1(9)=0.001378
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000321
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.3 .AND. TIM .LT. 0.4) THEN
           YEXP1(1)=0
      YEXP1(2)=0.037498
      YEXP1(3)=0.088588
      YEXP1(4)=0
      YEXP1(5)=0.0000802
      YEXP1(6)=0
YEXP1(7)=0.031231
      YEXP1(8)=0
```

```
      YEXP1(9)=0.00081
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000329
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.21 .AND. TIM .LT. 0.24) THEN
           YEXP1(1)=0
      YEXP1(2)=0.0352
      YEXP1(3)=0.084095
      YEXP1(4)=0
      YEXP1(5)=0.0000262
      YEXP1(6)=0
YEXP1(7)=0.029857
      YEXP1(8)=0
      YEXP1(9)=0.000484
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000158
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.1 .AND. TIM .LT. 0.20) THEN
           YEXP1(1)=0
      YEXP1(2)=0.036621
      YEXP1(3)=0.086467
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.030594
      YEXP1(8)=0
      YEXP1(9)=0.000301
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.0000575
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE
           GO TO 500

           END IF
```

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    ELSE IF (TEM .GT. 1199 .AND. TEM .LT. 1201 ) THEN
        IF (TIM .GT. 8.5 .AND. TIM .LT. 9.0) THEN
     YEXP1(1)=0
     YEXP1(2)=0.029661
     YEXP1(3)=0.027812
     YEXP1(4)=0
     YEXP1(5)=0.000949
     YEXP1(6)=0
YEXP1(7)=0.00367
     YEXP1(8)=0
     YEXP1(9)=0.000281
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0.000064
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0

          ELSE IF (TIM .GT. 4.1 .AND. TIM .LT. 4.5) THEN
          YEXP1(1)=0
     YEXP1(2)=0.031588
     YEXP1(3)=0.053182
     YEXP1(4)=0
     YEXP1(5)=0.0025
     YEXP1(6)=0
YEXP1(7)=0.008305
     YEXP1(8)=0
     YEXP1(9)=0.000539
     YEXP1(10)=0.0000317
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0.000352
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0

          ELSE IF (TIM .GT. 2.3 .AND. TIM .LT. 2.5) THEN
          YEXP1(1)=0
     YEXP1(2)=0.036882
     YEXP1(3)=0.084624
     YEXP1(4)=0
     YEXP1(5)=0.005511
     YEXP1(6)=0
YEXP1(7)=0.015259
     YEXP1(8)=0
     YEXP1(9)=0.000846
     YEXP1(10)=0.0000842
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0.000874
     YEXP1(16)=0
     YEXP1(17)=0
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           YEXP1(18)=0
           YEXP1(19)=0
           YEXP1(20)=0

                ELSE IF (TIM .GT. 1.2 .AND. TIM .LT. 1.3) THEN
                YEXP1(1)=0
           YEXP1(2)=0.041205
           YEXP1(3)=0.089856
           YEXP1(4)=0
           YEXP1(5)=0.004607
           YEXP1(6)=0
      YEXP1(7)=0.023285
           YEXP1(8)=0
           YEXP1(9)=0.002321
           YEXP1(10)=0.0000822
           YEXP1(11)=0
           YEXP1(12)=0
           YEXP1(13)=0
           YEXP1(14)=0
           YEXP1(15)=0.001211
           YEXP1(16)=0
           YEXP1(17)=0.0000758
           YEXP1(18)=0
           YEXP1(19)=0.0000675
           YEXP1(20)=0

                ELSE IF (TIM .GT. 0.80 .AND. TIM .LT. 0.85) THEN
                YPRIME(1)=1
                YEXP1(1)=YPRIME(1)
                YPRIME(2)=1
           YEXP1(2)=YPRIME(2)
                YPRIME(3)=1
           YEXP1(3)=YPRIME(3)
                YPRIME(4)=1
           YEXP1(4)=YPRIME(4)
                YPRIME(5)=1
           YEXP1(5)=YPRIME(5)
                YPRIME(6)=1
           YEXP1(6)=YPRIME(6)
                YPRIME(7)=1
      YEXP1(7)=YPRIME(7)
                YPRIME(8)=1
           YEXP1(8)=YPRIME(8)
                YPRIME(9)=1
           YEXP1(9)=YPRIME(9)
                YPRIME(10)=1
           YEXP1(10)=YPRIME(10)
                YPRIME(11)=1
           YEXP1(11)=YPRIME(11)
                YPRIME(12)=1
           YEXP1(12)=YPRIME(12)
                YPRIME(13)=1
           YEXP1(13)=YPRIME(13)
                YPRIME(14)=1
           YEXP1(14)=YPRIME(14)
                YPRIME(15)=1
           YEXP1(15)=YPRIME(15)
                YPRIME(16)=1
           YEXP1(16)=YPRIME(16)
                YPRIME(17)=1
           YEXP1(17)=YPRIME(17)
                YPRIME(18)=1
           YEXP1(18)=YPRIME(18)
```

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              YPRIME(19)=1
         YEXP1(19)=YPRIME(19)
              YPRIME(20)=1
         YEXP1(20)=YPRIME(20)

              ELSE IF (TIM .GT. 0.6 .AND. TIM .LT. 0.65) THEN
              YEXP1(1)=0
         YEXP1(2)=0.042121
         YEXP1(3)=0.091778
         YEXP1(4)=0
         YEXP1(5)=0.003447
         YEXP1(6)=0
    YEXP1(7)=0.026118
         YEXP1(8)=0
         YEXP1(9)=0.002289
         YEXP1(10)=0.0000715
         YEXP1(11)=0
         YEXP1(12)=0
         YEXP1(13)=0
         YEXP1(14)=0
         YEXP1(15)=0.00113
         YEXP1(16)=0
         YEXP1(17)=0.0000565
         YEXP1(18)=0
         YEXP1(19)=0.00005
         YEXP1(20)=0

              ELSE IF (TIM .GT. 0.48 .AND. TIM .LT. 0.52) THEN
              YPRIME(1)=1
              YEXP1(1)=YPRIME(1)
              YPRIME(2)=1
         YEXP1(2)=YPRIME(2)
              YPRIME(3)=1
         YEXP1(3)=YPRIME(3)
              YPRIME(4)=1
         YEXP1(4)=YPRIME(4)
              YPRIME(5)=1
         YEXP1(5)=YPRIME(5)
              YPRIME(6)=1
         YEXP1(6)=YPRIME(6)
              YPRIME(7)=1
    YEXP1(7)=YPRIME(7)
              YPRIME(8)=1
         YEXP1(8)=YPRIME(8)
              YPRIME(9)=1
         YEXP1(9)=YPRIME(9)
              YPRIME(10)=1
         YEXP1(10)=YPRIME(10)
              YPRIME(11)=1
         YEXP1(11)=YPRIME(11)
              YPRIME(12)=1
         YEXP1(12)=YPRIME(12)
              YPRIME(13)=1
         YEXP1(13)=YPRIME(13)
              YPRIME(14)=1
         YEXP1(14)=YPRIME(14)
              YPRIME(15)=1
         YEXP1(15)=YPRIME(15)
              YPRIME(16)=1
         YEXP1(16)=YPRIME(16)
              YPRIME(17)=1
         YEXP1(17)=YPRIME(17)
              YPRIME(18)=1
```

```
      YEXP1(18)=YPRIME(18)
           YPRIME(19)=1
      YEXP1(19)=YPRIME(19)
           YPRIME(20)=1
      YEXP1(20)=YPRIME(20)

           ELSE IF (TIM .GT. 0.3 .AND. TIM .LT. 0.4) THEN
           YEXP1(1)=0
      YEXP1(2)=0.037899
      YEXP1(3)=0.088671
      YEXP1(4)=0
      YEXP1(5)=0.001246
      YEXP1(6)=0
YEXP1(7)=0.029314
      YEXP1(8)=0
      YEXP1(9)=0.001081
      YEXP1(10)=0.0000365
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000887
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.20 .AND. TIM .LT. 0.22) THEN
           YEXP1(1)=0
      YEXP1(2)=0.037154
      YEXP1(3)=0.087353
      YEXP1(4)=0
      YEXP1(5)=0.000481
      YEXP1(6)=0
YEXP1(7)=0.029839
      YEXP1(8)=0
      YEXP1(9)=0.000794
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000625
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.1 .AND. TIM .LT. 0.19) THEN
           YEXP1(1)=0
      YEXP1(2)=0.03918
      YEXP1(3)=0.090987
      YEXP1(4)=0
      YEXP1(5)=0.000241
      YEXP1(6)=0
YEXP1(7)=0.031512
      YEXP1(8)=0
      YEXP1(9)=0.000633
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
```

```
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000439
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE
           GO TO 500

           END IF


     ELSE IF (TEM .GT. 1299 .AND. TEM .LT. 1301 ) THEN
         IF (TIM .GT. 8.0 .AND. TIM .LT. 9.0) THEN
      YEXP1(1)=0
      YEXP1(2)=0.021563
      YEXP1(3)=0.035802
      YEXP1(4)=0
      YEXP1(5)=0.000801
      YEXP1(6)=0
YEXP1(7)=0.001137
      YEXP1(8)=0
      YEXP1(9)=0.0000399
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 4.0 .AND. TIM .LT. 5.0) THEN
           YEXP1(1)=0
      YEXP1(2)=0.039751
      YEXP1(3)=0.090732
      YEXP1(4)=0
      YEXP1(5)=0.007581
      YEXP1(6)=0
YEXP1(7)=0.009045
      YEXP1(8)=0
      YEXP1(9)=0.000354
      YEXP1(10)=0.000116
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000663
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 2.2 .AND. TIM .LT. 2.4) THEN
           YEXP1(1)=0
      YEXP1(2)=0.039463
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```
      YEXP1(3)=0.089804
      YEXP1(4)=0
      YEXP1(5)=0.009988
      YEXP1(6)=0
YEXP1(7)=0.0104
      YEXP1(8)=0
      YEXP1(9)=0.000332
      YEXP1(10)=0.000165
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000932
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0.0000216
      YEXP1(20)=0

           ELSE IF (TIM .GT. 1.0 .AND. TIM .LT. 1.5) THEN
           YEXP1(1)=0
      YEXP1(2)=0.040765
      YEXP1(3)=0.088429
      YEXP1(4)=0
      YEXP1(5)=0.010321
      YEXP1(6)=0
YEXP1(7)=0.014118
      YEXP1(8)=0
      YEXP1(9)=0.002099
      YEXP1(10)=0.000195
      YEXP1(11)=0
      YEXP1(12)=0.000241
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.001232
      YEXP1(16)=0
      YEXP1(17)=0.00019
      YEXP1(18)=0
      YEXP1(19)=0.000157
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.70 .AND. TIM .LT. 0.80) THEN
           YPRIME(1)=1
           YEXP1(1)=YPRIME(1)
           YPRIME(2)=1
      YEXP1(2)=YPRIME(2)
           YPRIME(3)=1
      YEXP1(3)=YPRIME(3)
           YPRIME(4)=1
      YEXP1(4)=YPRIME(4)
           YPRIME(5)=1
      YEXP1(5)=YPRIME(5)
           YPRIME(6)=1
      YEXP1(6)=YPRIME(6)
           YPRIME(7)=1
YEXP1(7)=YPRIME(7)
           YPRIME(8)=1
      YEXP1(8)=YPRIME(8)
           YPRIME(9)=1
      YEXP1(9)=YPRIME(9)
           YPRIME(10)=1
      YEXP1(10)=YPRIME(10)
           YPRIME(11)=1
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```
      YEXP1(11)=YPRIME(11)
           YPRIME(12)=1
      YEXP1(12)=YPRIME(12)
           YPRIME(13)=1
      YEXP1(13)=YPRIME(13)
           YPRIME(14)=1
      YEXP1(14)=YPRIME(14)
           YPRIME(15)=1
      YEXP1(15)=YPRIME(15)
           YPRIME(16)=1
      YEXP1(16)=YPRIME(16)
           YPRIME(17)=1
      YEXP1(17)=YPRIME(17)
           YPRIME(18)=1
      YEXP1(18)=YPRIME(18)
           YPRIME(19)=1
      YEXP1(19)=YPRIME(19)
           YPRIME(20)=1
      YEXP1(20)=YPRIME(20)

           ELSE IF (TIM .GT. 0.55 .AND. TIM .LT. 0.6) THEN
           YEXP1(1)=0
      YEXP1(2)=0.042585
      YEXP1(3)=0.092583
      YEXP1(4)=0
      YEXP1(5)=0.009856
      YEXP1(6)=0
YEXP1(7)=0.016806
      YEXP1(8)=0
      YEXP1(9)=0.002425
      YEXP1(10)=0.000202
      YEXP1(11)=0
      YEXP1(12)=0.00028
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.001243
      YEXP1(16)=0
      YEXP1(17)=0.000215
      YEXP1(18)=0
      YEXP1(19)=0.000169
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.42 .AND. TIM .LT. 0.47) THEN
           YPRIME(1)=1
           YEXP1(1)=YPRIME(1)
           YPRIME(2)=1
      YEXP1(2)=YPRIME(2)
           YPRIME(3)=1
      YEXP1(3)=YPRIME(3)
           YPRIME(4)=1
      YEXP1(4)=YPRIME(4)
           YPRIME(5)=1
      YEXP1(5)=YPRIME(5)
           YPRIME(6)=1
      YEXP1(6)=YPRIME(6)
           YPRIME(7)=1
YEXP1(7)=YPRIME(7)
           YPRIME(8)=1
      YEXP1(8)=YPRIME(8)
           YPRIME(9)=1
      YEXP1(9)=YPRIME(9)
           YPRIME(10)=1
      YEXP1(10)=YPRIME(10)
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          YPRIME(11)=1
     YEXP1(11)=YPRIME(11)
          YPRIME(12)=1
     YEXP1(12)=YPRIME(12)
          YPRIME(13)=1
     YEXP1(13)=YPRIME(13)
          YPRIME(14)=1
     YEXP1(14)=YPRIME(14)
          YPRIME(15)=1
     YEXP1(15)=YPRIME(15)
          YPRIME(16)=1
     YEXP1(16)=YPRIME(16)
          YPRIME(17)=1
     YEXP1(17)=YPRIME(17)
          YPRIME(18)=1
     YEXP1(18)=YPRIME(18)
          YPRIME(19)=1
     YEXP1(19)=YPRIME(19)
          YPRIME(20)=1
     YEXP1(20)=YPRIME(20)

          ELSE IF (TIM .GT. 0.3 .AND. TIM .LT. 0.38) THEN
          YEXP1(1)=0
     YEXP1(2)=0.037673
     YEXP1(3)=0.08801
     YEXP1(4)=0
     YEXP1(5)=0.007797
     YEXP1(6)=0
YEXP1(7)=0.021627
     YEXP1(8)=0
     YEXP1(9)=0.000439
     YEXP1(10)=0.000206
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0.001136
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0.0000334
     YEXP1(20)=0

          ELSE IF (TIM .GT. 0.18 .AND. TIM .LT. 0.20) THEN
          YEXP1(1)=0
     YEXP1(2)=0.037166
     YEXP1(3)=0.08805
     YEXP1(4)=0
     YEXP1(5)=0.005468
     YEXP1(6)=0
YEXP1(7)=0.024221
     YEXP1(8)=0
     YEXP1(9)=0.000478
     YEXP1(10)=0.000306
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0.00104
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0.0000194
```

```
               YEXP1(20)=0

                    ELSE IF (TIM .GT. 0.1 .AND. TIM .LT. 0.165) THEN
                    YEXP1(1)=0
               YEXP1(2)=0.038857
               YEXP1(3)=0.089756
               YEXP1(4)=0
               YEXP1(5)=0.002294
               YEXP1(6)=0
          YEXP1(7)=0.028351
               YEXP1(8)=0
               YEXP1(9)=0.000626
               YEXP1(10)=0.000167
               YEXP1(11)=0
               YEXP1(12)=0
               YEXP1(13)=0
               YEXP1(14)=0
               YEXP1(15)=0.000866
               YEXP1(16)=0
               YEXP1(17)=0
               YEXP1(18)=0
               YEXP1(19)=0
               YEXP1(20)=0

                    ELSE
                    GO TO 500

                    END IF


              ELSE
              PRINT *,'SOMETHING WRONG'

              END IF

      ELSE
           IF (TEM .GT. 799 .AND. TEM .LT. 801) THEN
                  IF (TIM .GT. 13.0 .AND. TIM .LT. 13.2) THEN
               YEXP1(1)=0
               YEXP1(2)=0
               YEXP1(3)=0.034851
               YEXP1(4)=0
               YEXP1(5)=0
               YEXP1(6)=0
          YEXP1(7)=0.01246
               YEXP1(8)=0
               YEXP1(9)=0
               YEXP1(10)=0
               YEXP1(11)=0
               YEXP1(12)=0
               YEXP1(13)=0
               YEXP1(14)=0
               YEXP1(15)=0
               YEXP1(16)=0
               YEXP1(17)=0
               YEXP1(18)=0
               YEXP1(19)=0
               YEXP1(20)=0

                    ELSE IF (TIM .GT. 6.4 .AND. TIM .LT. 6.6) THEN
                    YEXP1(1)=0
               YEXP1(2)=0
               YEXP1(3)=0.036449
```

```
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.012861
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

            ELSE IF (TIM .GT. 3.5 .AND. TIM .LT. 3.7) THEN
            YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.037505
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.013221
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

            ELSE IF (TIM .GT. 1.7 .AND. TIM .LT. 1.9) THEN
            YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.037613
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.013259
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

            ELSE IF (TIM .GT. 1.1 .AND. TIM .LT. 1.3) THEN
```

```
          YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.037336
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.013374
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

          ELSE IF (TIM .GT. 0.8 .AND. TIM .LT. 1.0) THEN
          YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.035584
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.012748
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

          ELSE IF (TIM .GT. 0.6 .AND. TIM .LT. 0.8) THEN
          YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.036716
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.013084
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
```

```
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.4 .AND. TIM .LT. 0.6) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.037368
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.013243
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.3 .AND. TIM .LT. 0.4) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.036729
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.012882
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.1 .AND. TIM .LT. 0.3) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.060572
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.021132
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
```

```
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE
           GO TO 500

           END IF

    ELSE IF (TEM .GT. 899 .AND. TEM .LT. 901 ) THEN
        IF (TIM .GT. 11.0 .AND. TIM .LT. 12.0) THEN
      YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.030759
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.011394
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000095
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 5.0 .AND. TIM .LT. 6.0) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.036072
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.012903
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.0000313
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 3.0 .AND. TIM .LT. 3.7) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.038906
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.013316
```

```
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

            ELSE IF (TIM .GT. 1.5 .AND. TIM .LT. 1.9) THEN
            YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.037852
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.013368
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

            ELSE IF (TIM .GT. 1.0 .AND. TIM .LT. 1.2) THEN
            YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.03737
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.013344
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

            ELSE IF (TIM .GT. 0.8 .AND. TIM .LT. 0.9) THEN
            YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.037305
      YEXP1(4)=0
```

```
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.013268
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

            ELSE IF (TIM .GT. 0.6 .AND. TIM .LT. 0.7) THEN
            YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.036827
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.013056
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

            ELSE IF (TIM .GT. 0.4 .AND. TIM .LT. 0.5) THEN
            YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.03728
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.013212
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

            ELSE IF (TIM .GT. 0.25 .AND. TIM .LT. 0.3) THEN
            YEXP1(1)=0
```

```
     YEXP1(2)=0
     YEXP1(3)=0.036943
     YEXP1(4)=0
     YEXP1(5)=0
     YEXP1(6)=0
YEXP1(7)=0.012959
     YEXP1(8)=0
     YEXP1(9)=0
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0

          ELSE IF (TIM .GT. 0.1 .AND. TIM .LT. 0.25) THEN
          YEXP1(1)=0
     YEXP1(2)=0
     YEXP1(3)=0.061838
     YEXP1(4)=0
     YEXP1(5)=0
     YEXP1(6)=0
YEXP1(7)=0.021571
     YEXP1(8)=0
     YEXP1(9)=0
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0

          ELSE
          GO TO 500

          END IF


          ELSE IF (TEM .GT. 999 .AND. TEM .LT. 1001 ) THEN
        IF (TIM .GT. 10.0 .AND. TIM .LT. 11.0) THEN
     YEXP1(1)=0
     YEXP1(2)=0.00000201
     YEXP1(3)=0.033863
     YEXP1(4)=0
     YEXP1(5)=0.0000177
     YEXP1(6)=0
YEXP1(7)=0.011818
     YEXP1(8)=0
     YEXP1(9)=0.0000148
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0.000167
     YEXP1(13)=0
```

```
      YEXP1(14)=0
      YEXP1(15)=0.000433
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 5.0 .AND. TIM .LT. 6.0) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.03468
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.012044
      YEXP1(8)=0
      YEXP1(9)=0.0000105
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000207
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 2.5 .AND. TIM .LT. 3.7) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.037255
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.012843
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000088
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 1.4 .AND. TIM .LT. 1.9) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.036963
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.012992
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
```

```
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.0000465
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.85 .AND. TIM .LT. 0.99) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.032873
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.011513
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.0000275
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.7 .AND. TIM .LT. 0.8) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.036577
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.013019
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.55 .AND. TIM .LT. 0.6) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.036524
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.012961
```

```
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.4 .AND. TIM .LT. 0.5) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.036472
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.0129
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.23 .AND. TIM .LT. 0.27) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.036246
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.012716
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.1 .AND. TIM .LT. 0.22) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.057504
      YEXP1(4)=0
```

```
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.020184
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

            ELSE
            GO TO 500

            END IF


     ELSE IF (TEM .GT. 1099 .AND. TEM .LT. 1101 ) THEN
         IF (TIM .GT. 9.0 .AND. TIM .LT. 11.0) THEN
      YEXP1(1)=0
      YEXP1(2)=0.00016
      YEXP1(3)=0.033305
      YEXP1(4)=0
      YEXP1(5)=0.000575
      YEXP1(6)=0
YEXP1(7)=0.010136
      YEXP1(8)=0
      YEXP1(9)=0.0000873
      YEXP1(10)=0.000195
      YEXP1(11)=0
      YEXP1(12)=0.000668
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.001455
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

            ELSE IF (TIM .GT. 4.5 .AND. TIM .LT. 6.0) THEN
            YEXP1(1)=0
      YEXP1(2)=0.0000526
      YEXP1(3)=0.029286
      YEXP1(4)=0
      YEXP1(5)=0.000145
      YEXP1(6)=0
YEXP1(7)=0.007112
      YEXP1(8)=0
      YEXP1(9)=0.0000503
      YEXP1(10)=0.0000443
      YEXP1(11)=0
      YEXP1(12)=0.000333
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000494
      YEXP1(16)=0
```

```
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 2.3 .AND. TIM .LT. 3.0) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.037241
      YEXP1(4)=0
      YEXP1(5)=0.0000553
      YEXP1(6)=0
YEXP1(7)=0.012728
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0.000146
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000303
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 1.2 .AND. TIM .LT. 1.5) THEN
           YPRIME(1)=1
           YEXP1(1)=YPRIME(1)
           YPRIME(2)=1
      YEXP1(2)=YPRIME(2)
           YPRIME(3)=1
      YEXP1(3)=YPRIME(3)
           YPRIME(4)=1
      YEXP1(4)=YPRIME(4)
           YPRIME(5)=1
      YEXP1(5)=YPRIME(5)
           YPRIME(6)=1
      YEXP1(6)=YPRIME(6)
           YPRIME(7)=1
YEXP1(7)=YPRIME(7)
           YPRIME(8)=1
      YEXP1(8)=YPRIME(8)
           YPRIME(9)=1
      YEXP1(9)=YPRIME(9)
           YPRIME(10)=1
      YEXP1(10)=YPRIME(10)
           YPRIME(11)=1
      YEXP1(11)=YPRIME(11)
           YPRIME(12)=1
      YEXP1(12)=YPRIME(12)
           YPRIME(13)=1
      YEXP1(13)=YPRIME(13)
           YPRIME(14)=1
      YEXP1(14)=YPRIME(14)
           YPRIME(15)=1
      YEXP1(15)=YPRIME(15)
           YPRIME(16)=1
      YEXP1(16)=YPRIME(16)
           YPRIME(17)=1
      YEXP1(17)=YPRIME(17)
           YPRIME(18)=1
```

```
      YEXP1(18)=YPRIME(18)
           YPRIME(19)=1
      YEXP1(19)=YPRIME(19)
           YPRIME(20)=1
      YEXP1(20)=YPRIME(20)

           ELSE IF (TIM .GT. 0.85 .AND. TIM .LT. 0.99) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.036708
      YEXP1(4)=0
      YEXP1(5)=0.0000108
      YEXP1(6)=0
YEXP1(7)=0.013078
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.0000844
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.65 .AND. TIM .LT. 0.7) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.035159
      YEXP1(4)=0
      YEXP1(5)=0.012398
      YEXP1(6)=0
YEXP1(7)=0
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.0000438
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.50 .AND. TIM .LT. 0.55) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.035786
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.012679
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
```

```
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.3 .AND. TIM .LT. 0.4) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.035857
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.012681
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.21 .AND. TIM .LT. 0.24) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.037854
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.013254
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.1 .AND. TIM .LT. 0.20) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.0596
      YEXP1(4)=0
      YEXP1(5)=0
      YEXP1(6)=0
YEXP1(7)=0.020796
      YEXP1(8)=0
      YEXP1(9)=0
```

```
          YEXP1(10)=0
          YEXP1(11)=0
          YEXP1(12)=0
          YEXP1(13)=0
          YEXP1(14)=0
          YEXP1(15)=0
          YEXP1(16)=0
          YEXP1(17)=0
          YEXP1(18)=0
          YEXP1(19)=0
          YEXP1(20)=0

               ELSE
               GO TO 500

               END IF


         ELSE IF (TEM .GT. 1199 .AND. TEM .LT. 1201 ) THEN
             IF (TIM .GT. 8.5 .AND. TIM .LT. 9.0) THEN
          YEXP1(1)=0
          YEXP1(2)=0.000275
          YEXP1(3)=0.021071
          YEXP1(4)=0
          YEXP1(5)=0.00089
          YEXP1(6)=0
     YEXP1(7)=0.002864
          YEXP1(8)=0
          YEXP1(9)=0.0000992
          YEXP1(10)=0.000223
          YEXP1(11)=0
          YEXP1(12)=0.000185
          YEXP1(13)=0
          YEXP1(14)=0
          YEXP1(15)=0.000594
          YEXP1(16)=0
          YEXP1(17)=0
          YEXP1(18)=0
          YEXP1(19)=0.00000691
          YEXP1(20)=0

               ELSE IF (TIM .GT. 4.1 .AND. TIM .LT. 4.5) THEN
               YEXP1(1)=0
          YEXP1(2)=0.000103
          YEXP1(3)=0.027341
          YEXP1(4)=0
          YEXP1(5)=0.000517
          YEXP1(6)=0
     YEXP1(7)=0.004055
          YEXP1(8)=0
          YEXP1(9)=0.0000718
          YEXP1(10)=0.000181
          YEXP1(11)=0
          YEXP1(12)=0.000291
          YEXP1(13)=0
          YEXP1(14)=0
          YEXP1(15)=0.000597
          YEXP1(16)=0
          YEXP1(17)=0
          YEXP1(18)=0
          YEXP1(19)=0
          YEXP1(20)=0
```

```
          ELSE IF (TIM .GT. 2.3 .AND. TIM .LT. 2.5) THEN
          YEXP1(1)=0
     YEXP1(2)=0
     YEXP1(3)=0.037221
     YEXP1(4)=0
     YEXP1(5)=0.000024
     YEXP1(6)=0
YEXP1(7)=0.013059
     YEXP1(8)=0
     YEXP1(9)=0
     YEXP1(10)=0
     YEXP1(11)=0
     YEXP1(12)=0
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0.000158
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0

          ELSE IF (TIM .GT. 1.2 .AND. TIM .LT. 1.3) THEN
          YEXP1(1)=0
     YEXP1(2)=0.0000889
     YEXP1(3)=0.031331
     YEXP1(4)=0
     YEXP1(5)=0.000497
     YEXP1(6)=0
YEXP1(7)=0.009374
     YEXP1(8)=0
     YEXP1(9)=0.0000694
     YEXP1(10)=0.000149
     YEXP1(11)=0
     YEXP1(12)=0.000498
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0.000165
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0

          ELSE IF (TIM .GT. 0.80 .AND. TIM .LT. 0.85) THEN
          YEXP1(1)=0
     YEXP1(2)=0.0000541
     YEXP1(3)=0.035898
     YEXP1(4)=0
     YEXP1(5)=0.000275
     YEXP1(6)=0
YEXP1(7)=0.012148
     YEXP1(8)=0
     YEXP1(9)=0.0000371
     YEXP1(10)=0.0000587
     YEXP1(11)=0
     YEXP1(12)=0.00037
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0.000539
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
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      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.6 .AND. TIM .LT. 0.65) THEN
           YEXP1(1)=0
      YEXP1(2)=0.0000328
      YEXP1(3)=0.035719
      YEXP1(4)=0
      YEXP1(5)=0.000168
      YEXP1(6)=0
YEXP1(7)=0.012322
      YEXP1(8)=0
      YEXP1(9)=0.00002
      YEXP1(10)=0.0000256
      YEXP1(11)=0
      YEXP1(12)=0.000245
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.0000739
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.48 .AND. TIM .LT. 0.52) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.034634
      YEXP1(4)=0
      YEXP1(5)=0.0000703
      YEXP1(6)=0
YEXP1(7)=0.012152
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0.0000997
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000176
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.3 .AND. TIM .LT. 0.4) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.0359
      YEXP1(4)=0
      YEXP1(5)=0.000026
      YEXP1(6)=0
YEXP1(7)=0.012648
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.0000183
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      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.20 .AND. TIM .LT. 0.22) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.03534
      YEXP1(4)=0
      YEXP1(5)=0.0000179
      YEXP1(6)=0
 YEXP1(7)=0.010352
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.00000811
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE IF (TIM .GT. 0.1 .AND. TIM .LT. 0.19) THEN
           YEXP1(1)=0
      YEXP1(2)=0
      YEXP1(3)=0.055282
      YEXP1(4)=0
      YEXP1(5)=0.0000121
      YEXP1(6)=0
 YEXP1(7)=0.019467
      YEXP1(8)=0
      YEXP1(9)=0
      YEXP1(10)=0
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.0000131
      YEXP1(16)=0
      YEXP1(17)=0
      YEXP1(18)=0
      YEXP1(19)=0
      YEXP1(20)=0

           ELSE
           GO TO 500

           END IF


     ELSE IF (TEM .GT. 1299 .AND. TEM .LT. 1301 ) THEN
         IF (TIM .GT. 8.0 .AND. TIM .LT. 9.0) THEN
      YEXP1(1)=0
      YEXP1(2)=0.004247
      YEXP1(3)=0.042054
      YEXP1(4)=0
      YEXP1(5)=0.005843
```

```
      YEXP1(6)=0
YEXP1(7)=0.003349
      YEXP1(8)=0
      YEXP1(9)=0.000283
      YEXP1(10)=0.000356
      YEXP1(11)=0
      YEXP1(12)=0
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000823
      YEXP1(16)=0
      YEXP1(17)=0.0000848
      YEXP1(18)=0
      YEXP1(19)=0.0000306
      YEXP1(20)=0

            ELSE IF (TIM .GT. 4.0 .AND. TIM .LT. 5.0) THEN
            YEXP1(1)=0
      YEXP1(2)=0.002731
      YEXP1(3)=0.050966
      YEXP1(4)=0
      YEXP1(5)=0.007608
      YEXP1(6)=0
YEXP1(7)=0.006037
      YEXP1(8)=0
      YEXP1(9)=0.000298
      YEXP1(10)=0.000768
      YEXP1(11)=0
      YEXP1(12)=0.000264
      YEXP1(13)=0
      YEXP1(14)=0
      YEXP1(15)=0.000172
      YEXP1(16)=0
      YEXP1(17)=0.0000466
      YEXP1(18)=0
      YEXP1(19)=0.0000229
      YEXP1(20)=0

            ELSE IF (TIM .GT. 2.2 .AND. TIM .LT. 2.4) THEN
            YPRIME(1)=1
            YEXP1(1)=YPRIME(1)
            YPRIME(2)=1
      YEXP1(2)=YPRIME(2)
            YPRIME(3)=1
      YEXP1(3)=YPRIME(3)
            YPRIME(4)=1
      YEXP1(4)=YPRIME(4)
            YPRIME(5)=1
      YEXP1(5)=YPRIME(5)
            YPRIME(6)=1
      YEXP1(6)=YPRIME(6)
            YPRIME(7)=1
YEXP1(7)=YPRIME(7)
            YPRIME(8)=1
      YEXP1(8)=YPRIME(8)
            YPRIME(9)=1
      YEXP1(9)=YPRIME(9)
            YPRIME(10)=1
      YEXP1(10)=YPRIME(10)
            YPRIME(11)=1
      YEXP1(11)=YPRIME(11)
            YPRIME(12)=1
      YEXP1(12)=YPRIME(12)
```

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          YPRIME(13)=1
     YEXP1(13)=YPRIME(13)
          YPRIME(14)=1
     YEXP1(14)=YPRIME(14)
          YPRIME(15)=1
     YEXP1(15)=YPRIME(15)
          YPRIME(16)=1
     YEXP1(16)=YPRIME(16)
          YPRIME(17)=1
     YEXP1(17)=YPRIME(17)
          YPRIME(18)=1
     YEXP1(18)=YPRIME(18)
          YPRIME(19)=1
     YEXP1(19)=YPRIME(19)
          YPRIME(20)=1
     YEXP1(20)=YPRIME(20)

          ELSE IF (TIM .GT. 1.0 .AND. TIM .LT. 1.5) THEN
          YEXP1(1)=0
     YEXP1(2)=0.001752
     YEXP1(3)=0.051578
     YEXP1(4)=0
     YEXP1(5)=0.0066
     YEXP1(6)=0
YEXP1(7)=0.00837
     YEXP1(8)=0
     YEXP1(9)=0.000294
     YEXP1(10)=0.000951
     YEXP1(11)=0
     YEXP1(12)=0.000041
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0.002321
     YEXP1(16)=0
     YEXP1(17)=0.0000165
     YEXP1(18)=0
     YEXP1(19)=0.0000972
     YEXP1(20)=0

          ELSE IF (TIM .GT. 0.70 .AND. TIM .LT. 0.80) THEN
          YEXP1(1)=0
     YEXP1(2)=0.001499
     YEXP1(3)=0.052957
     YEXP1(4)=0
     YEXP1(5)=0.006233
     YEXP1(6)=0
YEXP1(7)=0.010036
     YEXP1(8)=0
     YEXP1(9)=0.000337
     YEXP1(10)=0.001037
     YEXP1(11)=0
     YEXP1(12)=0.000532
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0.002631
     YEXP1(16)=0
     YEXP1(17)=0.0000129
     YEXP1(18)=0
     YEXP1(19)=0.000099
     YEXP1(20)=0

          ELSE IF (TIM .GT. 0.55 .AND. TIM .LT. 0.6) THEN
          YEXP1(1)=0
```

```
     YEXP1(2)=0.000953
     YEXP1(3)=0.056777
     YEXP1(4)=0
     YEXP1(5)=0.004507
     YEXP1(6)=0
YEXP1(7)=0.013342
     YEXP1(8)=0
     YEXP1(9)=0.000364
     YEXP1(10)=0.00109
     YEXP1(11)=0
     YEXP1(12)=0.000865
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0.002972
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0.000107
     YEXP1(20)=0

          ELSE IF (TIM .GT. 0.42 .AND. TIM .LT. 0.47) THEN
          YEXP1(1)=0
     YEXP1(2)=0.000445
     YEXP1(3)=0.056447
     YEXP1(4)=0
     YEXP1(5)=0.002327
     YEXP1(6)=0
YEXP1(7)=0.016008
     YEXP1(8)=0
     YEXP1(9)=0.000299
     YEXP1(10)=0.000712
     YEXP1(11)=0
     YEXP1(12)=0.001028
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0.002055
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0.00000931
     YEXP1(20)=0

          ELSE IF (TIM .GT. 0.3 .AND. TIM .LT. 0.38) THEN
          YEXP1(1)=0
     YEXP1(2)=0.000179
     YEXP1(3)=0.055773
     YEXP1(4)=0
     YEXP1(5)=0.000973
     YEXP1(6)=0
YEXP1(7)=0.018032
     YEXP1(8)=0
     YEXP1(9)=0.000147
     YEXP1(10)=0.000262
     YEXP1(11)=0
     YEXP1(12)=0.000761
     YEXP1(13)=0
     YEXP1(14)=0
     YEXP1(15)=0.000997
     YEXP1(16)=0
     YEXP1(17)=0
     YEXP1(18)=0
     YEXP1(19)=0
     YEXP1(20)=0
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```
                  ELSE IF (TIM .GT. 0.18 .AND. TIM .LT. 0.20) THEN
                  YEXP1(1)=0
             YEXP1(2)=0.0000514
             YEXP1(3)=0.056242
             YEXP1(4)=0
             YEXP1(5)=0.000317
             YEXP1(6)=0
        YEXP1(7)=0.017106
             YEXP1(8)=0
             YEXP1(9)=0.0000448
             YEXP1(10)=0.0000464
             YEXP1(11)=0
             YEXP1(12)=0.000315
             YEXP1(13)=0
             YEXP1(14)=0
             YEXP1(15)=0.0000809
             YEXP1(16)=0
             YEXP1(17)=0
             YEXP1(18)=0
             YEXP1(19)=0
             YEXP1(20)=0

                  ELSE IF (TIM .GT. 0.1 .AND. TIM .LT. 0.165) THEN
                  YEXP1(1)=0
             YEXP1(2)=0
             YEXP1(3)=0.056291
             YEXP1(4)=0
             YEXP1(5)=0.000166
             YEXP1(6)=0
        YEXP1(7)=0.017663
             YEXP1(8)=0
             YEXP1(9)=0.0000259
             YEXP1(10)=0.0000209
             YEXP1(11)=0
             YEXP1(12)=0.0002
             YEXP1(13)=0
             YEXP1(14)=0
             YEXP1(15)=0.0000586
             YEXP1(16)=0
             YEXP1(17)=0
             YEXP1(18)=0
             YEXP1(19)=0
             YEXP1(20)=0

                  ELSE
                  GO TO 500

                  END IF


            ELSE
            PRINT *,'SOMETHING WRONG'

            END IF

      ENDIF
IF (YEXP1(2) .EQ. 0) THEN
      YEXP2(1) = YPRIME(2)
      ELSE
      YEXP2(1) = (YPRIME(2)-YEXP1(2))/YEXP1(2)
      END IF
      IF (YEXP1(3) .EQ. 0) THEN
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             YEXP2(2) = YPRIME(3)
             ELSE
             YEXP2(2) = (YPRIME(3)-YEXP1(3))/YEXP1(3)
             END IF
             IF (YEXP1(5) .EQ. 0) THEN
             YEXP2(3) = YPRIME(5)
             ELSE
             YEXP2(3) = (YPRIME(5)-YEXP1(5))/YEXP1(5)
             END IF
             IF (YEXP1(7) .EQ. 0) THEN
             YEXP2(4) = YPRIME(7)
             ELSE
           YEXP2(4) = (YPRIME(7)-YEXP1(7))/YEXP1(7)
             END IF
             IF (YEXP1(9) .EQ. 0) THEN
             YEXP2(5) = YPRIME(9)
             ELSE
             YEXP2(5) = (YPRIME(9)-YEXP1(9))/YEXP1(9)
             END IF
             IF (YEXP1(10) .EQ. 0) THEN
             YEXP2(6) = YPRIME(10)
             ELSE
             YEXP2(6) = (YPRIME(10)-YEXP1(10))/YEXP1(10)
             END IF
             IF (YEXP1(12) .EQ. 0) THEN
             YEXP2(7) = YPRIME(12)
             ELSE
             YEXP2(7) = (YPRIME(12)-YEXP1(12))/YEXP1(12)
             END IF
             IF (YEXP1(14) .EQ. 0) THEN
             YEXP2(8) = YPRIME(14)
             ELSE
             YEXP2(8) = (YPRIME(14)-YEXP1(14))/YEXP1(14)
             END IF
             IF (YEXP1(15) .EQ. 0) THEN
             YEXP2(9) = YPRIME(15)
             ELSE
             YEXP2(9) = (YPRIME(15)-YEXP1(15))/YEXP1(15)
             END IF
             IF (YEXP1(17) .EQ. 0) THEN
             YEXP2(10) = YPRIME(17)
             ELSE
             YEXP2(10) = (YPRIME(17)-YEXP1(17))/YEXP1(17)
             END IF
             IF (YEXP1(19) .EQ. 0) THEN
             YEXP2(11) = YPRIME(19)
             ELSE
             YEXP2(11) = (YPRIME(19)-YEXP1(19))/YEXP1(19)
             END IF

C            OPEN(UNIT=21,FORM='FORMATTED',STATUS='OLD',
C      1                  FILE='exprs.txt')

C            DO LOOP1=1,1000000
C            READ(21,'(F8.0,E14.7)',END=70),TEMP,TIME

C            IF (TEMP.EQ.TEM) .AND. (TIME.EQ.TIM) THEN

C          DO LOOP2=1,100
C          READ(21,'(F8.0,E14.7,F10.7)',END=50),TEMP,TIME,YEXP
C          END DO
C            END DO
C50      CLOSE(UNIT=21)
```

```
        LSQSUM =((YEXP2(1)**2)+(YEXP2(2)**2)+(YEXP2(3)**2)+(YEXP2(4)**2)
       1          +(YEXP2(5)**2)+(YEXP2(6)**2)+(YEXP2(7)**2)+(YEXP2(8)**2)
       1          +(YEXP2(9)**2)+(YEXP2(9)**2)+(YEXP2(10)**2)+
       1            (YEXP2(10)**2)+(YEXP2(1)**2)+(YEXP2(2)**2))
C        PRINT *,LSQSUM

C          LSQSUM = (ABS(YPRIME(2)-YEXP2(2)))**2+YPRIME(3)-YEXP2(3)))**2+
C      1             YPRIME(5)-YEXP2(5)))**2+YPRIME(7)-YEXP2(7)))**2+
C   2            YPRIME(9)-YEXP2(9)))**2+YPRIME(10)-YEXP2(10)))**2+
C   3            YPRIME(12)-YEXP2(12)))**2+YPRIME(14)-YEXP2(14)))**2+
C   4            YPRIME(15)-YEXP2(15)))**2+YPRIME(17)-YEXP2(17)))**2+
C   5            YPRIME(18)-YEXP2(18)))**2

C
C        LSQSUM = 0.1
500          END
C70      PRINT *,'problem: ctrl-c, please'
C        GO TO 50
```

Appendix III

The driver routine used in the parameter estimation software

```
FROM __FUTURE__ IMPORT PRINT_FUNCTION
FROM __FUTURE__ IMPORT DIVISION

FROM PYEVOLVE IMPORT G1DLIST, GSIMPLEGA, SELECTORS, SCALING, DBADAPTERS, MUTATORS,
INITIALIZATORS, CONSTS
FROM PYEVOLVE IMPORT GALLELE
FROM RANDOM IMPORT SEED, RANDINT, RANDOM

FROM PYLAB IMPORT *
IMPORT MATPLOTLIB.PYPLOT AS PLT

IMPORT OS
IMPORT SYS
IMPORT TIME
FROM NUMPY IMPORT *
IMPORT PARSER
FROM SCIPY IMPORT *
FROM PYLAB IMPORT *
FROM SCIPY IMPORT OPTIMIZE
FROM SCIPY IMPORT INTEGRATE
FROM SCIPY.INTEGRATE IMPORT ODEINT
FROM SCIPY.OPTIMIZE IMPORT LEASTSQ

DEF LSQ_100(TS,CONCS):
    #TEST_VAR = MIN(RANGE(LEN(TS)), KEY=LAMBDA I: ABS(TS[I]-SAMPLE_POINTS[2][0]))
    SAMPLING_TIMES = [TIMES[0] FOR TIMES IN SAMPLE_POINTS_1000]
    #PRINT(CONCS)
    TEST = []
    FOR I IN RANGE(0,LEN(SAMPLING_TIMES)):
        #PRINT(I,"LOOP")
        TEMP = MIN(ENUMERATE(TS), KEY=LAMBDA X: ABS(X[1]-SAMPLING_TIMES[I]))
        #PRINT(TEMP[0])
        IF TEMP[1] > SAMPLING_TIMES[I]:
            #PRINT("LARGER")
            TEMP_2 = [TEMP[0]-1,TEMP[0],TEMP[1],I]
            #PRINT(TEMP_2)
        ELSE:
            #PRINT("SMALLER")
            TEMP_2 = [TEMP[0], TEMP[0]+1, TEMP[1],I]
            #PRINT(TEMP_2)
```

```
        #test.append(min(enumerate(ts), key=lambda x: abs(x[1]-
sampling_times[i])))
        if i > 0:
            test.append(temp_2)
        #print(test)
        #test_var[i] = min(enumerate(ts), key=lambda x: abs(x[1]-
sampling_times[i]))
    #print(test)
    #print(ts[108],ts[109],sample_points[2][0])
    #print(concs[108][1],concs[108][3],concs[108][5],concs[108][7])
    #print(concs[109][1],concs[109][3],concs[109][5],concs[109][7])
    #normalizing1 = max([species[1] for species in concs])
    #normalizing2 = max([species[3] for species in concs])
    #normalizing3 = max([species[5] for species in concs])
    #normalizing4 = max([species[7] for species in concs])

    ss_sum = 0

    for time_point in test:

    #print(concs[time_point[0]][0],concs[time_point[0]][1],concs[time_point[0]][2],con
cs[time_point[0]][2],concs[time_point[0]][4])
        #raw_input("CTRL-C")
        sum1 = concs[time_point[0]][0]+(concs[time_point[1]][0]-
concs[time_point[0]][0])*(sample_points_1000[time_point[3]][0]-
ts[time_point[0]])/(ts[time_point[1]]-ts[time_point[0]])
        sum2 = concs[time_point[0]][1]+(concs[time_point[1]][1]-
concs[time_point[0]][1])*(sample_points_1000[time_point[3]][0]-
ts[time_point[0]])/(ts[time_point[1]]-ts[time_point[0]])
        sum3 = concs[time_point[0]][2]+(concs[time_point[1]][2]-
concs[time_point[0]][2])*(sample_points_1000[time_point[3]][0]-
ts[time_point[0]])/(ts[time_point[1]]-ts[time_point[0]])
        sum4 = concs[time_point[0]][3]+(concs[time_point[1]][3]-
concs[time_point[0]][3])*(sample_points_1000[time_point[3]][0]-
ts[time_point[0]])/(ts[time_point[1]]-ts[time_point[0]])
        sum5 = concs[time_point[0]][4]+(concs[time_point[1]][4]-
concs[time_point[0]][4])*(sample_points_1000[time_point[3]][0]-
ts[time_point[0]])/(ts[time_point[1]]-ts[time_point[0]])


        #print(sum3,sample_points_1000[time_point[3]][2])
        #print(sum1,sample_points[time_point[3]][3],normalizing1)
        #normss1 = ((sum1/normalizing1)-
(sample_points[time_point[3]][3]/normalizing1))**2
        #normss2 = ((sum2/normalizing2)-
(sample_points[time_point[3]][1]/normalizing2))**2
```

```
        #normss3 = ((sum3/normalizing3)-
(sample_points[time_point[3]][2]/normalizing3))**2
        #normss4 = ((sum4/normalizing4)-
(sample_points[time_point[3]][4]/normalizing4))**2
        ss1 = (sum1-sample_points_1000[time_point[3]][3])**2 #H2
        ss2 = (sum2-sample_points_1000[time_point[3]][5])**2 #CH4
        ss3 = (sum3-sample_points_1000[time_point[3]][1])**2 #C2H4
        ss4 = (sum4-sample_points_1000[time_point[3]][2])**2 #C2H6
        ss5 = (sum5-sample_points_1000[time_point[3]][4])**2 #C4H6
        #print(ss2)

        if ss1 < 1e-12:
            ss1 = 0.0
        if ss2 < 1e-12:
            ss2 = 0.0
        if ss3 < 1e-12:
            ss3 = 0.0
        if ss4 < 1e-12:
            ss4 = 0.0
        if ss5 < 1e-12:
            ss5 = 0.0

        ss_tot = (ss1+ss2+ss3+ss4+ss5)
        ss_sum = ss_sum + ss_tot

    if sum1 < 0 or sum2 < 0 or sum3 < 0 or sum4 < 0 or sum5 < 0:
        ss_sum = 50000
    #print(normalizing1,normalizing2,normalizing3,normalizing4)
    #sum1 = concs[108][1]+(concs[109][1]-concs[108][1])*(sample_points[2][0]-
ts[108])/(ts[109]-ts[108])
    #sum2 = concs[108][3]+(concs[109][3]-concs[108][3])*(sample_points[2][0]-
ts[108])/(ts[109]-ts[108])
    #sum3 = concs[108][5]+(concs[109][5]-concs[108][5])*(sample_points[2][0]-
ts[108])/(ts[109]-ts[108])
    #sum4 = concs[108][7]+(concs[109][7]-concs[108][7])*(sample_points[2][0]-
ts[108])/(ts[109]-ts[108])
    #print(sum1,sample_points[2][1])
    #ss1 = (sum1-sample_points[2][3])**2
    #ss2 = (sum2-sample_points[2][1])**2
    #ss3 = (sum3-sample_points[2][2])**2
    #ss4 = (sum4-sample_points[2][4])**2
    #print(ss1,ss2,ss3,ss4)
    #normss1 = ((sum1/normalizing1)-(sample_points[2][3]/normalizing1))**2
    #normss2 = ((sum2/normalizing2)-(sample_points[2][1]/normalizing2))**2
    #normss3 = ((sum3/normalizing3)-(sample_points[2][2]/normalizing3))**2
    #normss4 = ((sum4/normalizing4)-(sample_points[2][4]/normalizing4))**2
    #print(normss1,normss2,normss3,normss4)
```

```
    #ss_tot = 1000*(normss1+normss2+normss3+normss4)
    #print(ss_sum,"1000")
    return ss_sum

def deriv(x,t,k):
    #global k,soot
    #C12 = 4.04-(2*x[3]+2*x[5]+4*x[7]+x[2])
    #H2 = 8.08-(2*x[1]+4*x[3]+6*x[5]+6*x[7]+4*x[2])
    #print(x)
    #raw_input("enter")
    #if C12 == 0:
    #       rel_soot = 0
    #else:
    #       rel_soot = H2/C12

    #soot_line = [C12,H2,rel_soot]
    #soot.append(soot_line)
    #print(x[0],x[1],x[2],x[3],x[4],x[5],x[6],x[7],x[8])
    #print(x[0]+2*x[1]+3*x[2]+4*x[3]+5*x[4]+6*x[5]+5*x[6]+6*x[7]+6*x[8],2*x[2]+2*x[
3]+2*x[4]+2*x[5]+4*x[6]+4*x[7]+6*x[8])
    #raw_input("CTRL-C")
    return [k[8]*x[5]*x[5]-k[9]*x[0]*x[5],
                -k[2]*x[1]*x[5]+k[10]*x[5]*x[6],
                -2*k[0]*x[2]*x[2]-k[1]*x[2]*x[5]+k[7]*x[6]*x[5],
                k[4]*x[5]*x[6]-k[6]*x[3]*x[5],
                k[3]*x[5]*x[6]-k[5]*x[4]*x[5],
                8*k[0]*x[2]*x[2]+4*k[1]*x[2]*x[5]+4*k[2]*x[1]*x[5]-6*k[3]*x[5]*x[6]-
6*k[4]*x[5]*x[6]+6*k[5]*x[4]*x[5]+6*k[6]*x[3]*x[5]-4*k[7]*x[5]*x[6]-
2*k[8]*x[5]*x[5]+2*k[9]*x[0]*x[5]-4*k[10]*x[5]*x[6],
                4*k[0]*x[2]*x[2]+2*k[1]*x[2]*x[5]+k[2]*x[1]*x[5]-4*k[3]*x[5]*x[6]-
2*k[4]*x[5]*x[6]+4*k[5]*x[4]*x[5]+2*k[6]*x[3]*x[5]-2*k[7]*x[5]*x[6]-k[10]*x[5]*x[6]]

def func(k):
    #print(k)
    start=0
    end=2.2
    numsteps=10000
    times=linspace(start,end,numsteps)
    y0=array([0.0,10.2,2.02,0.0,0.0,0.0,0.0])
    #fitness_100 = 25000
    result_100,output_100 = integrate.odeint(deriv,y0,times,args=(k,), mxstep=5000,
full_output = 1)
    big_question_100 = output_100['message']
    if big_question_100 == 'Integration successful.':
        fitness_100 = lsq_100(times,result_100)
    #print(fitness_100,"BFGS")
    return fitness_100
```

```
def deriv_700(x,t):
        global k,soot
        C12 = 4.04-(2*x[3]+2*x[5]+4*x[7]+x[2])
        H2 = 8.08-(2*x[1]+4*x[3]+6*x[5]+6*x[7]+4*x[2])
        #print(x[1])
        if C12 == 0:
                rel_soot = 0
        else:
                rel_soot = H2/C12

        soot_line = [C12,H2,rel_soot]
        soot.append(soot_line)
        #print(x[0],x[1],x[2],x[3],x[4],x[5],x[6],x[7],x[8])
        #print(x[0]+2*x[1]+3*x[2]+4*x[3]+5*x[4]+6*x[5]+5*x[6]+6*x[7]+6*x[8],2*x[2]+2*x[
3]+2*x[4]+2*x[5]+4*x[6]+4*x[7]+6*x[8])
        #raw_input("CTRL-C")
        return [6*k[16]*x[3]*x[3]+2*k[17]*x[3]*x[3]+2*k[18]*x[3]*x[3]+2*k[19]*x[2]*x[4]-
2*k[21]*x[0]*x[0]+6*k[22]*x[5]+6*k[23]*x[7],
                        k[16]*x[3]*x[3]+k[19]*x[2]*x[4]+k[21]*x[0]*x[0]-2*k[20]*x[1]*x[4],
                        -k[19]*x[2]*x[4],
                        -2*k[16]*x[3]*x[3]-2*k[17]*x[3]*x[3]-
2*k[18]*x[3]*x[3]+k[20]*x[1]*x[4],
                        4*k[16]*x[3]*x[3]+2*k[17]*x[3]*x[3]-
2*k[20]*x[1]*x[4]+2*k[22]*x[5]+4*k[23]*x[7],
                        k[17]*x[3]*x[3]-k[22]*x[5],
                        0,
                        k[18]*x[3]*x[3]-k[23]*x[7],
                        0]


def deriv_800(x,t):
        global k,soot
        C12 = 4.04-(2*x[3]+2*x[5]+4*x[7]+x[2])
        H2 = 8.08-(2*x[1]+4*x[3]+6*x[5]+6*x[7]+4*x[2])
        #print(x[1])
        if C12 == 0:
                rel_soot = 0
        else:
                rel_soot = H2/C12

        soot_line = [C12,H2,rel_soot]
        soot.append(soot_line)
        #print(x[0],x[1],x[2],x[3],x[4],x[5],x[6],x[7],x[8])
        #print(x[0]+2*x[1]+3*x[2]+4*x[3]+5*x[4]+6*x[5]+5*x[6]+6*x[7]+6*x[8],2*x[2]+2*x[
3]+2*x[4]+2*x[5]+4*x[6]+4*x[7]+6*x[8])
        #raw_input("CTRL-C")
```

```
    return [6*k[8]*x[3]*x[3]+2*k[9]*x[3]*x[3]+2*k[10]*x[3]*x[3]+2*k[11]*x[2]*x[4]-
2*k[13]*x[0]*x[0]+6*k[14]*x[5]+6*k[15]*x[7],
                    k[8]*x[3]*x[3]+k[11]*x[2]*x[4]+k[13]*x[0]*x[0]-2*k[12]*x[1]*x[4],
                    -k[11]*x[2]*x[4],
                    -2*k[8]*x[3]*x[3]-2*k[9]*x[3]*x[3]-2*k[10]*x[3]*x[3]+k[12]*x[1]*x[4],
                    4*k[8]*x[3]*x[3]+2*k[9]*x[3]*x[3]-
2*k[12]*x[1]*x[4]+2*k[14]*x[5]+4*k[15]*x[7],
                    k[9]*x[3]*x[3]-k[14]*x[5],
                    0,
                    k[10]*x[3]*x[3]-k[15]*x[7],
                    0]



def lsq_1000(ts,concs):
    #test_var = min(range(len(ts)), key=lambda i: abs(ts[i]-sample_points[2][0]))
    sampling_times = [times[0] for times in sample_points_1000]
    #print(concs)
    test = []
    for i in range(0,len(sampling_times)):
        #print(i,"loop")
        temp = min(enumerate(ts), key=lambda x: abs(x[1]-sampling_times[i]))
        #print(temp[0])
        if temp[1] > sampling_times[i]:
            #print("larger")
            temp_2 = [temp[0]-1,temp[0],temp[1],i]
            #print(temp_2)
        else:
            #print("smaller")
            temp_2 = [temp[0], temp[0]+1, temp[1],i]
            #print(temp_2)
        #test.append(min(enumerate(ts), key=lambda x: abs(x[1]-
sampling_times[i])))
        if i > 0:
            test.append(temp_2)
        #print(test)
        #test_var[i] = min(enumerate(ts), key=lambda x: abs(x[1]-
sampling_times[i]))
    #print(test)
    #print(ts[108],ts[109],sample_points[2][0])
    #print(concs[108][1],concs[108][3],concs[108][5],concs[108][7])
    #print(concs[109][1],concs[109][3],concs[109][5],concs[109][7])
    #normalizing1 = max([species[1] for species in concs])
    #normalizing2 = max([species[3] for species in concs])
    #normalizing3 = max([species[5] for species in concs])
    #normalizing4 = max([species[7] for species in concs])
```

```
	ss_sum = 0

	for time_point in test:

	#print(concs[time_point[0]][0],concs[time_point[0]][1],concs[time_point[0]][2],con
cs[time_point[0]][2],concs[time_point[0]][4])
		#raw_input("CTRL-C")
		sum1 = concs[time_point[0]][0]+(concs[time_point[1]][0]-
concs[time_point[0]][0])*(sample_points_1000[time_point[3]][0]-
ts[time_point[0]])/(ts[time_point[1]]-ts[time_point[0]])
		sum2 = concs[time_point[0]][1]+(concs[time_point[1]][1]-
concs[time_point[0]][1])*(sample_points_1000[time_point[3]][0]-
ts[time_point[0]])/(ts[time_point[1]]-ts[time_point[0]])
		sum3 = concs[time_point[0]][2]+(concs[time_point[1]][2]-
concs[time_point[0]][2])*(sample_points_1000[time_point[3]][0]-
ts[time_point[0]])/(ts[time_point[1]]-ts[time_point[0]])
		sum4 = concs[time_point[0]][3]+(concs[time_point[1]][3]-
concs[time_point[0]][3])*(sample_points_1000[time_point[3]][0]-
ts[time_point[0]])/(ts[time_point[1]]-ts[time_point[0]])
		sum5 = concs[time_point[0]][4]+(concs[time_point[1]][4]-
concs[time_point[0]][4])*(sample_points_1000[time_point[3]][0]-
ts[time_point[0]])/(ts[time_point[1]]-ts[time_point[0]])


		#print(sum3,sample_points_1000[time_point[3]][2])
		#print(sum1,sample_points[time_point[3]][3],normalizing1)
		#normss1 = ((sum1/normalizing1)-
(sample_points[time_point[3]][3]/normalizing1))**2
		#normss2 = ((sum2/normalizing2)-
(sample_points[time_point[3]][1]/normalizing2))**2
		#normss3 = ((sum3/normalizing3)-
(sample_points[time_point[3]][2]/normalizing3))**2
		#normss4 = ((sum4/normalizing4)-
(sample_points[time_point[3]][4]/normalizing4))**2
		ss1 = (sum1-sample_points_1000[time_point[3]][3])**2 #H2
		ss2 = (sum2-sample_points_1000[time_point[3]][5])**2 #CH4
		ss3 = (sum3-sample_points_1000[time_point[3]][1])**2 #C2H4
		ss4 = (sum4-sample_points_1000[time_point[3]][2])**2 #C2H6
		ss5 = (sum5-sample_points_1000[time_point[3]][4])**2 #C4H6
		#print(ss2)

		if ss1 < 1e-12:
			ss1 = 0.0
		if ss2 < 1e-12:
			ss2 = 0.0
		if ss3 < 1e-12:
			ss3 = 0.0
```

```
        if ss4 < 1e-12:
            ss4 = 0.0
        if ss5 < 1e-12:
            ss5 = 0.0

        ss_tot = (ss1+ss2+ss3+ss4+ss5)
        ss_sum = ss_sum + ss_tot

    if sum1 < 0 or sum2 < 0 or sum3 < 0 or sum4 < 0 or sum5 < 0:
        ss_sum = 50000
    #print(normalizing1,normalizing2,normalizing3,normalizing4)
    #sum1 = concs[108][1]+(concs[109][1]-concs[108][1])*(sample_points[2][0]-
ts[108])/(ts[109]-ts[108])
    #sum2 = concs[108][3]+(concs[109][3]-concs[108][3])*(sample_points[2][0]-
ts[108])/(ts[109]-ts[108])
    #sum3 = concs[108][5]+(concs[109][5]-concs[108][5])*(sample_points[2][0]-
ts[108])/(ts[109]-ts[108])
    #sum4 = concs[108][7]+(concs[109][7]-concs[108][7])*(sample_points[2][0]-
ts[108])/(ts[109]-ts[108])
    #print(sum1,sample_points[2][1])
    #ss1 = (sum1-sample_points[2][3])**2
    #ss2 = (sum2-sample_points[2][1])**2
    #ss3 = (sum3-sample_points[2][2])**2
    #ss4 = (sum4-sample_points[2][4])**2
    #print(ss1,ss2,ss3,ss4)
    #normss1 = ((sum1/normalizing1)-(sample_points[2][3]/normalizing1))**2
    #normss2 = ((sum2/normalizing2)-(sample_points[2][1]/normalizing2))**2
    #normss3 = ((sum3/normalizing3)-(sample_points[2][2]/normalizing3))**2
    #normss4 = ((sum4/normalizing4)-(sample_points[2][4]/normalizing4))**2
    #print(normss1,normss2,normss3,normss4)
    #ss_tot = 1000*(normss1+normss2+normss3+normss4)
    #print(ss_sum,"1000")
    return ss_sum

def lsq_700(ts,concs):
    #test_var = min(range(len(ts)), key=lambda i: abs(ts[i]-sample_points[2][0]))
    sampling_times = [times[0] for times in sample_points_700]
    #print(concs)
    test = []
    for i in range(0,len(sampling_times)):
        #print(i,"loop")
        temp = min(enumerate(ts), key=lambda x: abs(x[1]-sampling_times[i]))
        #print(temp[0])
        if temp[1] > sampling_times[i]:
            #print("larger")
            temp_2 = [temp[0]-1,temp[0],temp[1],i]
            #print(temp_2)
```

```
        ELSE:
            #PRINT("SMALLER")
            TEMP_2 = [TEMP[0], TEMP[0]+1, TEMP[1],I]
            #PRINT(TEMP_2)
        #TEST.APPEND(MIN(ENUMERATE(TS), KEY=LAMBDA X: ABS(X[1]-
SAMPLING_TIMES[I])))
        IF I > 0:
            TEST.APPEND(TEMP_2)
        #PRINT(TEST)
        #TEST_VAR[I] = MIN(ENUMERATE(TS), KEY=LAMBDA X: ABS(X[1]-
SAMPLING_TIMES[I]))
    #PRINT(TEST)
    #PRINT(TS[108],TS[109],SAMPLE_POINTS[2][0])
    #PRINT(CONCS[108][1],CONCS[108][3],CONCS[108][5],CONCS[108][7])
    #PRINT(CONCS[109][1],CONCS[109][3],CONCS[109][5],CONCS[109][7])
    NORMALIZING1 = MAX([SPECIES[1] FOR SPECIES IN CONCS])
    NORMALIZING2 = MAX([SPECIES[3] FOR SPECIES IN CONCS])
    NORMALIZING3 = MAX([SPECIES[5] FOR SPECIES IN CONCS])
    NORMALIZING4 = MAX([SPECIES[7] FOR SPECIES IN CONCS])

    SS_SUM = 0

    FOR TIME_POINT IN TEST:
        SUM1 = CONCS[TIME_POINT[0]][1]+(CONCS[TIME_POINT[1]][1]-
CONCS[TIME_POINT[0]][1])*(SAMPLE_POINTS_700[TIME_POINT[3]][0]-
TS[TIME_POINT[0]])/(TS[TIME_POINT[1]]-TS[TIME_POINT[0]])
        SUM2 = CONCS[TIME_POINT[0]][3]+(CONCS[TIME_POINT[1]][3]-
CONCS[TIME_POINT[0]][3])*(SAMPLE_POINTS_700[TIME_POINT[3]][0]-
TS[TIME_POINT[0]])/(TS[TIME_POINT[1]]-TS[TIME_POINT[0]])
        SUM3 = CONCS[TIME_POINT[0]][5]+(CONCS[TIME_POINT[1]][5]-
CONCS[TIME_POINT[0]][5])*(SAMPLE_POINTS_700[TIME_POINT[3]][0]-
TS[TIME_POINT[0]])/(TS[TIME_POINT[1]]-TS[TIME_POINT[0]])
        SUM4 = CONCS[TIME_POINT[0]][7]+(CONCS[TIME_POINT[1]][7]-
CONCS[TIME_POINT[0]][7])*(SAMPLE_POINTS_700[TIME_POINT[3]][0]-
TS[TIME_POINT[0]])/(TS[TIME_POINT[1]]-TS[TIME_POINT[0]])
        SUM5 = CONCS[TIME_POINT[0]][2]+(CONCS[TIME_POINT[1]][2]-
CONCS[TIME_POINT[0]][2])*(SAMPLE_POINTS_700[TIME_POINT[3]][0]-
TS[TIME_POINT[0]])/(TS[TIME_POINT[1]]-TS[TIME_POINT[0]])

        #PRINT(SUM1,SUM2,SUM3,SUM4)
        #PRINT(SUM1,SAMPLE_POINTS[TIME_POINT[3]][3],NORMALIZING1)
        #NORMSS1 = ((SUM1/NORMALIZING1)-
(SAMPLE_POINTS[TIME_POINT[3]][3]/NORMALIZING1))**2
        #NORMSS2 = ((SUM2/NORMALIZING2)-
(SAMPLE_POINTS[TIME_POINT[3]][1]/NORMALIZING2))**2
        #NORMSS3 = ((SUM3/NORMALIZING3)-
(SAMPLE_POINTS[TIME_POINT[3]][2]/NORMALIZING3))**2
```

```
        #normss4 = ((sum4/normalizing4)-
(sample_points[time_point[3]][4]/normalizing4))**2
        ss1 = (sum1-sample_points_700[time_point[3]][3])**2
        ss2 = (sum2-sample_points_700[time_point[3]][1])**2
        ss3 = (sum3-sample_points_700[time_point[3]][2])**2
        ss4 = (sum4-sample_points_700[time_point[3]][4])**2
        ss5 = (sum5-sample_points_700[time_point[3]][5])**2
        #print(normss1,normss2,normss3,normss4)

        if ss1 < 1e-12:
            ss1 = 0.0
        if ss2 < 1e-12:
            ss2 = 0.0
        if ss3 < 1e-12:
            ss3 = 0.0
        if ss4 < 1e-12:
            ss4 = 0.0
        if ss5 < 1e-12:
            ss5 = 0.0

        ss_tot = (ss1+ss2+ss3+ss4+ss5)
        ss_sum = ss_sum + ss_tot

    if sum1 < 0 or sum2 < 0 or sum3 < 0 or sum4 < 0 or sum5 < 0:
        ss_sum = 50000
    #print(normalizing1,normalizing2,normalizing3,normalizing4)
    #sum1 = concs[108][1]+(concs[109][1]-concs[108][1])*(sample_points[2][0]-
ts[108])/(ts[109]-ts[108])
    #sum2 = concs[108][3]+(concs[109][3]-concs[108][3])*(sample_points[2][0]-
ts[108])/(ts[109]-ts[108])
    #sum3 = concs[108][5]+(concs[109][5]-concs[108][5])*(sample_points[2][0]-
ts[108])/(ts[109]-ts[108])
    #sum4 = concs[108][7]+(concs[109][7]-concs[108][7])*(sample_points[2][0]-
ts[108])/(ts[109]-ts[108])
    #print(sum1,sample_points[2][1])
    #ss1 = (sum1-sample_points[2][3])**2
    #ss2 = (sum2-sample_points[2][1])**2
    #ss3 = (sum3-sample_points[2][2])**2
    #ss4 = (sum4-sample_points[2][4])**2
    #print(ss1,ss2,ss3,ss4)
    #normss1 = ((sum1/normalizing1)-(sample_points[2][3]/normalizing1))**2
    #normss2 = ((sum2/normalizing2)-(sample_points[2][1]/normalizing2))**2
    #normss3 = ((sum3/normalizing3)-(sample_points[2][2]/normalizing3))**2
    #normss4 = ((sum4/normalizing4)-(sample_points[2][4]/normalizing4))**2
    #print(normss1,normss2,normss3,normss4)
    #ss_tot = 1000*(normss1+normss2+normss3+normss4)
    #print(ss_sum)
```

```
        #PRINT(SS_SUM,"700")
        RETURN SS_SUM

DEF LSQ_800(TS,CONCS):
        #TEST_VAR = MIN(RANGE(LEN(TS)), KEY=LAMBDA I: ABS(TS[I]-SAMPLE_POINTS[2][0]))
        SAMPLING_TIMES = [TIMES[0] FOR TIMES IN SAMPLE_POINTS]
        #PRINT(CONCS)
        TEST = []
        FOR I IN RANGE(0,LEN(SAMPLING_TIMES)):
                #PRINT(I,"LOOP")
                TEMP = MIN(ENUMERATE(TS), KEY=LAMBDA X: ABS(X[1]-SAMPLING_TIMES[I]))
                #PRINT(TEMP[0])
                IF TEMP[1] > SAMPLING_TIMES[I]:
                        #PRINT("LARGER")
                        TEMP_2 = [TEMP[0]-1,TEMP[0],TEMP[1],I]
                        #PRINT(TEMP_2)
                ELSE:
                        #PRINT("SMALLER")
                        TEMP_2 = [TEMP[0], TEMP[0]+1, TEMP[1],I]
                        #PRINT(TEMP_2)
                #TEST.APPEND(MIN(ENUMERATE(TS), KEY=LAMBDA X: ABS(X[1]-
SAMPLING_TIMES[I])))
                IF I > 0:
                        TEST.APPEND(TEMP_2)
                #PRINT(TEST)
                #TEST_VAR[I] = MIN(ENUMERATE(TS), KEY=LAMBDA X: ABS(X[1]-
SAMPLING_TIMES[I]))
        #PRINT(TEST)
        #PRINT(TS[108],TS[109],SAMPLE_POINTS[2][0])
        #PRINT(CONCS[108][1],CONCS[108][3],CONCS[108][5],CONCS[108][7])
        #PRINT(CONCS[109][1],CONCS[109][3],CONCS[109][5],CONCS[109][7])
        NORMALIZING1 = MAX([SPECIES[1] FOR SPECIES IN CONCS])
        NORMALIZING2 = MAX([SPECIES[3] FOR SPECIES IN CONCS])
        NORMALIZING3 = MAX([SPECIES[5] FOR SPECIES IN CONCS])
        NORMALIZING4 = MAX([SPECIES[7] FOR SPECIES IN CONCS])

        SS_SUM = 0

        FOR TIME_POINT IN TEST:
                SUM1 = CONCS[TIME_POINT[0]][1]+(CONCS[TIME_POINT[1]][1]-
CONCS[TIME_POINT[0]][1])*(SAMPLE_POINTS[TIME_POINT[3]][0]-
TS[TIME_POINT[0]])/(TS[TIME_POINT[1]]-TS[TIME_POINT[0]])
                SUM2 = CONCS[TIME_POINT[0]][3]+(CONCS[TIME_POINT[1]][3]-
CONCS[TIME_POINT[0]][3])*(SAMPLE_POINTS[TIME_POINT[3]][0]-
TS[TIME_POINT[0]])/(TS[TIME_POINT[1]]-TS[TIME_POINT[0]])
```

```
        sum3 = concs[time_point[0]][5]+(concs[time_point[1]][5]-
concs[time_point[0]][5])*(sample_points[time_point[3]][0]-
ts[time_point[0]])/(ts[time_point[1]]-ts[time_point[0]])
        sum4 = concs[time_point[0]][7]+(concs[time_point[1]][7]-
concs[time_point[0]][7])*(sample_points[time_point[3]][0]-
ts[time_point[0]])/(ts[time_point[1]]-ts[time_point[0]])
        sum5 = concs[time_point[0]][2]+(concs[time_point[1]][2]-
concs[time_point[0]][2])*(sample_points[time_point[3]][0]-
ts[time_point[0]])/(ts[time_point[1]]-ts[time_point[0]])
        #print(sum1,sum2,sum3,sum4)
        #print(sum1,sample_points[time_point[3]][3],normalizing1)
        #normss1 = ((sum1/normalizing1)-
(sample_points[time_point[3]][3]/normalizing1))**2
        #normss2 = ((sum2/normalizing2)-
(sample_points[time_point[3]][1]/normalizing2))**2
        #normss3 = ((sum3/normalizing3)-
(sample_points[time_point[3]][2]/normalizing3))**2
        #normss4 = ((sum4/normalizing4)-
(sample_points[time_point[3]][4]/normalizing4))**2
        ss1 = (sum1-sample_points[time_point[3]][3])**2
        ss2 = (sum2-sample_points[time_point[3]][1])**2
        ss3 = (sum3-sample_points[time_point[3]][2])**2
        ss4 = (sum4-sample_points[time_point[3]][4])**2
        ss5 = (sum5-sample_points[time_point[3]][5])**2
        #print(normss1,normss2,normss3,normss4)

        if ss1 < 1e-12:
            ss1 = 0.0
        if ss2 < 1e-12:
            ss2 = 0.0
        if ss3 < 1e-12:
            ss3 = 0.0
        if ss4 < 1e-12:
            ss4 = 0.0
        if ss5 < 1e-12:
            ss5 = 0.0

        ss_tot = (ss1+ss2+ss3+ss4+ss5)
        ss_sum = ss_sum + ss_tot

    if sum1 < 0 or sum2 < 0 or sum3 < 0 or sum4 < 0 or sum5 < 0:
        ss_sum = 50000
    #print(normalizing1,normalizing2,normalizing3,normalizing4)
    #sum1 = concs[108][1]+(concs[109][1]-concs[108][1])*(sample_points[2][0]-
ts[108])/(ts[109]-ts[108])
    #sum2 = concs[108][3]+(concs[109][3]-concs[108][3])*(sample_points[2][0]-
ts[108])/(ts[109]-ts[108])
```

```
        #SUM3 = CONCS[108][5]+(CONCS[109][5]-CONCS[108][5])*(SAMPLE_POINTS[2][0]-
TS[108])/(TS[109]-TS[108])
        #SUM4 = CONCS[108][7]+(CONCS[109][7]-CONCS[108][7])*(SAMPLE_POINTS[2][0]-
TS[108])/(TS[109]-TS[108])
        #PRINT(SUM1,SAMPLE_POINTS[2][1])
        #SS1 = (SUM1-SAMPLE_POINTS[2][3])**2
        #SS2 = (SUM2-SAMPLE_POINTS[2][1])**2
        #SS3 = (SUM3-SAMPLE_POINTS[2][2])**2
        #SS4 = (SUM4-SAMPLE_POINTS[2][4])**2
        #PRINT(SS1,SS2,SS3,SS4)
        #NORMSS1 = ((SUM1/NORMALIZING1)-(SAMPLE_POINTS[2][3]/NORMALIZING1))**2
        #NORMSS2 = ((SUM2/NORMALIZING2)-(SAMPLE_POINTS[2][1]/NORMALIZING2))**2
        #NORMSS3 = ((SUM3/NORMALIZING3)-(SAMPLE_POINTS[2][2]/NORMALIZING3))**2
        #NORMSS4 = ((SUM4/NORMALIZING4)-(SAMPLE_POINTS[2][4]/NORMALIZING4))**2
        #PRINT(NORMSS1,NORMSS2,NORMSS3,NORMSS4)
        #SS_TOT = 1000*(NORMSS1+NORMSS2+NORMSS3+NORMSS4)
        #PRINT(SS_SUM,"800")
        RETURN SS_SUM

DEF EVAL_ODE(COEFFICIENTS):
        GLOBAL BEST
        #SOOT = [0.0,0.0]
        #SOOT[2] = SOOT[0]+SOOT[1]
        #K = COEFFICIENTS
        LOWER = [0.12383158860828203, 0.0082889278632296056, 0.064548634394218415,
96.546963522128578, 752.48863740816182, 0.00076575280707778272,
0.0012263260030934081, 0.037061857125076647]
        K = [1]*8
        KS = [0.001,
                        0.005,
                        0.9,
                        0.4,
                        0.001,
                        150.0,
                        0.1,
                        2.5]

        #KPRIME =[0.11328835771394888, 0.33263377629458646, 1.1640089079868086,
2.0667372877095214, 0.41012816741839597, 0.10000000000000001]

        #K[0] = 0.0001
        #K[1] = 0.00050000000000000001
        #K[2] = 3.7331083789351216
        #K[3] = KS[3]*COEFFICIENTS[0]
        #K[4] = 0.10000000000000001
        #K[5] = KS[5]*COEFFICIENTS[1]
        #K[6] = 0.012967137223098181
```

```
    #k[7] = 0.77350066708682985
    for line in range(0,len(ks)):
        k[line] = coefficients[line]*ks[line]
        #k[line] = kprime[line]*ks[line]
    #k[5] = k[5] * coefficients[0]


    fitness_800 = 10000
    fitness_700 = 10000
    fitness_1000 = 10000
    #raw_input("enter")
    #deriv = -2*k[0]*y[0]*y[0]-k[1]*y[0]*y[1]-k[2]*y[0]*y[4]-k[3]*y[0]*y[4],
k[0]*y[0]*y[0]+k[2]*y[0]*y[4]-k[1]*y[0]*y[1]-k[4]*y[1]*y[3], k[0]*y[0]*y[0]-
k[5]*y[6]*y[2]+k[3]*y[0]*y[4], k[1]*y[0]*y[1]-k[4]*y[1]*y[3],
k[1]*y[0]*y[1]+k[5]*y[6]*y[2]-k[2]*y[0]*y[4]-k[3]*y[0]*y[4], k[4]*y[1]*y[3],
k[2]*y[0]*y[4]-k[5]*y[6]*y[2], k[5]*y[6]*y[2]]
    start=0
    end=2.2
    numsteps=10000
    times=linspace(start,end,numsteps)
    y0=array([0.0,10.2,2.02,0.0,0.0,0.0,0.0])
    #try:
    k = [1.2258349879616048, 7.3573498930818539, 0.5655378938692821,
0.24190720312068753, 0.072096923193689905, 9.0958851170494324, 16.791712803451617,
0.2903035978514783, 8.5373138448440482, 9.533406414781723, 0.26863078207250535]
    x0 = (k[0],k[1],k[2],k[3],k[4],k[5],k[6],k[7],k[8],k[9],k[10])

    result_1000,output_1000 = integrate.odeint(deriv,y0,times, args=(k,),
mxstep=5000, full_output = 1)
    big_question_1000 = output_1000['message']

    if big_question_1000 == 'Integration successful.':
        fitness_1000 = lsq_1000(times,result_1000)
    opt_value = [0.0]*8
    total_fitness = fitness_1000
    bounds =
[(0.1*k[0],10.0*k[0]),(0.1*k[1],10.0*k[1]),(0.1*k[2],10.0*k[2]),(0.1*k[3],10.0*k[3]),(0.1*k[4],1
0.0*k[4]),(0.1*k[5],10.0*k[5]),(0.1*k[6],10.0*k[6]),(0.1*k[7],10.0*k[7])]
    if total_fitness < best:
        #print("FMIN")
        sol = optimize.fmin(func,x0,maxfun = 500000, maxiter = 500000 )
        #print(sol)
        #best = sol[1]
        #print(best,"after BFGS")
        opt_value = str(sol[1]) + str(sol[0]) + " \n"
        #total_fitness = sol[1]
        f = open("optim.txt","a")
```

```
                F.WRITE(OPT_VALUE)
                F.CLOSE()

        #RESULT_700,OUTPUT_700 = INTEGRATE.ODEINT(DERIV,Y0,TIMES, MXSTEP=5000,
FULL_OUTPUT = 1)
        #BIG_QUESTION_700 = OUTPUT_700['MESSAGE']

        #IF BIG_QUESTION_700 == 'INTEGRATION SUCCESSFUL.':
        #       FITNESS_700 = LSQ_700(TIMES,RESULT_700)

        #RESULT_800,OUTPUT_800=INTEGRATE.ODEINT(DERIV,Y0,TIMES, MXSTEP=5000,
FULL_OUTPUT = 1)
        #BIG_QUESTION_800 = OUTPUT_800['MESSAGE']

        #IF BIG_QUESTION_800 == 'INTEGRATION SUCCESSFUL.':
        #       FITNESS_800 = LSQ_800(TIMES,RESULT_800)
        #ELSE:
        #       PASS
        #EXCEPT EXCEPTION:
        #       PRINT("FAILED")
        #RAW_INPUT("CTRL-C")
         #FITNESS_1000 #+ FITNESS_700 + FITNESS_800
        #PRINT(K[0],K[7])

        #FOR LOOP IN RANGE(0,):
        #       IF K[LOOP]<LOWER[LOOP]:
        #               TOTAL_FITNESS = 100000
        #               PRINT(LOOP)

        PRINT(TOTAL_FITNESS)

        RETURN TOTAL_FITNESS


SAMPLE_POINTS = [[0,2.02,0,0,0,10.2],
                                        [0.0211,1.9968,0,0,0,10.007],
                                        [0.0238,1.9885,0,0,0,10.078],
                                        [0.0319,1.9768,0,0,0,9.7744],
                                        [0.0383,1.9768,0,0,0,9.7563],
                                        [0.0503,1.9355,0,0,0.00354,9.5978],
                                        [0.0616,2.0351,0,0,0.00681,9.0885],
                                        [0.1183,1.9791,0,0,0.02445,9.126],
                                        [0.2317,1.7245,0.00742,0.11565,0.04053,8.0976],
                                        [0.4099,1.5839,0.01273,0.34817,0.11791,8.101],
                                        [0.815,1.3282,0.01757,0.76986,0.13657,8.3721],
                                        [1.625,0.94035,0.01222,1.1069,0.0908,6.1623]]
```

```
sample_points_700 =          [[0.0,2.02,0.0,0.0,0.0,10.2],
                              [0.02,1.941,0.0,0.0,0.0,9.6696],
                              [0.023,1.9809,0.0,0.0,0.0,9.8734],
                              [0.0319,2.0085,0.0,0.0,0.0,9.9297],
                              [0.0389,2.0176,0.0,0.0,0.0,9.9424],
                              [0.0521,2.0265,0.0,0.0,0.0,9.9556],
                              [0.0646,1.8057,0.0,0.0,0.00224,9.8341],
                              [0.0854,2.0209,0.0,0.0,0.00375,10.054],
                              [0.127,1.9968,0.0,0.0,0.00709,10.129],
                              [0.2517,1.8823,0.00153,0.0,0.01676,9.4775],
                              [0.4477,1.8499,0.00216,0.00438,0.03512,9.2688],
                              [0.88874515,1.7663,0.00619,0.10863,0.02562,8.875],
                              [1.7843,1.4695,0.011,0.20582,0.02019,8.434]]


sample_points_1000 = [[0.0,2.02,0.0,0.0,0.0,10.2],
                              [0.0209,1.6933,0.00232,0.0,0.00292,9.5231],
                              [0.0232,1.639,0.00401,0.06851,0.00402,9.3432],
                              [0.03,1.7266,0.01309,0.23804,0.04949,9.3384],
                              [0.0354,1.528,0.02659,0.59076,0.10173,9.4216],
                              [0.0456,1.2657,0.03221,1.2582,0.14623,9.4185],
                              [0.0552,0.94797,0.02967,1.9695,0.1289,8.7469],
                              [0.0712,0.78873,0.02588,2.2974,0.11345,8.4992],
                              [0.1991,0.30803,0.0243,5.4354,0.03927,6.7635],
                              [0.3499,0.1772,0.0049,7.8337,0.02031,5.8438],
                              [0.6926,0.13798,0.00296,8.9574,0.01153,4.8415],
                              [1.3781,0.09141,0.00172,9.831,0.00691,3.2477]]


#pars = [2.0, 3.0, 4.0, 5.0, 6.0, 7.0,]
#ethene = [point[1] for point in sample_points]
#print(ethene)
#setOfAlleles = GAllele.GAlleles()
#for i in range(0,8):
#       if i == 2 or i == 5:
#               a = GAllele.GAlleleRange(0.05,5.0,real=True)
#       elif i == 4:
#               a = GAllele.GAlleleRange(0.5,50.0,real=True)
#       else:
#               a = GAllele.GAlleleRange(0.1,10.0,real=True)
best = 1500
genome = G1DList.G1DList(11)
```

```
genome.evaluator.set(eval_ode)
genome.setParams(rangemin=0.1, rangemax=10.0)
#genome.setParams(allele=setOfAlleles)
genome.mutator.set(Mutators.G1DListMutatorRealGaussian)
genome.initializator.set(Initializators.G1DListInitializatorReal)


ga = GSimpleGA.GSimpleGA(genome)

#ga.nGenerations = 2
ga.setMinimax(Consts.minimaxType["minimize"])
ga.selector.set(Selectors.GRouletteWheel)
ga.setGenerations(10)
ga.setCrossoverRate(0.7)
ga.setPopulationSize(5)
ga.setMutationRate(0.3)

sqlite_adapter = DBAdapters.DBSQLite(identify="ex2")
ga.setDBAdapter(sqlite_adapter)
#print(pop)
        #print(ga)


#pop.scaleMethod.set(Scaling.LinearScaling)


#ga.step()
#raw_input("enter")
ga.evolve(2)
print(ga.bestIndividual())

#winner = ga.bestIndividual()
#print(winner)
```

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