DETAILED KINETICS OF THE PYROLYSIS AND OXIDATION OF ANISOLE

Emma Barker Hemings, Giulia Bozzano, Mario Dente, Eliseo Ranzi[*]

Department of Chemistry, Materials and Chemical Engineering,
Politecnico di Milano, P.zza Leonardo da Vinci 32, 20133 Milano (Italy)
[*]eliseo.ranzi@polimi.it

Thermal conversion of biomass to produce bio-fuels represents a promising opportunity in the field of alternative energy sources. Typical thermal processes are pyrolysis, gasification and combustion, in which the original biomass undergoes decomposition to char, gaseous and tar products. The detailed product distribution is strongly dependent on the feedstock and the operating conditions, namely temperature, pressure and contact time. The understanding of the reaction mechanism is crucial in the design and optimization of large-scale units for biomass treatment. In this framework, this paper aims at proposing a comprehensive and detailed kinetic model for the pyrolysis and oxidation of anisole. This component is generally acknowledged as a model compound for the lignin fraction of biomass, and could therefore offer a starting point for the modeling of similar substituted aromatics. The reaction mechanism is centered around the formation and reaction of the stable and highly resonant phenoxy radical. Particularly, its recombinations with methyl and hydrogen radicals are relevant in the formation of cresols and phenol, that constitute important intermediates. Moreover, the decomposition to CO and cyclopentadienyl, successive reactions to form cyclopentadiene and methyl-cyclopentadiene play an important role contributing to PAH formation. The model predictions are compared to a wide range set of experimental data. This kinetic study clearly confirms not only the importance of phenol and cresols but mainly the role of resonantly stabilized radicals such as benzyl and phenoxyl radicals. This issue is indeed crucial in the pyrolysis and oxidation of aromatic species and it requires further modeling studies and experimental investigation.

1. INTRODUCTION AND MOTIVATION OF THE WORK

Recent reports indicate that the current world energy demand reaches 32 quadrillion BTU, and projections up to 2035 indicate a generalized trend of growth in energy consumption. In this scenario, liquid fuels are of great interest as they can represent an easy-to-transport and store source of energy. Particularly, bio-fuels are expected to gain significant relevance in the upcoming future, eventually accounting for 80 percent of the growth in liquid fuel consumption. This fact goes with the decline of fossil fuels, mainly related to the increase in oil prices, the limited availability and the concerns on environmental sustainability (Demirbas, 2007). In addition, diversification and decentralization of energy supplies for energy self-sufficiency is envisaged as a strategic goal (Naik et al., 2010).

Biomass can represent a valid alternative source of energy, due to its availability (Anon, 2004), no net CO_2 emissions and lower NO_x and SO_x emissions. The term "biomass" is largely comprehensive, and generally used to identify all types of organic matter. In terms of major components, biomass is composed of a mixture of cellulose, hemicellulose and lignin (Zhang et al., 2010), together with extractives, inorganic constituents (ashes) and water. The effective exploitation of biomass potential, mainly through thermal processes of either pyrolysis, combustion or gasification, has seen several promising attempts, still these solutions are suitable of further improvement and optimization. Particularly, the physical and chemical transformations occurring in biomass processing need a fundamental and detailed understanding (U.S. Department of Energy, 2007), in order to develop large scale processes and define optimal operating conditions (Bridgewater et al., 1999).

Chemical kinetics, coupled with transport phenomena, are determinant to characterize the extent of primary and secondary decomposition of the feedstock. Several models of both are reported in literature, and extensively

revised by Di Blasi (2008). Decomposition rates are generally well predicted by most, but comprehensive models that offer a detailed product distribution are not available to our knowledge. This deficiency is pointed out by Moghtaderi (2006), with the indication that further investigation in kinetic modeling of biomass conversion would be beneficial.

In this perspective, the paper aims at the presentation of a comprehensive kinetic modeling of the pyrolysis and oxidation of anisole, which is considered a model compound for the components released by the lignin fraction. Details on the overall kinetic model which has been used in the present work have been extensively reported elsewhere (Ranzi et al., 2008; Calonaci et al., 2010).

The modeling approach basically goes through the identification of anisole as model compound of lignin, and the study of its reactivity. The choice of anisole was made upon the consideration of lignin structure (Hurff and Klein, 1983; Freudenberg and Neish, 1968; Klein and Virk, 2008). Lignin is an aromatic-based polymer, in which aromatic units possess a set of propanoid and methoxy-phenol substituents. In this light, anisole is the first aromatic component with the methoxy group. The relative simplicity of the molecule allows for the development of manageable kinetic schemes. It is generally acknowledged that the reactivity of lignin is mainly due to the substituents, the aromatic rings being relatively inert. The reactivity of each substituent can also be considered as relatively independent from the others. Confirmation of this approach can be found in works on the kinetic modelling of hydrocarbon pyrolysis (Dente et al., 1979; Campbell et al., 2009).

The systematic hierarchical modularity of detailed kinetic schemes first suggests that the comprehensive sub-model of anisole can be coupled with a more general kinetic scheme of pyrolysis and oxidation of hydrocarbon fuels. Secondly, this kinetic sub-model can be considered as a first step towards the kinetic description of similar, and eventually more substituted compounds. This approach is useful in the effective development of large reaction networks that account for the entire slate of products deriving from biomass decomposition. Besides, this kinetic study of anisole pyrolysis and oxidation highlighted the relevant role of other compounds, such as phenol and cresol. These components require a detailed kinetic study, as they represent important intermediates necessary to account for the product distribution arising from anisole thermal processing. The investigation of the reactivity of other substituted aromatics therefore represents an interesting extension of the present study.

2. KINETIC MECHANISM OF PYROLYSIS AND OXIDATION OF ANISOLE

Both from an experimental and a theoretical point of view, many kinetic studies of pyrolysis and oxidation of anisole discuss the different reaction paths as well as the open issues relating this reaction system. Table 1 summarizes the relevant reactions of anisole pyrolysis and oxidation. As already mentioned and accordingly to the recognized hierarchical modularity (Westbrook and Dryer, 1984), this reaction subset has been directly coupled with a more general and validated kinetic scheme of pyrolysis and oxidation of hydrocarbons (Ranzi et al., 2008; Ranzi et al., 2001), very recently extended also to alcohol fuels (Frassoldati et al., 2010; Grana et al., 2010). While the overall kinetic scheme is available on the web (http://creckmodeling.chem.polimi.it/), Table 1 reports, together with anisole reactions, also the relevant reactions of phenol and cresol, due to their important impact on this reaction system. Note that in order to avoid an excessive number of reactions, recombination reactions of resonantly stabilized radicals are not reported.

It is generally agreed that anisole decomposition is initiated through the thermal homolysis of the relatively weak C-O bond in the methoxy group, according to the following reaction:

$$C_6H_5OCH_3 \rightarrow C_6H_5O + CH_3 \qquad (1)$$

Colussi et al. (1977), as well as Suryan et al. (1989), already observed that the fission of the C-O bond accounts for the extensive conversion of anisole. This reaction is thermodynamically favoured because of the formation of the resonantly stabilized phenoxy radical C_6H_5O. The resonance energy for phenoxy radical is estimated to be

17.5 kcal/mol. Following previous discussions (Mackie at al., 1989; Pecullan et al., 1997), it is relevant to observe that the unpaired electron of the phenoxy radical is indeed also associated with the C atoms in the ring:
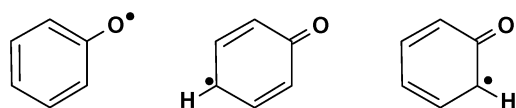

Fig. 1: Resonant structures of the phenoxy radical. .

The reactivity of the phenoxy radical plays a crucial role in anisol pyrolysis and oxidation. This radical can follow three prevailing reaction pathways with the formation of cresol, phenol and cyclopentadienyl radical. The radical recombination reaction with CH_3 to form o- and p-cresols (through a cyclohexadienyl intermediate), the H-recombination to form phenol and the decomposition to cyclopentadienyl radical and CO are the three main reaction paths of phenoxy radical.

The methyl radical can either go through H-abstraction reactions to form methane, or recombine with cyclopentadienyl radicals to form methylcyclopentadiene, or eventually recombine with another CH_3 radical to form ethane. The phenoxy radical can also react to form benzofuran and dibenzofuran through different recombination and condensation reactions. Cyclopentadienyl radicals further contribute to the formation of polycyclic aromatic species (PAHs).

The reactivity of phenoxy radical is a crucial issue in the anisole system and investigation on its decomposition to cyclopentadienyl radical and CO is extensively reported in literature (Lin and Lin, 1985; Lin and Lin, 1986). A simplified kinetic model, including four major reactions, was proposed to account for the product distribution. The decomposition of phenoxy radical shows low values for the collision factor A in the Arrhenius expression. This might account for a very tight transition state, going through a bicyclic (5C- and 3C-ring) intermediate. A confirmation of this tight structure for the transition state is given in recent works using ab-initio calculations (Olivella ey al., 1995; Xu and Lin, 2006).

Table 1: Relevant reactions in pyrolysis and combustion of anisole.

	Reactions	A [s^{-1}]	Eact [cal/mol]
1	$C_6H_5OCH_3 \rightarrow C_6H_5O+CH_3$	3.00E+15	63000
2	$CH_3+C_6H_5O \rightarrow CH_3C_6H_4OH$	4.00E+09	0
3	$H+C_6H_5OCH_3 \rightarrow C_6H_6+CH_3O$	1.00E+09	8000
4	$H+C_6H_5OCH_3 \rightarrow C_6H_5OH+CH_3$	1.00E+10	6000
5	$H+C_6H_5OCH_3 \rightarrow H+CH_3C_6H_4OH$	1.00E+09	5000
6	$OH+C_6H_5OCH_3 \rightarrow C_6H_5OH+CH_3O$	1.00E+09	0
7	$H+C_6H_5OCH_3 \rightarrow H_2+C_6H_5OCH_2$	7.10E+10	10500
8	$CH_3+C_6H_5OCH_3 \rightarrow CH_4+C_6H_5OCH_2$	1.20E+09	11500
9	$OH+C_6H_5OCH_3 \rightarrow H_2O+C_6H_5OCH_2$	1.20E+10	3500
10	$HO_2+C_6H_5OCH_3 \rightarrow H_2O_2+C_6H_5OCH_2$	1.60E+09	19000
11	$O_2+C_6H_5OCH_3 \rightarrow HO_2+C_6H_5OCH_2$	5.00E+10	49000
12	$H+C_6H_5O \rightarrow C_6H_5OH$	6.00E+11	0
13	$C_6H_5O \rightarrow$ cyclic-C_5H_5+CO	5.00E+11	43920
14	$H+C_6H_5O \rightarrow$ cyclic-C_5H_6+CO	1.50E+11	0

The kinetic mechanism developed to describe the thermal decomposition of anisole is tested against three independent sets of experimental data available in literature. Particularly, the model is validated in a wide range of operating conditions, which are described in the following.

3. COMPARISON BETWEEN MODEL PREDICTIONS AND EXPERIMENTAL DATA

3.1 Pyrolysis and oxidation of anisole in a plug-flow reactor

The comprehensive reaction mechanism of anisole, with the relevant intermediate of the phenoxy radical, is well described by the flux analysis schematically reported in Fig. 2. This analysis refers to the results of the pyrolysis experiments conducted in the Princeton atmospheric pressure flow reactor reported by Pecullan et al. (1997). This experimental and theoretical work discuss and support the above reaction mechanism on the basis of different experimental measurements at about 1000 K, in pyrolysis and oxidation conditions (Φ=1.7, Φ=1 and Φ=0.6). The authors also propose a detailed kinetic model for the anisole sub-system, containing 66 reversible reactions involving 31 species. This work was a very useful starting point for the sub-mechanism reported in Table 1. The cited paper (Pecullan et al., 1997) also highlights the role of cyclopentadiene, methyl-cyclopentadiene and cyclopentadienyl radicals to form PAHs and benzene.
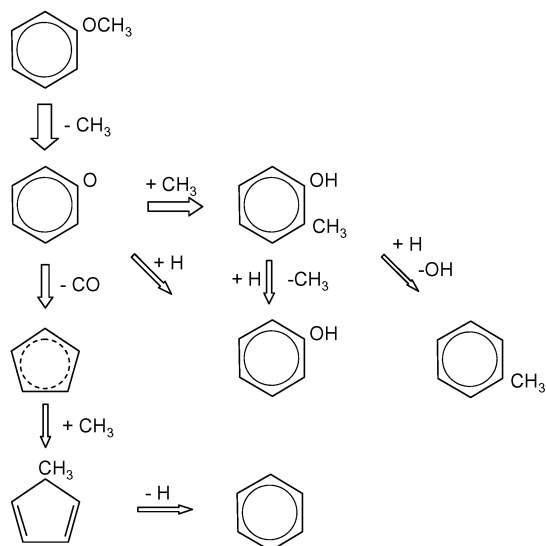

Fig. 2: Reaction flux analysis for the pyrolysis of anisole at T =1000K, contact time = 20ms, conversion =60%. Arrow thickness stands for the relative importance of different reaction paths.

Fig. 3 shows a comparisons between experimental measurements (Pecullan et al., 1997) and model predictions both in pyrolysis and oxidation conditions. Note that, following usual practice employed for comparison with flow reactor data (Frassoldati et al., 2010), predicted profiles are shifted of roughly 10-15 ms in order to match the fuel conversion. This approach and similar corrections, due to non-ideal reactant mixing and/or catalytic effects, were discussed and verified both numerically and experimentally in the literature (Zhao et al., 2008). Both experiments and model predictions confirm that anisole decomposition is not extensively influenced by the presence of oxygen in these operating conditions. Methylcyclopentadiene predictions well agree with experimental measurements, while the successive benzene formation seems underestimated. CO and cyclopentadiene yields are in good agreement with the experimental measurements, thus suggesting that the kinetics of the phenoxy radical decomposition is treated with good accuracy.

While the general agreement is to some extent satisfactory, two major deviations need to be highlighted. The first one refers to the yields of cresol and phenol. Phenol is notably underestimated, in a similar way cresol consumption is underestimated, even if an high rate value is assumed for the substitutive addition reaction of H to cresol, with subsequent demethylation and phenol formation:

$$H + CH_3C_6H_4OH \rightarrow CH_3 + C_6H_5OH \tag{2}$$

Fig. 3 shows a comparison of experimental data and model prediction for both phenol and cresol yields. The model results cannot be considered satisfactory at the moment, and indicate that a deeper insight in the reactivity of phenol and cresol is necessary. Particularly, reaction paths that lead to a rapid and primary formation of phenol might be envisaged, as indicated by the tight slope of the phenol experimental curve. Conversely, cresol yield is correctly predicted at short residence times, but the excess of cresol which is evident at high residence times suggests that secondary decomposition reaction should be revised in order to increase cresol reactivity. Unfortunately, there is a lack of reliable experimental information regarding cresol pyrolysis, to our knowledge. A similar limited agreement with the experimental data was also observed by Pecullan et al. (1997): low phenol yields, together with the overestimation of cresol. A possible explanation for the higher than predicted yield of phenol was seen in the presence of condensed carbonaceous species absorbed on the reactor wall, which could act as a source of hydrogen. This way, phenol formation from recombination of phenoxy and hydrogen radicals would be enhanced. The authors also searched, with poor success, for exotic reaction pathways to form phenol, such as a unimolecular elimination of the methylene singlet from anisole or the recombination of phenoxy radicals with subsequent consumption of the dimer, without appreciable results.
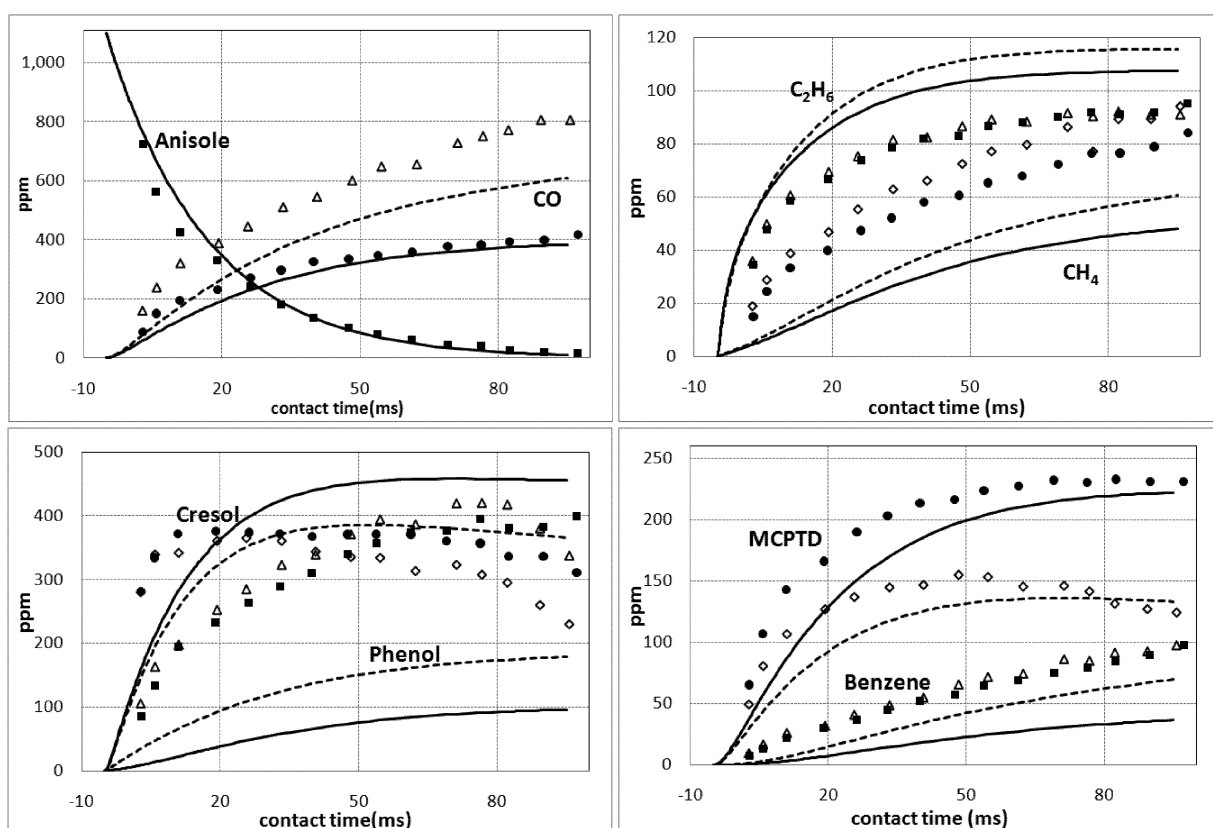

Fig. 2: Comparison between experimental measurements(Pecullan et al., 1997) and model predictions. Pyrolysis: solid lines and symbols; oxidation, $\Phi=0.62$: dashed lines and empty symbols.

A second point relates to the underestimation of methane, as shown in Fig. 3. Primary methyl radicals is mainly formed by the initial anisole decomposition (1). Ethane formation is solely due to methyl radicals recombination and the slight ethane overestimation seems to indicate a corresponding over-estimation of methyl radical. On the

contrary, the underestimation of methane, obtained by H abstraction reactions of methyl radical, suggests an insufficient formation of methyl radical. Very similar deviations were also observed and discussed by Pecullan et al. (1997).

3.2 Hydrogenolysis of anisole

The H abstraction reactions on anisole to form the reactive anisyl radical ($C_6H_5OCH_2$) are of negligible importance in the operating conditions of the Princeton flow reactor. Rearrangement and dehydrogenation reactions of anisyl radical form benzaldehyde: $C_6H_5OCH_2 \rightarrow H + C_6H_5CHO$. Mulcahy et al. (1967) investigated CH_3 reactions with anisole, confirming the high reactivity of the anisyl radical. Benzaldehyde and methane are found to be the major products, suggesting that the reaction goes through the above mentioned steps. CH_3 addition on anisyl, or on the aromatic ring are of very limited importance. Arends et al. (1993), studied the gas-phase thermal decomposition of anisole diluted in a 10-fold excess of hydrogen at atmospheric pressure in a tubular flow reactor over the temperature range 793-1020 K. Due to the large excess of H_2, and the high H radical concentration, the role of H abstraction reactions on anisole and successive reaction of anisyl radical becomes more evident. The formation of phenol, both from phenoxy radical recombination with H radicals and from H-abstraction of phenoxy radical on H_2, are also enhanced. Another relevant reaction path is the addition of H atoms on anisole: $H+ C_6H_5OCH_3 \rightarrow CH_3 + C_6H_5OH$.

Fig. 4 shows the reaction flux analysis in these conditions. Cresol and cyclopentadiene reaction paths become of limited importance, while H abstraction with anisyl radical and benzaldehyde formation account for ~20-30% of anisole decomposition.
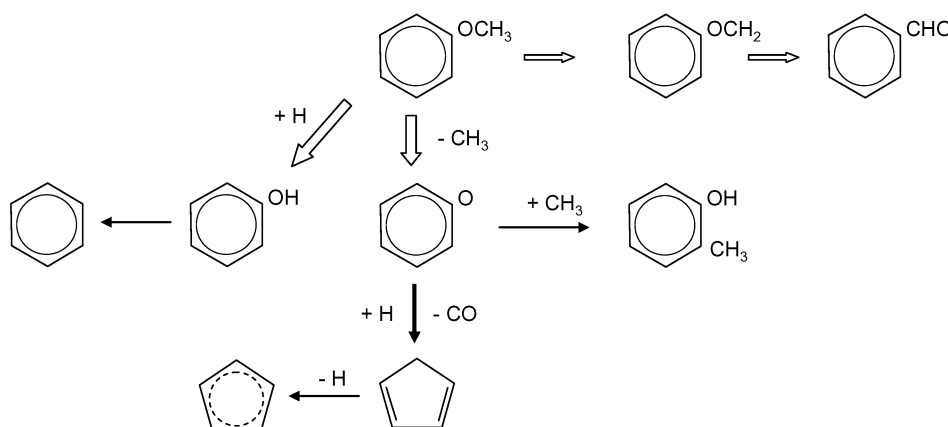

Fig. 4: Reaction flux analysis at T = 813K, contact time = 3.5s, conversion = 30%.Arrow thickness stands for the relative importance of different reaction paths.

Table 2 shows the comparison between predicted and measured selectivities of major products, both for the low and the high temperature regions reported (Arends et al., 1993).

A general agreement is found and the model seems to accurately predict the product distribution under these operating conditions. The major product gases ae CO and CH_4, which are correctly predicted by the model. Yields of phenol and cresol are satisfactory and the high concentration of H radical in the system accounts for the high production of phenol, either by addition on the aromatic ring, or radical recombination.

Table 2: Hydrogenolysis of anisole. Comparison between model predictions and experimental selectivities of major species (Arends et al., 1993).

	813K		873K		1007K	
	exp	mod	exp	mod	exp	mod
CO	22.21	17.25	34.4	22.78	27.7	19.47
CH4	70.44	70.1	87	84.05	76.3	79.6
Phenol	63.72	63.97	60.4	67.27	56.26	64.18
Cresol	16.32	3.74	1.1	0.62	8.8	5.74
Benzaldehyde	11.93	10.27	4.1	2.63	5.36	5.78
Benzene	16.32	16.67	17.3	17.73	9.8	4.4
Cyclopentadiene	0.35	2.91	5	7.46	9.9	13.36
Me-cyclopentadiene	nc	0.21	nc	0.11	3.18	1.64
Naphtalene	nc	0.16	0.3	1.38	0.09	0.18
Dibenzofuran	0.48	0.55	0.8	0.31	0.65	1.09

3.3 Pyrolysis of anisole at high severity

An experimental study of the pyrolysis of anisole has been reported by Platonov et al. (2001). These data refer to the pyrolysis of anisole in conditions of high severity, i.e. T=1023-1173 K and contact times up to 4.5 s. This work reports a large detail of PAH and tar components in the product stream; the distribution of oxygen in different functional groups is also underlined. The severe pyrolysis conditions of these experiments allow to better analyse the role of successive reactions of resonantly stabilized radicals such as phenoxy and benzyl like radicals.

Fig. 5 shows the predicted yields of relevant intermediates versus contact time at temperatures of 1073 and 1173 K. Anisole decompose in few milliseconds at these temperatures. Successive reactions of o- and p-cresol and phenol become of crucial interest in describing the evolution of this reacting system. Cresol is the first intermediate at these temperatures. At 1073 K it decomposes with large phenol and benzene formation. At higher temperatures, not only cresol, but also phenol is largely decomposed with the successive formation of naphthalene, PAH and soot precursors.

Fig. 5 also shows a comparison between experimental measurements and model predictions of major gas components. Pyrographite and gas products increase by increasing the severity of the thermal process, i.e. by increasing temperature or contact time. Conversely, there is a clear decrease in tar components.
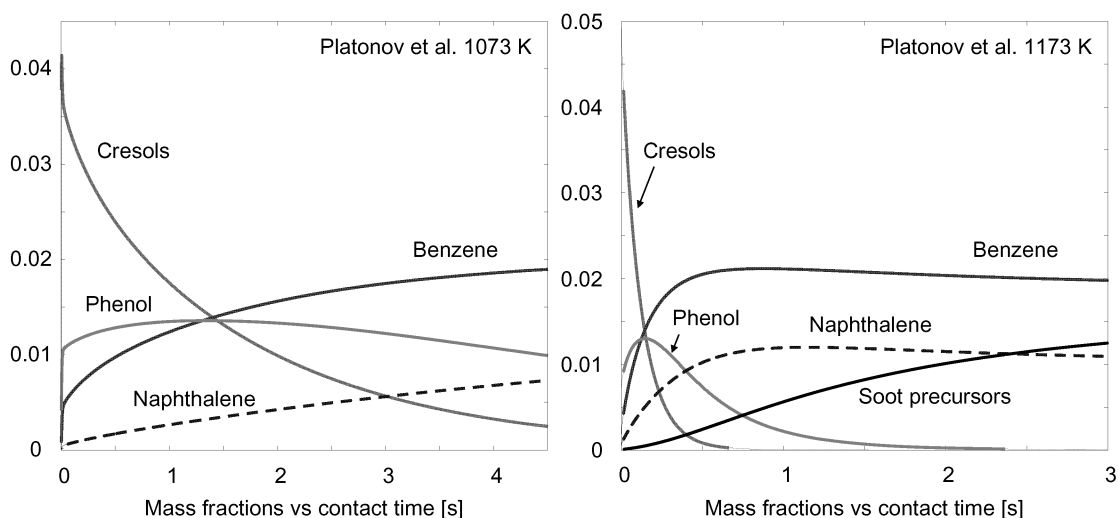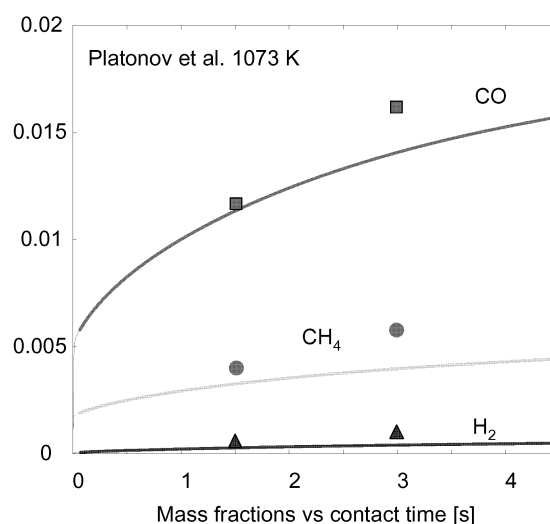
Fig. 5: Pyrolysis of anisole. Predicted yields of intermediates vs time at1073K - 1173K. Comparison of experimental data and model prediction for the major gaseous products.

4. CONCLUSIONS

A detailed kinetic model of anisole pyrolysis and oxidation is proposed and discussed in this paper. Comparison with literature experimental data enables to verify the validity and the limits of the kinetic model under various conditions of operation. Conversely, relevant information on the actual reaction mechanism, with highlights on the major reaction paths and intermediates, can be taken from this kinetic modelling work, which is useful to interpret experimental evidences. The model also enables to make predictions in a wide range of operating conditions, thus helping in the design and characterization of reactor systems and process configurations. The definition of optimal operating conditions, based on model predictions, can be inferred and represents the ultimate goal of the modelling work.

With specific reference to the reported results, the kinetic model tested in the present work is fairly acceptable under different working conditions. The comparison with experimental data suggest that the phenoxy radical is a crucial intermediate in anisole pyrolysis, and that phenol and cresols are two relevant products. The investigation of the reactivity of these compounds is therefore interesting in the light of further development and improvement of the proposed reaction mechanism.

It might be worthy to remind the importance of the choice of anisole as a model compound for the present study. Relying on the assumption that the reactivity of the molecule is concentrated in the substituents on the aromatic ring and that substituents are not strongly affected by the presence and nature of other groups on the ring, the work made for anisole can be extended and generalized to similar components and analogous reactions. Examples of this approach can be found in literature, for instance Shin et al. (2001) (Shin et al. 2001) propose a reaction mechanism for the pyrolysis of vanillin, suggesting that the reaction proceeds via breaking of the C-O bond of the methoxy substituents, as for anisole. The validity of this assumption might be questioned (Mulcahy et al. S.d.) in the case of special stabilization of the radicals through H-bonding, still it offers a strong guideline for the development of other reaction mechanism for lignin model compounds.

5. REFERENCES

Anon, 2004. Survey of energy resources, World Energy Council. Oxford Elsevier Ltd, pag 267.

Arends, I.W.C.., Louw, R. and Mulder, P., 1993, Kinetic study of the thermolysis of anisole in a hydrogen atmosphere, The Journal of Physical Chemistry, 97(30), 7914–7925.

Di Blasi, C., 2008, Modeling chemical and physical processes of wood and biomass pyrolysis, Progress in Energy and Combustion Science, 34(1), 47–90.

Bridgwater, A.V., Meier, D. and Radlein, D., 1999, An overview of fast pyrolysis of biomass, Organic Geochemistry, 30(12), 1479–1493.

Calonaci, M., Grana, R., Barker Hemings, E., Bozzano, G., Dente, M., and Ranzi, E., 2010, Comprehensive Kinetic Modeling Study of Bio-oil Formation from Fast Pyrolysis of Biomass, Energy & Fuels, 24, 4265–4273.

Campbell, D.M., Bennett, C., Hou, Z. and Klein, M.T., 2009, Attribute-Based Modeling of Resid Structure and Reaction, Industrial & Engineering Chemistry Research, 48(4), 1683–1693.

Colussi, A.J., Zabel, F. and Benson, S.W., 1977, The very low-pressure pyrolysis of phenyl ethyl ether, phenyl allyl ether, and benzyl methyl ether and the enthalpy of formation of the phenoxy radical, International Journal of Chemical Kinetics, 9(2), 161–178.

Demirbas, A., 2007, Progress and recent trends in biofuels, Progress in energy and combustion science, 33(1), 1–18.

Dente, M., Ranzi, E. and Goossens, A.G., 1979, Detailed prediction of olefin yields from hydrocarbon pyrolysis through a fundamental simulation model (SPYRO), Computers & Chemical Engineering, 3(1-4), 61–75.

Frassoldati, A., Cuoci, A., Faravelli, T., Niemann, U., Ranzi, E., Seiser, R. and Seshadri, K., 2010, An experimental and kinetic modeling study of n-propanol and iso-propanol combustion, Combustion and Flame, 157(1), 2–16.

Freudenberg, K. and Neish, A.C., 1968, Constitution and biosynthesis of lignin, Molecular Biology, Biochemistry and Biophysics, 2, 784.

Grana, R., Frassoldati, A., Faravelli, T., Niemann, U., Ranzi, E., Seiser, R., Cattolica, R. and Seshadri, K., 2010, An experimental and kinetic modeling study of combustion of isomers of butanol, Combustion and Flame, 157 (11), 2137-2154.

Hurff, S.J. and Klein, M.T., 1983, Reaction pathway analysis of thermal and catalytic lignin fragmentation by use of model compounds, Industrial & Engineering Chemistry Fundamentals, 22(4), 426–430.

Klein, M.T. and Virk, P.S., 2008, Modeling of lignin thermolysis, Energy & Fuels, 22(4), 2175–2182.

Lin, C.Y. and Lin, M.C., 1986, Thermal decomposition of methyl phenyl ether in shock waves: The kinetics of phenoxy radical reactions, The Journal of Physical Chemistry, 90(3), 425–431.

Lin, C.Y. and Lin, M.C., 1985, Unimolecular decomposition of the phenoxy radical in shock waves., International Journal of Chemical Kinetics, 17(10), 1025–1028.

Mackie, J.C., Doolan, K.R. and Nelson, P.F., 1989, Kinetics of the thermal decomposition of methoxybenzene (anisole), The Journal of Physical Chemistry, 93(2), 664–670.

Moghtaderi, B., 2006, The state-of-the-art in pyrolysis modelling of lignocellulosic solid fuels, Fire and Materials, 30(1), 1–34.

Mulcahy, M.F.R., Tucker, B.G., Williams, D.J. and Wilmshurst, J.R., 1965, Decomposition and rearrangement of free radicals from alkyl phenyl ethers, Chemical Communications (London), 23, 609–610.

Mulcahy, M.F.R. , B.G., Williams, D.J. and Wilmshurst, J.R., Reactions of free radicals with aromatic compounds in the gaseous phase. III. Kinetics of the reaction of methyl radicals with anisole (methoxybenzene), Australian Journal of Chemistry, 20(6), 1155–1171.

Naik, S., Goud, V.V., Rout, P.K., Jacobson, K. and Dalai, A.K., 2010, Characterization of Canadian biomass for alternative renewable biofuel, Renewable Energy, 35(8), 1624–1631.

Olivella, S., Sole, A. and Garcia-Raso, A., 1995, Ab initio calculations of the potential surface for the thermal decomposition of the phenoxyl radical, The Journal of Physical Chemistry, 99(26), 10549–10556.

Pecullan, M., Brezinsky, K. and Glassman, I., 1997, Pyrolysis and Oxidation of Anisole near 1000 K., J. Phys. Chem. A, 101(18), 3305–3316.

Platonov, V.V., Proskuryakov, V.A., Ryltsova, S.V. and Popova, Y.N., 2001, Homogeneous Pyrolysis of Anisole, Russian Journal of Applied Chemistry, 74(6), 1047–1052.

Ranzi, E., Cuoci, A., Faravelli, T., Frassoldati, A., Migliavacca, G., Pierucci, S. and Sommariva, S., 2008, Chemical kinetics of biomass pyrolysis, Energy & Fuels, 22(6), 4292–4300.

Ranzi, E., Dente, M., Goldaniga, A., Bozzano, G. and Faravelli, T., 2001, Lumping procedures in detailed kinetic modeling of gasification, pyrolysis, partial oxidation and combustion of hydrocarbon mixtures, Progress in Energy and Combustion Science, 27(1), 99.

Shin, E.J., Nimlos, M.R. and Evans, R.J., 2001, A study of the mechanisms of vanillin pyrolysis by mass spectrometry and multivariate analysis, Fuel, 80(12), 1689–1696.

Suryan, M.M., Kafafi, S.A. and Stein, S.E., 1989, The thermal decomposition of hydroxy-and methoxy-substituted anisoles, Journal of the American Chemical Society, 111(4), 1423–1429.

U.S. Department of Energy, 2007. Basic research needs: catalysis for energy.

Westbrook, C.K. and Dryer, F.L., 1984, Chemical kinetic modeling of hydrocarbon combustion, Progress in Energy and Combustion Science, 10(1), 1–57.

Xu, Z.F. and Lin, M.C., 2006, Ab Initio Kinetics for the Unimolecular Reaction C6H5OH→ CO+ C5H6, J. Phys. Chem. A, 110(4), 1672–1677.

Zhang, L., Xu, C.C. and Champagne, P., 2010, Overview of recent advances in thermo-chemical conversion of biomass, Energy Conversion and Management, 51(5), 969–982.

Zhao, Z., Chaos, M., Kazakov, A. and Dryer, F.L., 2008, Thermal decomposition reaction and a comprehensive kinetic model of dimethyl ether, International Journal of Chemical Kinetics, 40(1), 1–18.