

Environmental effects of volatile organic compounds on ozone layer

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ABSTRACT

Effect of Volatile Organic compounds (VOCs) such as benzene, toluene, ethylbenzene, xylene and other hazardous volatile organic materials on the ozone layer by studying the advantages and disadvantages of this material upon the production of ozone by NO_x gases. The rate of reaction, selectivity and optimum concentration of VOCs which can be used to protect the ozone layer and maximize the accumulation of ozone in the stratosphere using several numerical method. It is found that the rate of accumulation can be controlled by concentration VOCs materials in stratosphere layer.

Key words: Environmental Effect, Ozone Layer, Volatile Organic compounds (VOCs), chlorofluorocarbons (CFCs), rate of reaction, selectivity, polymath software.

INTRODUCTION

Modernization and progress has many disadvantages and one of the main aspects of concern is the pollution, the pollution reaches all of our resources: land, air, and water. The populations are increasing rapidly all over the world and hence the demand for food and other essentials is increasing too, the amount of waste being generated daily by each household is also increasing. One of the most harmful air pollutants are volatile organic compounds (VOCs), which can be evaporated and transport to atmosphere at ambient conditions. Such materials have been making many pollution risks such as: their ability to forming undesired photochemical ozone smog, and the potential to cause carcinogenic and mutagenic. [1] It is worth to mention that VOCs consist typically of light organic substances such as: propane, ether, benzene, methanol, ethanol, carbon tetrachloride and vinyl chloride; however the VOCs which come from crude oil may include many individual VOCs that cannot be determined [2].

In other hand, these materials effect on the human health such as: tiredness, dizziness, confusion, nausea and other problems to humans exposed to VOCs, and cause many diseases like: Anemia, Liver damage, Dysfunction of the central nervous system and Cancer; specifically leukemia. Also VOCs react with stratospheric ozone causing destroying in this sphere and increasing the hole in ozone layer which protect us from ultra violet rays. [3] This will expose people to dangerous ultra violet rays and cause eyes and skin cancer. The most hazard products include hazard VOCs are; hair sprays, petroleum paints, foam plastic products and carburetor. These industries including the hazard Methyl chloroform (1,1,1-trichloro-Methyl chloroethane), which was phased out in 1996, as a very common-used solvent found in such products.

According to the year 2003 official records the local fleet was then composed of 70.2% light-duty vehicles (LDV), 5.8% heavy-duty vehicles (HDV) and 8.8% motorcycles. Relative to the LDV fleet at that time, roughly 82% of the vehicles were powered by gasohol (77-79 % vol gasoline, 21-23% ethanol), 15% ran on hydrated ethanol (95% vol ethanol, 5% water) and ca 0,1 powered by flex-fuel (a mixture of ethanol in gasoline, with concentrations ranging between 0, 50 or 100%) [4]

The modern studies showed that it can be reacted with nitrogen monoxide (NO) and produces nitrogen dioxide (NO₂) which considered as a raw material to produce ozone (O₃) in addition to avoiding the reaction of degradation of ozone by NO as discussed in this research.

2-Literature Review

By May 1993, consumer products containing VOCs and CFCs and related chemicals identified in the 1990 Clean Air Act as most hazard destroying material to the ozone stratosphere are required to have a warning label. The 1990 Clean Air Act orders Environment Protection Agency (EPA) to study VOC used in different industrial fields and report to Congress by 1993 on whether such material must be regulated. By April 1994 EPA listed the consumer products that account for at least 80 % of VOCs released from factories, and classified the regulation issues for such compounds, starting with the worst polluters. Labeling, repackaging, chemical formula changes, fees or other procedures may be used to reduce VOC releases [5].

On January, 20, 1994, William P. L. Carter study the methods of ozone photochemical ranking of VOCs. In his study, he used the mechanism of photochemistry to study the reactions may be occurred in the atmospheric layers for 118 VOCs under different NO_x conditions. By using several measuring model, William could measure the different peak levels of ozone at different 39 different areas in USA. The study carried out that the study of VOCs in their effects on ozone need using quantitative reactivity measurements in addition to incremental reactivity. The results showed that the availability of NO_x in the atmosphere plays major role in reactivity ranking of VOCs with ozone [6].

In 2001, the mechanism and kinetic model of degradation and oxidation of VOCs in the troposphere were introduced using numerical method to analyze the effect of VOCs on ozone layer. Jenkin M. E., Aunders S. M. and Pilling M. J studied the effect of secondary oxides which can be formed from VOCs on the ozone layer by using several numerical method based on data collected from the sphere above Europe. It is worth to mention that studying chemical mechanism of this phenomena is very complex because there are huge number of reactions can be occurred depending on different organic compound and environmental conditions [7].

Altenstedt J., and Pleijel K. studied the potential creation of photochemical ozone for 83 VOCs and calculated their potential to creation at different conditions. The results showed that there is a large variation in the potential of photochemical ozone for VOCs at different conditions. They conclude that using ranking scale will be more useful and the theoretical calculations can typically equal to measuring data. Also, they concluded that the most efficient producers of ozone molecules were isoprene, 2-methyl-2-butene, and acroleine [8].

Butler T.M. and others introduced a new approach to ozone production potential of VOCs using several chemical mechanisms, where the direct effects of VOC on ozone were calculated due to single methodology. The calculations deliver additional detailed information about the intermediate oxidation products of VOC related to ozone production. They found that the potential of producing will be effected by the type of VOCs cause such potential. For example, reactive aromatic and alkenes VOCs produc ozone molecules rapidly, while alkanes need for time to start producing ozone increases in the day after they are emitted [9].

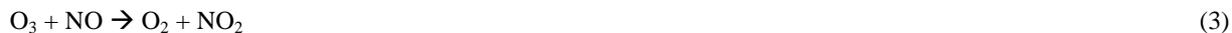
MATERIALS AND METHODS

3- RESEARCH METHODOLOGY

The NO_x is a definition of the mixture of NO₂ and NO, which considered one of the most important to form ozone (O₃) according to Equation (1) and (2). Even when (VOCs) are not present,



Unfortunately, ozone cannot be accumulated in the air sphere because it will be consumed in the reaction represented in Equation (3):



The role of VOC can be summarized in reduce the amount of nitrogen monoxide to prevent occurring of reaction (3) as shown in Equation (4).



VOCs will react with NO to produce NO₂ which is the reactant for ozone production reaction as mentioned in Equation (1) and (2), in other and the ozone will build up. It is worth to mention that OH radicals are also generated among these reactions radicals, which then regenerate NO₂.

As shown above, the formation of ozone depends on the concentration of VOCs and the percent of NO_x in the atmosphere, where if the concentration of VOCs is larger than the concentration of NO_x, the limiting reactant of the reaction is NO_x, while if the concentration of NO_x is larger than the concentration of VOCs, the limiting reactant will be the VOCs and the formation and accumulation of ozone will depend on the concentration of VOCs [10,11]. To control the reactions and make the rate of reaction 2 and 4, the concentration of VOCs should be controlled within the acceptable limits of pollutant VOCs. The rate of ozone accumulation (r_{acc}) can be determined as following:

r_{acc} = rate of reaction 2 – rate of reaction 3

$$r_{\text{acc}} = r_2 - r_3 \quad (5)$$

$$r_2 = k_2 [\text{O}] [\text{O}_2] \quad (6)$$

$$r_3 = k_3 [\text{O}] [\text{NO}] \quad (7)$$

But these concentrations are related to other limiting concentration (NO₂) due to the previous reaction equations.

$$[\text{O}] = [\text{NO}_2] \text{ due to Equation [1]; } [\text{O}_2] \gg [\text{NO}_2]$$

where the percent of oxygen is approximately 21%. (it will not be effective on the reaction rate). So:

$$r_{\text{acc}} = k'_2 [\text{NO}_2] - k_3 [\text{NO}_2] [\text{NO}] = [\text{NO}_2] (k'_2 - k_3 [\text{NO}]) \quad (8)$$

From this approach, the rate of ozone formation depends only on the reduction of NO which described in Equation 4. Then Equation 8 can be written as:

$$r_{\text{acc}} = [\text{NO}_2] (k'_2 - k_3 [\text{VOCs}]) \quad (9)$$

The challenge of this approach is to control the concentration of VOCs to achieve high selectivity and rate of ozone and do not exceed the universal limitation of [NO₂] and [VOCs]. This can be achieved by calculating the optimum concentration of [VOCs] by calculating the selectivity of ozone (O₃) which produced by Equation 2 and consumed by Equation 3 with respect to nitrogen dioxide (NO₂) which produced by Equation 3 & 4 and consumed by Equation 4, with taking into account that the [VOCs] is the limiting reactant for these set of reactions. The mathematical model of this behavior can be determined as following:

$$-d[\text{NO}_2]/dt = k_1 [\text{NO}_2] + k_4 [\text{VOC}]^2 - k_3 [\text{O}_3] [\text{VOC}] \quad (10)$$

$$-d[\text{VOC}]/dt = k_1 [\text{NO}_2] - k_4 [\text{VOC}]^2 - k_3 [\text{O}_3] [\text{VOC}] \quad (11)$$

$$-d[\text{O}_3]/dt = -k_3 [\text{O}_3] [\text{VOC}] \quad (12)$$

The specific reaction constants k_1 , k_3 and k_4 can be determined from Arrhenius law of mechanism:

$$k = A \times \exp (-E/RT) \quad (13)$$

The previous differential equations can be solved by numerical techniques using Polymath software to determine the optimum concentrations of [VOC] with respect to universal limits [11].

RESULTS AND DISCUSSION

The initial conditions of the problem are selected to be as the maximum acceptable concentration of [VOCs], [NO₂] and the natural concentration of ozone [O₃] in stratosphere as shown in Table 1.

Table 1: Initial Conditions [10]

[VOCs]	1000 ppm (average)
[NO ₂]	20 ppm
[O ₃]	0.3 ppm (average)

The values of activation energy (E) and pre-exponential factor (A) are listed in Table. 2.

Table 2: Activation energy (E) and pre-exponential factor (A) for studied reactions. [11]

Reaction	E (KJ/mol)	A × 10 ⁻¹²
1	56.57	1.32
3	80.9	20
4	70 (average)	42

By applying Equation 13 at temperature of 300K, the specific rate of reaction for reactions 1, 3 and 4 are summarized in Table3.

Table 3: The specific rate of reaction for reactions 1, 3 and 4

Reaction	Specific rate of reaction
1	186.63
3	0.164
4	27.25

Now, the results of optimum [NO₂] and [VOCs] will be determined by Polymath Software also the rate of reaction will be determined between t= 0 and t= 10 day,

CONCLUSION

- 1-The NO_x considered one of the most important to form ozone (O₃) Even when (VOCs) are not present,
- 2 - VOCs will react with NO to produce NO₂ which is the reactant for ozone production reaction .
- 3 - the formation of ozone depends on the concentration of VOCs and the percent of NO_x in the atmosphere.
- 4 - where if the concentration of VOCs is larger than the concentration of NO_x, the limiting reactant of the reaction is NO_x, while if the concentration of NO_x is larger than the concentration of VOCs, the limiting reactant will be the VOCs and the formation and accumulation of ozone will depend on the concentration of VOCs.
- 5 - the concentration of VOCs should be controlled within the acceptable limits of pollutant VOCs.
- 6 - the results of optimum [NO₂] and [VOCs] will be determined by Polymath Software also the rate of reaction will be determined between t= 0 and t= 10 day.

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