

# NUMERICAL SIMULATION OF THE THERMAL DESTRUCTION OF ORGANOPHOSPHOROUS

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## ABSTRACT

*The organophosphorus class of compounds has several usages nowadays. Some halogenated organophosphorus are used as flame retardants, and others are used as pesticides worldwide. In the last case, those compounds are subject to law regulation. They are now used as chemical weapons in many wars and terrorist attacks. Due to this variety of usages and the high toxicity of such compounds, the study of the proper treatment for residues containing those substances is significant to prevent the degradation of soil, water, and the atmosphere. For these reasons, the present study conducted numeric simulations of the incineration of organophosphorus compounds using kinetic models of combustion and pyrolysis found in the literature. The study of the degradation of this class of substances and the pollutant formation was made by simulating a homogeneous zeroth-order reactor and a continuous stirred tank reactor model. Due to the results of the simulations, the degradation made with the batch mode operation is efficient in the degradation of the substances considered in this work. The stream-containing process products have CO<sub>2</sub>, CO, HF, HOPO, and HOPO<sub>2</sub>. The three last cited have no determination about the emission ranges in the legislation, but their concentrations indicate the necessity of treatment for them. Furthermore, it was possible to evaluate the negative influence of the hydrocarbon used as fuel and the presence of CO<sub>2</sub> in the degradation of the organophosphate compounds.*

## KEYWORDS

*Organophosphorus compounds, numerical simulation, pollutants, incineration*

## 1. INTRODUCTION

Organophosphorus compounds are a class of chemicals widely used in various industries, including agriculture, pharmaceuticals, and manufacturing<sup>1,2</sup>. Also, some organophosphorus was used as chemical weapons<sup>3–5</sup>. These chemicals are known to be highly toxic and can cause severe health effects if ingested or inhaled<sup>4,6</sup>. Due to their toxicity, organophosphorus compounds are often classified as hazardous waste and must be appropriately disposed of to prevent environmental contamination and human exposure.

One method of disposing of organophosphorus compounds is incineration<sup>3,6–12</sup>, which involves burning the waste at high temperatures and converting it into ash and gases. This process can effectively destroy the hazardous components of the waste and reduce its volume but requires careful consideration due to the potential risks and challenges associated with this method. The incineration process involves several stages: waste handling, pre-treatment, combustion, and emission control<sup>9,13,14</sup>. During the waste handling stage, the organophosphorus waste is received and stored securely before being transported to the incineration facility. After the waste

has been pre-treated, it is loaded into the incinerator and burned at high temperatures, typically between 800-1200°C. The combustion process converts the organophosphorus compounds into carbon dioxide, water, and other gases, producing heat that can be used in other plant process 7,13 .

One challenge of incinerating organophosphorus compounds is the release of toxic gases during the combustion process. The combustion of these compounds can produce harmful gases, adversely affecting human health and the environment. Until now, diverse groups have investigated the inactivation and destruction of organophosphorus compounds<sup>1–3,15</sup>. Some studies focus on the combustions and pyrolysis of such compounds because some molecules are used as flame retardants. Therefore, it is essential to ensure that the incinerator is adequately designed, operated, and maintained to minimize the release of these gases. It is necessary to maintain high temperatures and sufficient oxygen levels during the incineration process to prevent the formation of these byproducts.

## 2. METHODS

The present study used Glaude's kinetic mechanism<sup>8</sup> to study the thermal degradation (incineration) of the following compounds: dimethyl methylphosphonate (DMMP), diisopropyl methylphosphonate (DIMP), trimethyl phosphate (TMP), and Sarin. The kinetic model was described previously, but it is based on the junction of three submodels: Warnatz's model that includes the C/H/O chemistry, the Gri-Mech 3.016 to describe the chemistry of molecules containing up to two carbon atoms, and a surrogate model based on the iso-octane model containing 397 reactions and 76 species. Also, a kinetic model containing 174 reactions and 63 species was included to describe the organophosphorus chemistry.

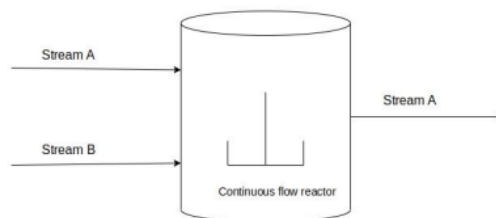
First, considering different fuels, a well-stimulated homogeneous reactor was simulated to study organophosphorus degradation. The simulations were conducted at the stoichiometric ratio between fuel and air, in the range of 800 – 2000 K and 1.0 atm. The fuels considered are listed in Table 1. It was considered gaseous fossil fuels and biogas with the composition of 65% methane and 35% CO<sub>2</sub>. Biogas was included in the present study due to the environmental questions associated with their use as an alternative fuel in the future. 17–20 .

**Table1:** Different fuel compositions considered in the present study. The organophosphorus combustion was simulated in the presence of each gaseous fuel blend.

Fuel	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CO <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	O <sub>2</sub>	N <sub>2</sub>
F1. Biogas	0.65	-	0.35	-	1.30	6.39
F2.Ethane	-	1.00	-	-	3.50	13.67
3.Ethane+ Methane	0.94	0.06	-	-	2.03	7.54
F4. Propane	-	-	-	1.0	5.00	18.00

The second step was the simulation of a continuous reactor considering only gaseous species. Since some of the studied species are flame retardants, it is important to evaluate how the mass flow from the reservoir containing the organophosphorus to the reactor impacts the thermal degradation. The flow reactor's scheme is shown in Figure 1. Two different inlets were considered: the first containing only the organophosphorus, and the second containing a mixture of fuel and air at stoichiometry ratio. The residence time varied in the range of 0.5 - 2.0 s, and the temperature ranged from 800 K to 2000 K. The combustion mechanism of all species in different

fuels was investigated via flow analysis of pollutant formation during the mixture ignition. All numerical simulations were conducted at Cantera 2.5 software<sup>21</sup>, using the Python environment.



**Figure 1:** Scheme of the well-stirred reactor studied. Streams A and B are the reactor's organophosphorus and fuel/air entrances. Stream C is the combustion products.

### 3. RESULTS

#### 3.1. Well-Stirred batch Reactor

Previously, Glaude<sup>8,22</sup> studied the thermal destruction of DIMP, TMP, DMMP, and Sarin, considering natural gas (methane) as fuel. According to its results, the model predicts the almost complete degradation of the studied compounds, reproduced by our simulations considering only methane as fuel, Table 2. However, the change in fuel type alters the thermal degradation of the considered compounds. The CO<sub>2</sub> presence in the biogas influences the thermal degradation of all compounds, mainly TMP, lowering its decomposition. As expected, the temperature elevation increases the decomposition of all compounds, except in some specific cases. As a partial conclusion, it is possible to infer that the fuel alters the thermal degradation mechanism of the studied compounds. Despite almost destroying the desired compounds, the incinerator developments should consider the fuel that will be used in its operation.

**Table 2:** Molar fraction of each organophosphorus at the end of simulations, considering the different fuel blends, F1-4, described in Table 1. All simulations were conducted at 1.0 atm.

Temperature (K)	Sarin	TMP	DIMP	DMMP
<b>F1</b>				
800	$1.65 \times 10^{-12}$	$1.15 \times 10^{-04}$	$1.48 \times 10^{-12}$	$2.01 \times 10^{-14}$
900	$2.94 \times 10^{-13}$	$1.14 \times 10^{-04}$	$1.14 \times 10^{-04}$	$1.78 \times 10^{-12}$
1000	$1.33 \times 10^{-14}$	$1.04 \times 10^{-04}$	$1.04 \times 10^{-04}$	$1.05 \times 10^{-04}$
<b>F2</b>				
800	$9.26 \times 10^{-14}$	$5.66 \times 10^{-05}$	$9.26 \times 10^{-14}$	$5.66 \times 10^{-05}$
900	$6.08 \times 10^{-16}$	$5.40 \times 10^{-05}$	$6.08 \times 10^{-16}$	$5.66 \times 10^{-05}$
1000	$3.61 \times 10^{-59}$	$5.48 \times 10^{-54}$	$3.61 \times 10^{-59}$	$8.07 \times 10^{-48}$
<b>F3</b>				
800	$1.12 \times 10^{-12}$	$9.46 \times 10^{-05}$	$1.42 \times 10^{-13}$	$9.46 \times 10^{-05}$
900	$1.95 \times 10^{-13}$	$9.38 \times 10^{-05}$	$7.97 \times 10^{-16}$	$9.39 \times 10^{-05}$
1000	$6.95 \times 10^{-47}$	$2.41 \times 10^{-53}$	$1.74 \times 10^{-55}$	$1.57 \times 10^{-48}$
<b>F4</b>				
800	$3.57 \times 10^{-13}$	$4.03 \times 10^{-05}$	$7.78 \times 10^{-14}$	$4.03 \times 10^{-05}$
900	$1.29 \times 10^{-45}$	$4.37 \times 10^{-54}$	$-2.08 \times 10^{-52}$	$-1.54 \times 10^{-48}$
1000	$8.94 \times 10^{-47}$	$3.58 \times 10^{-54}$	$-3.91 \times 10^{-60}$	$2.91 \times 10^{-48}$

The simulations can also help predict the pollutants formed during incineration. The pollutant formation was investigated considering the four fuel blends in Table 1. The major pollutants observed at the end of all simulations were CO<sub>2</sub>, CO, HPO<sub>2</sub>, HOPO, and HOPO<sub>2</sub>. In the Sarin case, a considerable amount of HF (3-100 ppm of products), an acidic species as a product, is also observed, which cannot be released into the environment. The literature reports a similar problem is observed in Tabun's incineration, which forms HCN and Sulfur Mustard gas, which releases H<sub>2</sub>S [23]. In all cases, the thermal degradation process releases poisonous and toxic gases as products, and a specific pollutant control strategy should be adopted.

The phosphorus-bearing molecules appear as reactive species [24] due to its open shell character and the little information about that species in the literature. However, those species have been observed in flames in the postflame zone [25]. They are associated with the combustion inhibition properties of some organophosphorus compounds [24,26,27] and are key intermediates that should be included in combustion models [26,28]. Also, some studies report that PO is the main product of DMMP decomposition [28], indicating that the model considered in the present study should be improved. These phosphorus-bearing species can react with H and OH radicals, acting as a sink of these free radicals, impacting ignition and flame propagation [27].

Table 3 shows the high fraction of CO<sub>2</sub> in the combustion products. Carbon dioxide is a completely oxidized molecule that does not burn during combustion. All CO<sub>2</sub> included in biogas is released and summed up with the CO<sub>2</sub> produced during combustion. Since CO<sub>2</sub> is a greenhouse gas associated with climate change, it can contribute to the atmosphere's carbon budget despite biogas being a renewable fuel source. For this reason, if the biogas is used for combustion, it should have a small fraction of CO<sub>2</sub>.

**Table 3:** Molar fraction of some pollutants at the end of the simulation, considering the biogas (F1) as fuel. All simulations were conducted at 1.0 atm.

<b>Sarin</b>						
Temperature (K)	HOPO <sub>2</sub>	HPO <sub>2</sub>	HOPO	HF	CO <sub>2</sub>	CO
800	1.04 × 10 <sup>-12</sup>	9.06 × 10 <sup>-16</sup>	1.46 × 10 <sup>-13</sup>	2.79 × 10 <sup>-06</sup>	4.02 × 10 <sup>-02</sup>	8.36 × 10 <sup>-10</sup>
900	2.56 × 10 <sup>-09</sup>	1.52 × 10 <sup>-12</sup>	1.25 × 10 <sup>-09</sup>	6.32 × 10 <sup>-05</sup>	4.02 × 10 <sup>-02</sup>	5.52 × 10 <sup>-07</sup>
1000	1.06 × 10 <sup>-10</sup>	1.57 × 10 <sup>-10</sup>	1.81 × 10 <sup>-08</sup>	1.09 × 10 <sup>-04</sup>	4.02 × 10 <sup>-02</sup>	6.66 × 10 <sup>-05</sup>
<b>TMP</b>						
800	4.52 × 10 <sup>-13</sup>	1.78 × 10 <sup>-18</sup>	1.31 × 10 <sup>-15</sup>		4.02 × 10 <sup>-02</sup>	4.77 × 10 <sup>-12</sup>
900	3.17 × 10 <sup>-09</sup>	1.09 × 10 <sup>-11</sup>	3.41 × 10 <sup>-10</sup>		4.02 × 10 <sup>-02</sup>	3.11 × 10 <sup>-07</sup>
1000	8.26 × 10 <sup>-08</sup>	3.02 × 10 <sup>-10</sup>	1.49 × 10 <sup>-08</sup>		4.02 × 10 <sup>-02</sup>	5.90 × 10 <sup>-05</sup>
<b>DIMP</b>						
800	4.40 × 10 <sup>-13</sup>	2.79 × 10 <sup>-18</sup>	7.15 × 10 <sup>-14</sup>		4.02 × 10 <sup>-02</sup>	1.76 × 10 <sup>-09</sup>
900	3.78 × 10 <sup>-09</sup>	1.76 × 10 <sup>-11</sup>	1.54 × 10 <sup>-08</sup>		4.02 × 10 <sup>-02</sup>	8.10 × 10 <sup>-07</sup>
1000	6.97 × 10 <sup>-08</sup>	4.42 × 10 <sup>-10</sup>	2.96 × 10 <sup>-09</sup>		4.02 × 10 <sup>-02</sup>	8.03 × 10 <sup>-05</sup>
<b>DMMP</b>						
800	4.40 × 10 <sup>-13</sup>	2.79 × 10 <sup>-18</sup>	7.15 × 10 <sup>-14</sup>		4.02 × 10 <sup>-02</sup>	5.17 × 10 <sup>-12</sup>
900	3.78 × 10 <sup>-09</sup>	1.76 × 10 <sup>-11</sup>	1.54 × 10 <sup>-08</sup>		4.02 × 10 <sup>-02</sup>	6.35 × 10 <sup>-07</sup>
1000	6.97 × 10 <sup>-06</sup>	4.42 × 10 <sup>-10</sup>	2.96 × 10 <sup>-07</sup>		4.02 × 10 <sup>-02</sup>	8.57 × 10 <sup>-05</sup>

### 3.2. Continuum Flow Reactor

The preliminary result obtained with the simulations is the effect of the temperature of the organophosphorus stream on the reactor temperature. Since some of the considered organophosphorus are flame retardants, their entrance into the reactor consumes free radicals responsible for the propagation of combustion chain reaction, lowering the temperature and interrupting the combustion. For this reason, all inlets containing organophosphorus have a temperature higher than 800 K, which is the minimum temperature not to quench the reactor. We assumed it is necessary to vaporize and warm the gaseous phosphorus bearing molecules before entering the combustion chamber. This process is well known in the incineration of liquid species<sup>29</sup>.

Another partial conclusion is that the destruction efficiency is reduced in the continuum reactor. It is possible to consider that incineration is an efficient method to remove the considered molecules. Still, the species increased by 2-3 orders of magnitude at the end of simulations. The less affected molecule was Sarin, while the other species showed a molar fraction of  $10^{-4}$  -  $10^{-6}$ . Only the temperature increase lowered the remaining molar fractions of all compounds. A preliminary parameters optimization was conducted to investigate the optimum values for the temperature, reactant mass flow, and fuel type. This study should be revisited and deepened to include the residence time because this parameter should significantly impact the incinerator efficiency, and more simulations should be included in the optimization to avoid bias.

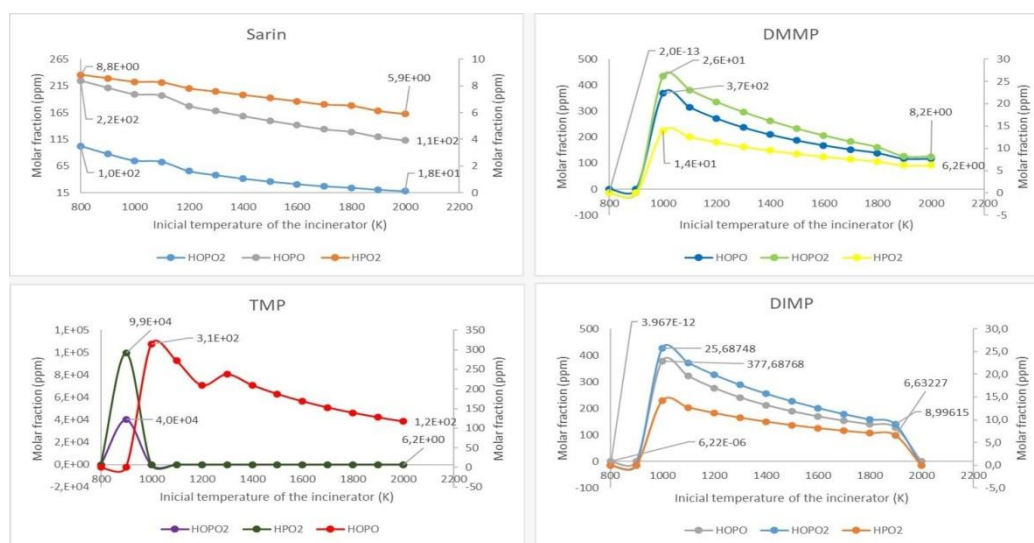
The pollutant molar fraction at the end of the simulation is shown in Table 4. The comparison between the results in Tables 2 and 3 indicates that the flow reactor is less effective in pollutant removal since the combustion products are higher in the continuum system. However, all incinerators work on continuous regime<sup>14,29</sup>, which implicates the optimization of the operational parameters: inlet temperatures, residence time, and reactants mas flow.

**Table 4:** Molar fraction of some pollutants at the end of simulation, considering the biogas (F1) as fuel. All simulations were conducted at 1.0 atm.

Temperature (K)	Sarin					
	HOPO <sub>2</sub>	HPO <sub>2</sub>	HOPO	HF	CO <sub>2</sub>	CO
800	$3.85 \times 10^{-4}$	$1.13 \times 10^{-6}$	$1.87 \times 10^{-5}$	$4.52 \times 10^{-4}$	$9.07 \times 10^{-2}$	$4.25 \times 10^{-3}$
900	$6.53 \times 10^{-4}$	$2.16 \times 10^{-6}$	$5.19 \times 10^{-5}$	$8.85 \times 10^{-4}$	$9.40 \times 10^{-2}$	$2.84 \times 10^{-3}$
1000	$4.33 \times 10^{-4}$	$4.33 \times 10^{-4}$	$9.12 \times 10^{-5}$	$8.96 \times 10^{-4}$	$9.26 \times 10^{-2}$	$4.06 \times 10^{-3}$
	TMP					
800	$3.42 \times 10^{-14}$	$1.02 \times 10^{-17}$	$9.26 \times 10^{-16}$		$3.28 \times 10^{-2}$	$9.94 \times 10^{-11}$
900	$2.11 \times 10^{-11}$	$4.43 \times 10^{-16}$	$1.76 \times 10^{-13}$		$3.28 \times 10^{-2}$	$6.24 \times 10^{-11}$
1000	$2.71 \times 10^{-5}$	$2.24 \times 10^{-11}$	$1.54 \times 10^{-9}$		$3.28 \times 10^{-2}$	$1.36 \times 10^{-5}$
	DIMP					
800	$2.20 \times 10^{-14}$	$1.93 \times 10^{-15}$	$2.93 \times 10^{-11}$		$1.16 \times 10^{-9}$	$4.15 \times 10^{-10}$
900	$2.02 \times 10^{-11}$	$1.17 \times 10^{-11}$	$1.79 \times 10^{-9}$		$1.42 \times 10^{-9}$	$3.57 \times 10^{-9}$
1000	$9.58 \times 10^{-9}$	$2.28 \times 10^{-9}$	$3.94 \times 10^{-8}$		$1.59 \times 10^{-7}$	$2.49 \times 10^{-6}$

	DMMP				
800	$3.63 \times 10^{-14}$	$8.24 \times 10^{-18}$	$3.27 \times 10^{-15}$	$3.28 \times 10^{-02}$	$9.93 \times 10^{-11}$
900	$4.88 \times 10^{-09}$	$1.23 \times 10^{-09}$	$1.10 \times 10^{-11}$	$3.28 \times 10^{-02}$	$2.96 \times 10^{-09}$
1000	$4.34 \times 10^{-06}$	$5.53 \times 10^{-07}$	$6.47 \times 10^{-10}$	$3.28 \times 10^{-02}$	$3.01 \times 10^{-06}$

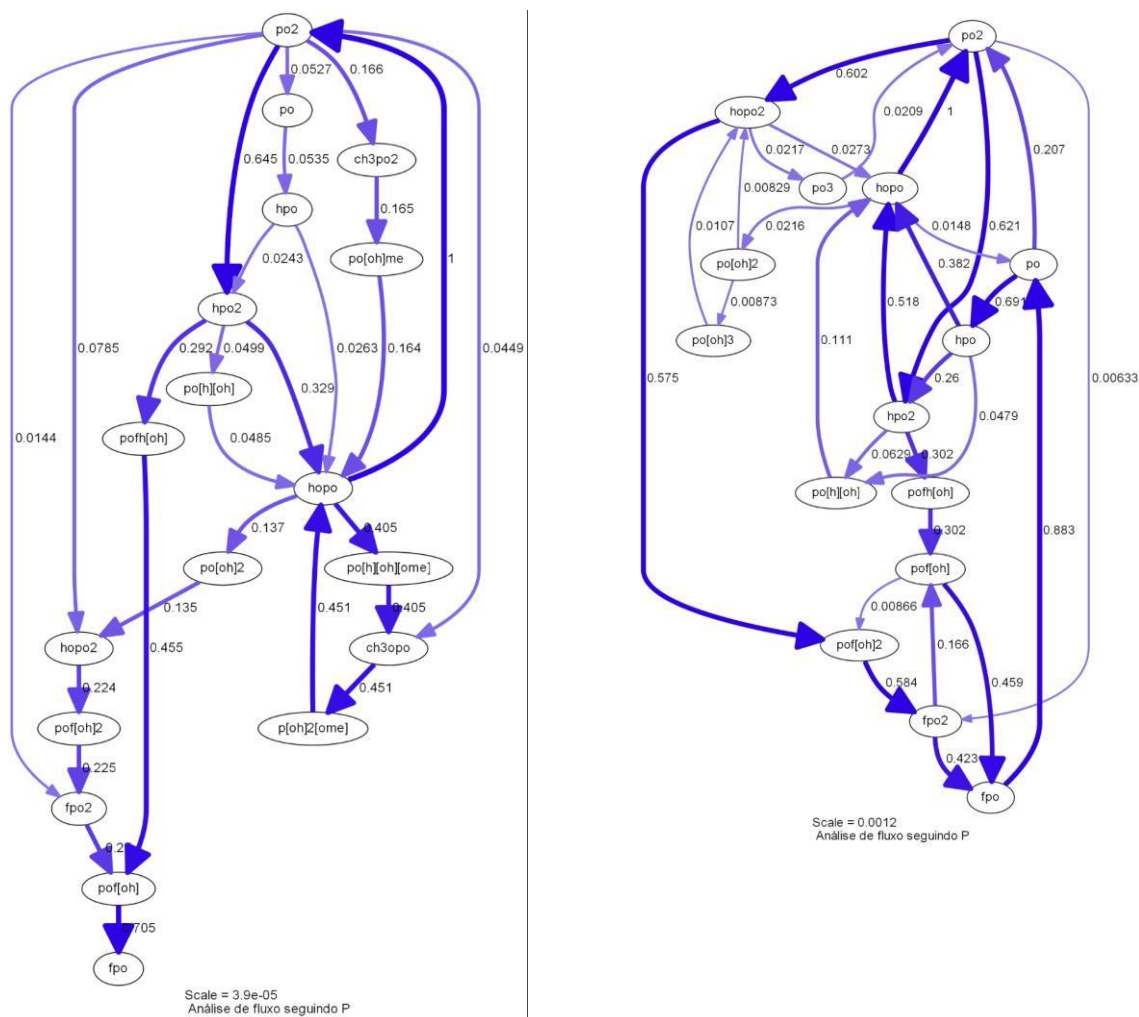
Figure 2 presents the phosphorous-bearing pollutants in a large range of temperatures (values in parts per million, ppm). In all cases, the temperature increment lowers all species' molar fraction, independent of the original organophosphorus. Except for the Sarin case, the pollutants peak near 1000K. At higher and lower temperatures, their molar fraction decreases. The pollutants formed from Sarin peak at 800 K, indicating that the molecules have different decomposition channels.



**Figure 2:** Pollutant molar fraction, in ppm, at the end of simulations in function of the initial temperature. The simulations were conducted with biogas as fuel and 1.0 atm.

### 3.3. Flow Analysis

The results of the flow analysis of the Sarin decomposition in the presence of F1 and F2 are shown in Figure 3. The flow analysis of the other organophosphorus will not be shown due to space limitations. The schemes show each fuel blend's impact on the formation of organophosphorus compounds during the combustion. Depending on the fuel used, the atomic flux of phosphorus changes. We can observe in both graphs the critical intermediates for the phosphorous flux, like PO, PO<sub>2</sub>, and HPO. All these species were identified previously by experiments<sup>24,28</sup>. The change in fuel from biogas to ethane changes the flow of species. For example, in the presence of ethane, PO can be formed from PO<sub>2</sub> and decomposes back into PO<sub>2</sub>. While in the presence of biogas, the reaction sequence is PO<sub>2</sub> → PO → HPO. Both flow analyses help the identification of intermediates during ignition and the formation FPO intermediate. The flow analysis considering carbon confirmed the participation of CH<sub>3</sub> radical during ignition, leading to CO, which will be converted into CO<sub>2</sub> as the reaction chain proceeds.



**Figure 3:** Flow analyses of the phosphorous atom during Sarin thermal degradation at the fuel ignition.

## 4. CONCLUSIONS

A kinetic model proposed in the literature was tested to evaluate the incineration of organophosphorus compounds. The thermal decomposition of four different compounds with four different fuel blends was investigated. The temperature effect and two distinct combustion regimes (batch and continuous) were also investigated.

As expected, the higher temperatures provide the most effective thermal destruction of the pollutants. But except Sarin, DMP, DIMP, and TMMP are less reactive and not prone to complete degradation at  $T < 1000$  K. But at higher temperatures, as indicated by the literature, thermal degradation is a good method to remove organophosphorus compounds.

The investigation of different fuel blends showed that the organophosphorus decomposition depends on the chosen fuel. Biogas can produce more  $\text{CO}_2$  in the product stream, while other fuels are not so effective in decomposing the compounds. The flow analyses pointed out that the  $\text{CO}$  and  $\text{CO}_2$  affect the decomposition mechanism of the organophosphorus.

The following molecules were found as the main combustion products:  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{HOPO}$ ,  $\text{HOPO}_2$ , and  $\text{HPO}_2$ . According to the pollutants' molar fraction at the end of all simulations, all

incineration processes need flue gas treatment after combustion because these pollutants cannot be directly released into the atmosphere.

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