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Novel aspects in the pyrolysis and oxidation of 2,5-dimethylfuran

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Abstract

In order to contribute to the study of the behavior of 2,5-dimethylfuran (2,5-DMF), a promising biofuel to be used as fuel or additive in automotive applications, an experimental and kinetic modeling study of the pyrolysis and oxidation of 2,5-DMF has been carried out using well controlled flow reactor installations. The influence of temperature, stoichiometry, 2,5-DMF concentration, and pressure has been analyzed. A detailed chemical kinetic mechanism built from different literature sources was used to describe the pyrolysis and oxidation of 2,5-DMF under the experimental conditions studied. Results attained extend the existing experimental database on 2,5-DMF and, for the first time, its tendency to form soot is analyzed. Additionally, the effect of pressure, which would be of interest for the use of this compound as a part of diesel fuels, has been evaluated.

Keywords

2,5-dimethylfuran, oxidation, pyrolysis, soot, pressure

1. Introduction

Oxygenated additives, such as alcohols, esters and ethers, are an interesting alternative to make part of reformulated fuels, both gasoline and diesel fuels [1-4]. Among these, a possible new candidate is 2,5-dimethylfuran (2,5-DMF). This compound has not received much interest until recently because it was difficult to synthesize. Nevertheless, significant progress has been made and 2,5-DMF can be now obtained by catalytic processes from fructose or glucose [5,6]. 2,5-DMF has properties that makes it attractive, such as: high boiling point, insolubility in water, high energetic density and oxygen content.

Because of this, in the very recent years, many investigations have addressed the study on different aspects related to 2,5-DMF, including fundamental studies of kinetic parameters and thermochemistry [7-12]; laboratory studies, such as studies in flames [13-15], in shock tube, plug flow or perfect stirred reactors [e.g. 13,16-19], as well as more applied studies addressing the performance of gasoline and diesel engines fueled with 2,5-DMF mixtures [e.g. 20-22]. Through all these studies, the knowledge related to the conversion of 2,5-DMF has progressively increased. However, and despite the extensive related literature, there are still aspects of interest not yet resolved.

In this context, the objective of the present work is to study the conversion of 2,5-DMF in a carefully controlled plug flow reactor installation, under different operating conditions, analyzing the effect of temperature (in the 500-1400 K interval), 2,5-DMF concentration, stoichiometry (from pyrolysis to very fuel-lean conditions) and pressure (in the 1-40 bar interval). Additionally, the soot formation tendency of 2,5-DMF has been evaluated. To our knowledge, this is the first study that includes data on soot formation from 2,5-DMF pyrolysis and on the influence of pressure on its conversion. The experimental results obtained have been interpreted in terms of a detailed kinetic model built from different literature subsets.

2. Experimental procedure

Table 1 shows the experimental conditions of this study. Experiments were conducted in three different experimental facilities: the so-called atmospheric-pressure gas-phase installation, the soot formation installation and the high-pressure gas-phase installation.

Experiments at atmospheric pressure were performed in the atmospheric-pressure gas-phase installation, which has been described in earlier publications (e.g. [23-25]) and only a brief description is given here. A quartz flow reactor with a reaction zone of 8.7 mm inside diameter and 200 mm in length is used. This tubular reactor is placed in a three-zone electrically heated furnace, ensuring a uniform temperature profile (± 10 K) along the reaction zone. The 2,5-DMF and oxygen flows are introduced in the reactor from gas cylinders using mass flow controllers. The oxygen concentration is related to the air excess ratio (λ), which is defined by the ratio between the fed oxygen and the stoichiometric oxygen amount. Also, water vapor is introduced in the reactor by saturating a nitrogen stream through a water bubbler. A total flow rate of 1000 mL(STP)/min is used, N_2 is fed to close the balance, and it results in a gas residence time as a function of the temperature, $t_r(s)=195/T(K)$. The product gases are quenched at the outlet of the reaction zone and conditioned before analysis. The outlet gas is analyzed by gas chromatography and continuous CO/CO_2 analyzers. The uncertainty of the concentration measurements is estimated as ±5% but not less than 10 ppm.

An experiment of soot formation was conducted in the soot formation installation. A full explanation of the installation can be seen in previous works (e.g [26]). The gases are led into a quartz flow reactor, which is placed in a one-zone electrically heated furnace, with an inner diameter of 45 mm and a reaction zone defined for a length of 160 mm. 2,5-DMF has been fed to the reactor, in a concentration of 6000 ppm, using an isocratic HPLC pump and a thermally insulated line. N_2 is added to make up a total flow rate of 1000 mL(STP)/min, and the resulting residence time is $t_r(s)=4168/T(K)$. The soot formed during the experiment is collected in a quartz fiber filter, with a pore size less than 1 µm and gases are analyzed in the same way as mentioned above.

The high-pressure gas-phase installation was used to carry out the oxidation experiments of 2,5-DMF at high-pressure. Fig. 1 shows the scheme of this experimental setup, which consists primarily of three sections: feeding section, reaction section, and conditioning and gas measurement section. The feeding section includes the gases, high-pressure flow controllers and a Controlled Evaporator Mixer (CEM), in order to feed 2,5-DMF into the reaction system, using N_2 as a carrier gas, by using a mini CORI-FLOW flow meter/controller and a EL-FLOW flow meter/controller, respectively. The rest of gases (O_2 and N_2) are fed as well into the reactor. The reactor is a quartz tube of 5 mm inside diameter and 1500 mm in length located within an AISI 316L stainless steel tube, which acts as a shell to maintain pressure. This pressure shell is placed inside a three-zone electrically heated furnace with individual temperature control. To assure the pressure inside in both the reactor and the pressure shell, pressure is monitored by two differential pressure transducers located at the reactor entrance and two pressure Badger valves situated at the outlet of the installation, allowing a maximum pressure of 80 bar. N_2 is released into the shell to avoid the existence of sudden pressure gradients on both sides of the reactor. The reactor-furnace system ensures an isothermal reaction zone of 560 mm (±5 K), and allows a maximum temperature over the whole pressure range of up 1100 K. The residence time in the reaction zone is function of the temperature and the pressure in this zone, i.e, t_r (s)=261 P(bar)/T(K) (for a total flow of 1000 mL(STP)/min). The conditioning and gas measurement section is formed by a condenser and various measuring equipments (gas chromatography and CO, CO_2, and NO continuous analyzers and FTIR spectrometer). The outlet gases pass through the pressure valve to reduce the system pressure to atmospheric pressure, subsequently gases are conditioned and finally analyzed. To prevent condensation of reactants and products, all gas flow lines are thermally insulated.

3. Modeling procedure

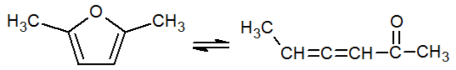
The experimental results have been analyzed in terms of a detailed gas-phase chemical kinetic model for the pyrolysis and oxidation of 2,5-DMF. The mechanism used includes the 2,5-DMF subset developed by Sirjean et al. [27], which was proposed for the decomposition and oxidation of 2,5-DMF, and was validated using their shock tube ignition delay measurements and the measurements of speciation of 2,5-DMF pyrolysis of

Lifshitz et al. [16]. This 2,5-DMF subset has been added to the mechanism progressively developed by our group, and that has been described and updated until now [28-31]. The full model includes 255 species and 1314 reactions. The reaction mechanism and the thermodynamic data can be found in the supplementary material. Calculations have been performed with Senkin, the plug flow reactor code which runs in conjunction with the CHEMKIN-II library [32].

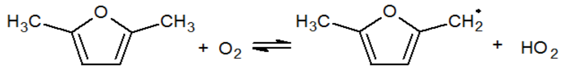
4. Results and discussion

Table 1 lists the experimental conditions used in the present work. Experiments address the study of the conversion of 2,5-DMF at different temperatures from fuel-rich to fuel-lean conditions for two 2,5-DMF concentrations (100 and 300 ppm), the formation of soot from 6000 ppm of 2,5-DMF under given conditions and the study of the influence of pressure (1-40 bar) on 2,5-DMF at stoichiometric conditions. Experimental data are shown as symbols and model calculations as lines. In general, the model predictions are in good agreement with the experimental results, even though the agreement is comparatively worse for the high-pressure conditions studied.

Different values of air excess ratio (λ) have been used to study the influence of the stoichiometry on the oxidation of 2,5-DMF at different temperatures. Fig. 2 shows the influence of the stoichiometry on the experimental data with 100 ppm 2,5-DMF at atmospheric pressure. As seen, under fuel-rich and stoichiometric conditions, there is no appreciable influence of the stoichiometry on the conversion of 2,5-DMF. In these cases, the onset of the consumption of 2,5-DMF occurs approximately at 1073 K. Nevertheless, under fuel-lean conditions, there is an appreciable influence of the stoichiometry. In these conditions, the onset temperature for the consumption of 2,5-DMF is 998 and 973 K for λ=5 and 30, respectively. Model calculations indicate that during the early stages of the conversion of 2,5-DMF, for all the stoichiometries studied, except for λ=30, the main reaction pathway is the thermal decomposition resulting in ring-opening (reaction (r.1)), while for λ=30 the 2,5-DMF+O_2 bimolecular initiation appears to be important (reaction (r.2)). The 5-methyl-2-furanylmethyl radical ($R1C_6H_7O$), formed in (r.2), follows a complex reaction sequence prior to its final conversion into CO and eventually in CO_2, as found in Sirjean et al. [27], and will be seen later.



(r.1)



(r.2)

Furthermore, with increasing λ, the maximum concentration of CO is shifted to lower temperatures. For λ=1, 5 and 30, 2,5-DMF is completely oxidized and converted to CO_2 at the highest temperature studied (1400 K), whereas for λ=0.3 and 0.7, the lack of oxygen prevents complete oxidation of 2,5-DMF. It is remarkable that for λ=0, no formation of CO_2 was found, while little amounts of CO were detected for the highest temperatures studied. H_2 is found to be formed in the temperature range studied only for fuel-rich conditions.

In order to study the influence of the 2,5-DMF concentration on its oxidation, experiments with two different initial 2,5-DMF concentrations (100 and 300 ppm) at atmospheric pressure and for λ=0.3, 1 and 30 have been carried out. The trend of the profiles when feeding 300 ppm of 2,5-DMF (not shown) is exactly the same as for 100 ppm (Fig. 2). In order to compare properly the results of the experiments carried out for the two concentration levels considered, Fig. 3 illustrates the $[2,5\text{-DMF}]_{out}/[2,5\text{-DMF}]_{in}$ ratio as a function of temperature for both concentrations of 2,5-DMF. Only for λ =30, the increase of the concentration of 2,5-DMF is seen to have an appreciable effect on its conversion, with the onset for 2,5-DMF consumption shifted to lower temperatures. It is worth mentioning that for the highest concentration of 2,5-DMF studied (300 ppm), other hydrocarbons such as ethylene, ethane and acetylene, are formed as products for the stoichiometries of λ=0.3 and 1. The concentration of these products increases with the decrease of the oxygen concentration.

Figure 4 shows the reaction pathway diagram for the conversion of 2,5-DMF, obtained with the mechanism compiled in the present work and applied to the conditions of atmospheric pressure, corresponding to consumption of 50 % 2,5-DMF. Note that the nomenclature used is the same used by Sirjean et al. [27]. The main paths determining the consumption of 2,5-DMF depend on the amount of oxygen present, as explained as follows:

Pathway 1. For all conditions, except for λ=30, the main channel for 2,5-DMF consumption is the abstraction of hydrogen from the methyl group to yield the resonance-stabilized 5-methyl-2-furanylmethyl radical ($R1C_6H_7O$). Subsequent H-atom transfer and ring enlargement result in the radical $R4C_6H_7O$ and the posterior formation of 2,4-cyclohexadien-1-one ($DM2C_6H_6O$) by β-scission of the C-H bond. $R4C_6H_7O$ can also decompose into $R6C_6H_7O$ or $R9C_6H_7O$ radicals. In the first case, there are two paths for decomposition: (i) ring opening thus forming the radical $R7C_6H_7O$ and subsequent formation of penta-1,4-dien-1-yl radical (C_5H_7-1s) by CO-elimination; and (ii) formation of cyclohexa-2,5-dien-1-one ($DM3C_6H_6O$), leading to further formation of cyclohexa-2,4-dien-1-one ($DM2C_6H_6O$)/cyclopentadiene (C_5H_6#) via the formation of the biradical $B1C_6H_6O$, or giving the subsequent formation of phenoxy (C_6H_5O#) by reaction with a third body or with atoms or radicals such as H or OH, respectively. If $R4C_6H_7O$ decomposes into $R9C_6H_7O$, the 2-cyclopenten-1-yl radical (C_5H_7#Y) is formed by CO-elimination.

Pathway 2. For λ≤1, 2,5-DMF can decompose by ring opening yielding hexa-3,4-dien-2-one ($DM4C_6H_8O$), which may react with a third body suffering C-C bond breaking, thus forming the buta-1,2-dien-1-yl radical (C_4H_5-1s) and the acetyl radical. In turn, C_4H_5-1s forms vinylacetylene and an H atom. This pathway is the second more important for the decomposition of 2,5-DMF under pyrolysis conditions, and the third most important channel for the rest of conditions.

Pathway 3. Both 2-methylfuran (2-MF) and methyl radical are formed by H-addition to 2,5-DMF. This pathway occurs for all conditions, except for λ=30, and represents the second channel in importance for the consumption of 2,5-DMF, except for λ=0 and 5. Once formed, 2-MF reacts or decomposes to yield: (i) furan and CH_3 by reaction with the hydrogen radical. Furan can decompose to give propyne and CO, or can react with OH-atom until form vinyl radical and CO; (ii) penta-2,3-dienal ($CH_3CHCCHCHO$) by 2-MF decomposition; (iii) penta-4,5-dien-2-one ($CH_3COCHCCH_2$); (iv) the resonance-stabilized 2-furylmethyl radical (furylCH_2) due to H-abstraction by OH, CH_3 radicals or H atoms from the methyl group of 2-MF. FurylCH_2 ring is opened up to form intermediaries and originate the radical nC_4H_5 and CO.

Pathway 4. Rearrangements of 2,5-DMF to yield 1,3-butadiene and the acetyl radical occur for all the conditions studied, except for λ=30.

Pathway 5. Another important channel for the decomposition of 2,5-DMF for λ≥5, is the OH-addition to form acetylene, the acetyl radical and acetaldehyde. For λ=30 this pathway represents the major channel for the consumption of 2,5-DMF. However, as the oxygen concentration decreases, its importance is diminished, and for λ=5 it represents the second channel most important for the consumption of 2,5-DMF.

A first-order sensitivity analysis for CO has been performed for the onset of 2,5-DMF consumption in each experiment at atmospheric pressure (i.e. 1073 K for λ=0, 0.3, 0.7 and 1, 998 K for λ=5 or 973 K for λ= 30). This analysis allows us to conclude that the results are most sensitive to various reactions according to the amount of oxygen present. Selected sensitivity plots carried out to atmospheric pressure are shown in the supplementary material. Results are found to be most sensitive to the reaction (r.3), and the evolution of $R1C_6H_7O$, except for λ=0, in which the results are mostly sensitive to the reaction (r.4)

$$2,5\text{-DMF}+O_2 \rightleftarrows R1C_6H_7O+HO_2 \qquad (r.3)$$

$$R1C_6H_7O+H(+M) \rightleftarrows 2,5\text{-DMF}(+M) \qquad (r.4)$$

Other reactions that also appear to be important in the sensitivity analysis include a variety of reactions, involving the isomerization of R1C_6H_7O species and the decompositions and reaction of intermediates with a number of radicals configuring the H/O radical pool.

Since one of the main properties, in the possible use of 2,5-DMF as fuel constituent, is its oxygenated character, the pyrolysis of 2,5-DMF has been performed in order to quantify its tendency to form soot. To do that, 6000 ppm of 2,5-DMF diluted in nitrogen were pyrolyzed at the temperature of 1473 K at atmospheric pressure, following the experimental procedure described by Ruiz et al. [33]. In this experiment, which was maintained during 3 hours at steady state in order to collect a quantifiable amount of soot, outlet gases were analyzed and the soot was collected. The gas composition was found to be: 4503 ppm CO, 96 ppm CO_2, 48 ppm C_2H_4, 1423 ppm C_2H_2, 16127 ppm H_2, 1874 ppm CH_4 and the amount of soot collected was 1.42 g.

With the aim of evaluating the potential for soot formation of 2,5-DMF, Table 2 shows the yields to soot obtained from different compounds [29, 33-36]. Even though the data shown in Table 2 include different specific operating conditions, it is noticeable the significant yield to soot attained in the conversion of 6000 ppm of 2,5-DMF (i.e. 36000 ppm of C) of 40.8 % compared to the yields of C_2H_2 and C_2H_4 (traditionally considered as soot precursors) of 43.3 and 38.7 %, respectively, for an inlet concentration of 15000 ppm (i.e. 30000 ppm C). Additionally, if compared with other oxygenated compounds, 2,5-DMF is found to generate more soot than ethanol and than methylformate that does not generate any soot [29,36].

To study the influence of the pressure on the oxidation of 2,5-DMF, experiments at atmospheric (1 bar) and high-pressure (20 and 40 bar) have been performed. Pressure may be of interest if 2,5-DMF is used as fuel constituent in diesel engines. Results on the conversion of 2,5-DMF and formation of products as a function of temperature are shown in Fig. 5. The pressure is seen to have an important impact on the conversion of 2,5-DMF, shifting the concentration profiles to lower temperatures. The model is seen to reproduce reasonably well the experimental data, even though the discrepancies observed are larger compared to the results obtained at atmospheric pressure. Calculations made at different pressures indicate that the only reaction pathway controlling the conversion of 2,5-DMF is the OH-addition to form acetylene, acetaldehyde and the acetyl radical (*pathway 5* in Fig. 4). On the other hand, sensitivity analysis for CO applied to the experiments at high-pressure allows us to conclude that the results are most sensitive to the reactions (r.5)-(r.7).

$2CH_3O_2 \rightleftarrows O_2+2CH_3O$ (r.5)

$CH_3CO(+M) \rightleftarrows CH_3+CO(+M)$ (r.6)

$CH_3O_2+HO_2 \rightleftarrows CH_3OOH+O_2$ (r.7)

It is noteworthy that at atmospheric pressure, besides the formation of the products shown in Fig. 5, the formation of ethane and acetylene was also observed, contrarily to the results obtained at higher pressures where these products were not detected.

5. Conclusions

A study on the conversion of 2,5-DMF, analyzing the influence of temperature, stoichiometry, 2,5-DMF concentration and pressure, has been performed in different flow reactor experimental installations. The results have been interpreted in terms of a detailed kinetic mechanism. In general, the experimental findings were found in good agreement with the model predictions. Results indicate a significant influence of stoichiometry on the onset temperature for the conversion of 2,5-DMF, only for fuel-lean conditions, while the effect is less important under fuel-rich or stoichiometric conditions. The variation of the concentration of 2,5-DMF in the experiments, of 100 and 300 ppm, indicates that no appreciable changes occur. The experiment performed under pyrolysis conditions and a significant concentration of 2,5-DMF (6000 ppm) reveals that a significant amount of soot is generated, with soot yield comparable to those attained in the pyrolysis of well-known soot precursors, such as C_2H_4 and C_2H_2, and much higher compared to other oxygenated compounds. Thus, this compound should be considered with caution as fuel additive if it is aimed to contribute to soot reduction. Increasing the pressure at which the 2,5-DMF oxidation is produced results in shifting the conversion regime of 2,5-DMF to lower temperatures. The main reactions pathways controlling the conversion of 2,5-DMF include the abstraction of hydrogen from the methyl group and the addition of OH radicals to the C2 position to form C_2H_2, CH_3HCO and the CH_3CO radicals.

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Table 1.

Experimental conditions. All experiments are done with a total flow rate of 1000 mL (STP)/min. N_2 is used to close the balance.

Set	λ	2,5-DMF (ppm)	O_2 (ppm)	P (bar)	T (K)	Installation
1A	0	100	0	1	800-1400	Atmospheric-pressure gas phase
2A	0.3	100	225	1		
3A	0.7	100	525	1		
4A	1	100	750	1		
5A	5	100	3750	1		
6A	30	100	22500	1		
7A	0.3	300	675	1		
8A	1	300	2250	1		
9A	30	300	67500	1		
1B	0	6000	0	1	1473	Formation of soot
1C	1	4500	33750	1	500-1100	High-pressure gas-phase
2C	1	4500	33750	20		
3C	1	2500	18750	40		

Table 2.

Yields to soot obtained from different compounds.

Compound	Concentration (ppm)	t_r (s)	Yield to soot (%)	Reference
2,5-DMF	6000	2.83	40.8	Present work
C_2H_2	15000	2.70	43.3	[34]
C_2H_4	15000	3.09	38.7	[34]
C_2H_2	50000	1.16	62.2	[35]
C_2H_4	50000	1.16	41.1	[33]
C_2H_5OH	50000	1.16	28.7	[36]
$C_2H_4O_2$ (methyl formate)	2515	2.00	0	[29]

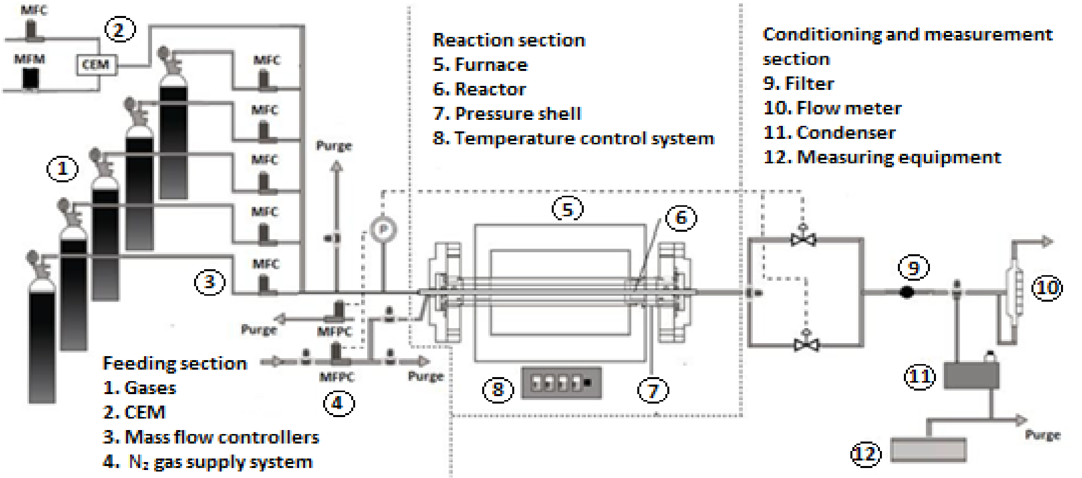

Fig. 1. High-pressure gas-phase installation scheme.

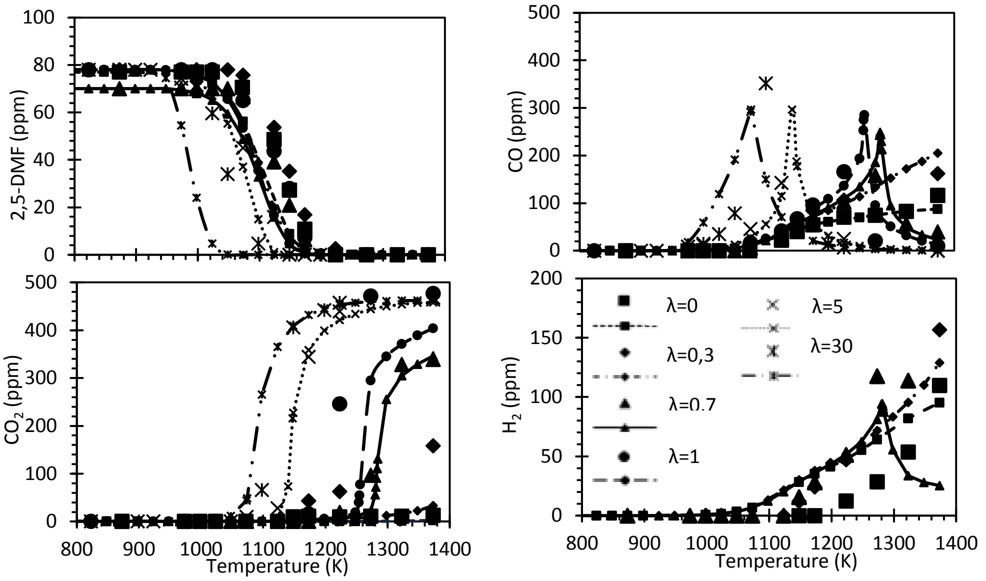

Fig. 2. Influence of the stoichiometry on the conversion of 2,5-DMF for 100 ppm at atmospheric pressure (sets 1A-6A in Table 1).

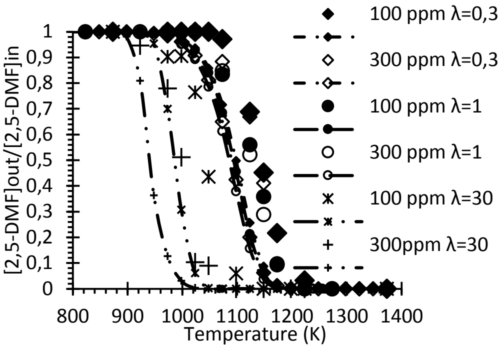

Fig. 3. Influence of the concentration of 2,5-DMF on its oxidation for λ=0.3, 1 and 30, at atmospheric pressure (sets 2A, 4A, 6A-9A in Table 1).

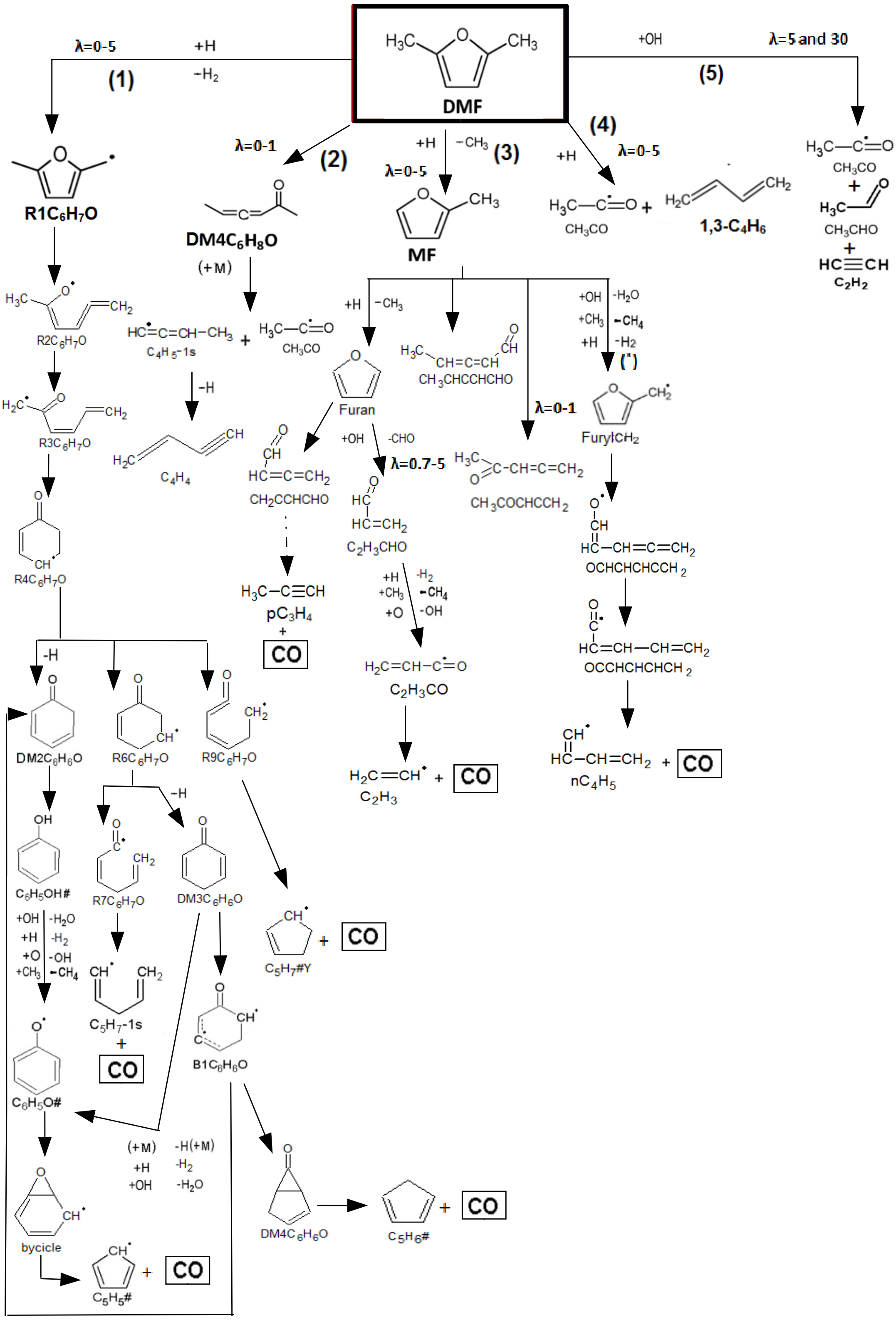

Fig. 4. Reaction pathway diagram for the conversion of 2,5-DMF under atmospheric pressure conditions.

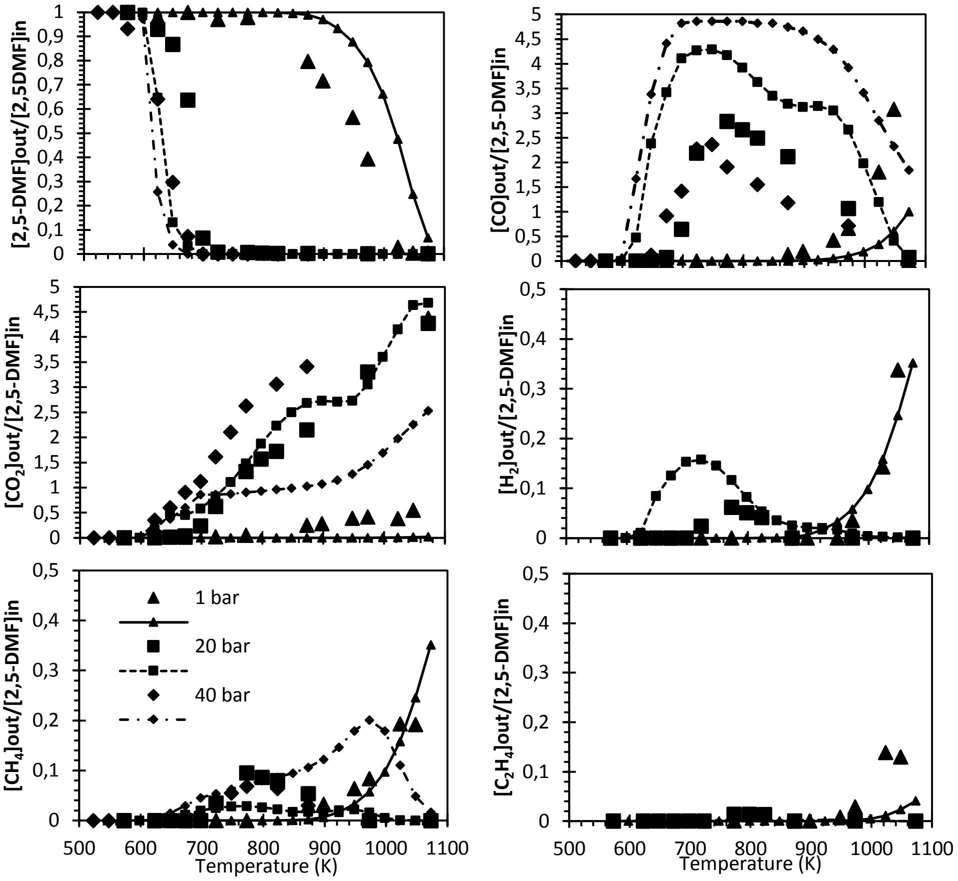

Fig. 5. Influence of the pressure on the oxidation of 2,5-DMF for λ=1 (sets 1C-3C in Table 1).

Figure captions

Fig.1. High-pressure gas-phase installation scheme.

Fig. 2. Influence of the stoichiometry on the conversion of 2,5-DMF for 100 ppm at atmospheric pressure (sets 1A-6A in Table 1).

Fig. 3. Influence of the concentration of 2,5-DMF on its oxidation for λ=0.3, 1 and 30, at atmospheric pressure (sets 2A, 4A, 6A-9A in Table 1).

Fig. 4. Reaction pathway diagram for the conversion of 2,5-DMF under atmospheric conditions.

Fig. 5. Influence of the pressure on the oxidation of 2,5-DMF for λ=1 (sets 1C-3C in Table 1).

Supplemental material

Kinetic Mechanism (mech_2,5-DMF.mec)

Thermodynamic (thermdat)

Sensitivity plots (Sens_plot)