Prediction of Uncontrolled Refueling Emissions from Gasoline Vehicles Based on Mathematical Models

Daming Liu¹*, Xianglin Zhong², Yaqi Li³, Xudong Zhen¹, Shaoyun Lu¹, Yuanyuan Xue¹

¹School of Automobile and Transportation, Tianjin University of Technology and Education, Tianjin, 300222, China
²National Engineering Laboratory for Mobile Source Emission Control Technology, China Automotive Technology and Research Center Co. Ltd, Tianjin, 300300, China
³Department of Railway Engineering, Tianjin Railway Technical and Vocational College, Tianjin 300240, China

*Corresponding author’s e-mail: ldam@tju.edu.cn

Abstract. The prediction of the uncontrolled refueling vapor generation of gasoline vehicles is the basis of the refueling emission control. It is of great significance to understand the mechanism of the gasoline vapor generation during the refueling process and to develop the refueling emission control devices. In this paper, the prediction of the refueling vapor generation of gasoline vehicles under uncontrolled conditions was conducted by using the empirical models, the steady state model and the time-varying diffusion model, respectively, and the prediction results were verified with the test results. The research results showed that the time-varying diffusion model had better adaptability and prediction accuracy than the empirical model. And the more influencing factors can be considered. But the verification and correction for this model were also needed by using experimental data. The empirical models had better prediction accuracy under specific conditions. However, due to the limitations of experimental conditions, the models lacked universality, which was an inherent defect of the empirical models. The steady-state model ignored the non-uniformity of fuel vapor concentration distribution in the fuel tank, resulting in a large error in the prediction results.

1. Introduction

At the end of 2019, the number of civilian vehicles in China had reached 260 million [1]. While vehicles bring convenience to our lives, they also cause problems such as energy crisis and environmental pollution. As the exhaust emission is removed from the source of automobile, the proportion of fuel evaporative emission is increasing. The Limits and Measurement Methods for Emissions from Light-duty Vehicles (China 6) promulgated in 2016 made stricter limits on the test requirements and evaporative emissions. And the refueling emission test was added to limit the fuel evaporative pollutant during the vehicle refueling process [2]. The prediction of refueling vapor generation under uncontrolled conditions is the basis of pollutant emission control. It is of great significance to understand the refueling emission mechanism and formulate control measures.

In 1972, California took the lead in writing fuel vapor recovery into the state bill, prompting researchers to start paying attention to the refueling emissions from gasoline vehicles. In 1972, Smith put the fuel tank of a gasoline vehicle in mini-SHED, changed the Reid vapor pressure (RVP) and the...
temperature of gasoline for multiple tests, and finally proposed an empirical model of refueling emissions under uncontrolled conditions [3]. In 1976, Hochhouser and Campion conducted a test similar to Smith’s test, measured the mass and volume of the fuel vapor at the same time, and obtained the specific mass (g/gallon) and specific volume (gallon/gallon) form of refueling emissions [4]. In 1985, Rothman and Johnson conducted the refueling tests on 8 different vehicles and 4 fuels with different RVP, fuel temperatures and tank temperatures. Based on the test results, a refueling emission empirical model was obtained [5]. In 1988, Cingle et al. also conducted refueling tests on 22 different vehicles and 3 fuels with different RVP, refueling temperatures and tank temperatures, and obtained another empirical model for predicting refueling emissions [6]. In 2007, Quigley conducted multiple uncontrolled refueling emissions studies on 12 vehicles to analyse the emissions of pollutants during refueling of gasoline vehicles [7]. In 2010, Reddy derived the steady-state model of fuel vapor generation by using the gasoline vapor-liquid equilibrium equation [8].

In China, Zhong and Huang studied the fuel vapor volatilization in the gasoline storage and transportation, and established a mathematical model to evaluate the fuel evaporative emissions during the refueling process of tank trucks [9]. In 2010, He et al. used the principle of molecular diffusion mass transfer to establish a mathematical model for the refueling process, and analysed the effects of factors such as the average tank temperature, the RVP, and the fuel temperature [10-12]. In 2015, Liu et al. analysed the current status of China's gasoline vehicle evaporative emissions, compared evaporative emission control with foreign countries, and combined with China's specific national conditions, pointed out that the adoption of ORVR system can effectively control the problem of refueling emissions in China [13].

This paper aims to predict the refueling emissions of gasoline vehicles under uncontrolled conditions with different models, analyse the advantages and disadvantages of each model by comparing the proposed conditions, principles and prediction results of different models, in order to further improve the prediction models.

2. Uncontrolled Refueling Emission Prediction Models

2.1. Empirical models

The empirical models were obtained by curve fitting using experimental data. Since the data can only cover limited test conditions, the application of the models has certain limitations.

1) Smith proposed an uncontrolled refueling emission model as follows [3]:

\[
E1 = \exp(-0.02645 + 0.01155 T_D - 0.01226 T_f + 0.002246 RVP)
\]

where \(E1\) is the refueling vapor generation (g/gallon); \(T_D\) is the dispensed fuel temperature (°F); \(T_f\) is the tank temperature (°F); \(RVP\) is the Reid vapor pressure of the fuel (psi).

2) Hochhauser and Campion proposed a refueling emissions model as follows [4]:

\[
E2 = \exp(-1.23 + 0.0185 T_D + 0.0017 T_f + 0.118 \cdot RVP)
\]

where \(E2\) is the refueling vapor generation (g/gallon); \(T_D\) is the dispensed fuel temperature (°F); \(T_f\) is the tank temperature (°F); \(RVP\) is the Reid vapor pressure of the fuel (psi).

Since the specific volume model is not widely used, it is not listed here. For details, please refer to Reference [4].

3) The empirical model of uncontrolled refueling emissions proposed by Rothman and Johnson is as follows [5]:

\[
E3 = -5.909 - 0.0949 \Delta T + 0.0884 T_D + 0.485 \cdot RVP
\]
where $E_3$ is the refueling vapor generation (g/gallon); $\Delta T = T_f - T_d$, $T_d$ is the dispensed fuel temperature of the (°F); $T_f$ is the temperature of the fuel in tank (°F); $RVP$ is the Reid vapor pressure of the fuel (psi).

(4) The empirical model obtained by Cingle et al. based on the experimental data is as follows [6]:

$$E_4 = \exp(-1.2798 - 0.0049\Delta T + 0.0203T_d + 0.1315RVP) \quad (4)$$

where $E_4$ is refueling vapor generation (g/gallon); $\Delta T = T_f - T_d$, $T_d$ is the temperature of the dispensed fuel (°F); $T_f$ is the tank temperature (°F); $RVP$ is the Reid vapor pressure of the fuel (psi).

The above empirical models can only characterize the influence of RVP, fuel temperature, and tank temperature on refueling emissions. Due to fitting based on limited experimental data, the universality of the models needs to be verified.

2.2. Steady-state model

Sam R. Reddy used the gasoline vapor-liquid equilibrium equation to establish a mathematical model to estimate the refueling vapor generation as a function of tank and dispensed fuel RVPs and temperatures, and air entrainment [8].

The gasoline vapor pressure equation was used as follows:

$$P_{HCdisp} = A \cdot T_{disp} \cdot RVP \cdot \exp\left(-\frac{B}{T_{disp}}\right) \quad (5)$$

where $P_{HCdisp}$ is the vapor pressure of the fuel (psi); $T_{disp}$ is the dispensed fuel temperature (°F); $RVP$ is the Reid vapor pressure of the fuel (psi); $A$ and $B$ are constants 25.61 and 2789.78, respectively.

Using equation (5), combined with the ideal gas state equation, the mass of fuel vapor in the top space of the tank can be obtained as follows.

$$E_5 = M_{HC} \cdot \left(\frac{fP_{atm}}{RT_{disp}} + \frac{P_{atm} - P_{HCtank}}{RT_{tank}}\right) \cdot \frac{P_{HCdisp}}{P_{atm} - P_{HCdisp}} \quad (6)$$

where $f$ is the volume ratio of air entrainment to dispensed fuel, $f=0$ in our calculations; $R$ is the universal gas constant 0.3187; $P_{atm}$ is the atmospheric pressure (psi); $T_{disp}$ is the dispensed fuel temperature (°F); $T_{tank}$ is the tank temperature (°F); $P_{HCdisp}$ is the dispensed fuel vapor pressure (psi); $P_{HCtank}$ is the vapor pressure of the fuel in tank (psi).

2.3. Time-varying diffusion model

During the refueling process, as the liquid fuel is dispensed into the fuel tank, the fuel level continues to rise, and the mixture of air and fuel vapor in the fuel tank moves upward. At the same time, the liquid fuel in the fuel tank further evaporates; the fuel vapor diffuses in the gas space, and finally is expelled from the fuel tank. Therefore, the fuel vapor emission process from the tank is a time-varying diffusion problem with an unfixed mass transfer interface (fuel surface).

Since the air is insoluble in liquid fuel, the refueling emissions problem reduces to the diffusion problem of one component A (fuel vapor) through another stagnant component B (air). According to the continuity equation and Fick diffusion law, the differential equation of fuel vapor mass transfer can be obtained. Solving this equation can obtain the molar concentration distribution of fuel vapor in the top space of the tank and its change with the refueling time. The molar flux $N_{HC}$ at the fuel vapor outlet of the tank (connected to the canister) can be obtained from the fuel vapor concentration distribution in the vertical direction of the tank.
where $c_{A,\text{surf}}$ is the molar concentration of fuel vapor at the fuel surface (mol/m$^3$), which depends on the temperature and RVP of the dispensed fuel; $c_{\text{av}}$ is the molar concentration of the average fuel vapor in the top space of the tank (mol/m$^3$), which depends on the temperature and RVP of the fuel in the tank; $D_{\text{m}}$ is the gas molecule diffusion coefficient; $t$ is the refueling time; $H_0$ is the height of the fuel level in the tank before dispensing fuel(m); $H_1$ is the height of the fuel vapor outlet of the tank (m); $u_{\text{surf}}$ is the rising velocity of the fuel level (m/s), which depends on the refueling rate and fuel tank shape; $\phi$ is the dimensionless molar average velocity (m/s).

Integrating equation (7) within the total refueling time $\tau$, the total mass of the fuel vapor escaping from the fuel vapor outlet of the tank can be obtained:

$$E_{6} = M_{\text{HC}} \int_{0}^{\tau} N_{\text{HC}} S_{\text{surf}} \, dt$$

where $M_{\text{HC}}$ is the molar mass of gasoline vapor (g/mol); $S_{\text{surf}}$ is the area of the fuel surface (m$^2$).

It can be seen that the time-varying diffusion model can describe the refueling emission process in more detail compared with the empirical model and the steady-state model. It can not only reflect the effects of the dispensed fuel temperature, tank temperature and RVP, but also reflect the refueling rate, fuel tank shape, the height of the fuel vapor outlet, and the remaining fuel in the tank.

3. Simulation conditions

In order to compare the prediction capabilities of the above models for the refueling emissions, the test conditions in [10] were selected as the simulation conditions, and the experiment results were used to verify the simulation results. The basic test conditions were shown in Table 1. When changing the simulation conditions by changing a certain parameter, the other parameters still maintained the values in Table 1. The molar mass of gasoline vapor was based on the data given in [9].

| Item                       | Value  |
|----------------------------|--------|
| Tank volume (L)            | 67     |
| Diameter of fuel inlet (mm)| 36     |
| Diameter of fuel vapor outlet (mm) | 6     |
| Refueling rate (L/min)     | 40     |
| Refueling volume (L)       | 50     |
| Remaining fuel in tank (L) | 12     |
| Molar mass of gasoline vapor (g/mol) | 65.51 |
| RVP (kPa)                  | 61     |
| Tank temperature (K)       | 293    |
| Dispensed fuel temperature (K) | 299   |

4. Results and discussion

4.1. The influence of the tank temperature on refueling emission

Figure 1 showed the effect of the tank temperature on the refueling emissions. Maintaining the RVP to 61 kPa and the dispensed fuel temperature at 299 K, the tank temperature was changed to values of 293,
295, 297, 299, 301, and 303 K, respectively. Substituting the above data into each prediction model, the refueling emissions at the corresponding tank temperature were obtained.

![Figure 1. The influence of the tank temperature on the refueling emission](image)

The tank temperature was changed drastically with the changes in the ambient temperature and the driving conditions. Therefore, it is very important for the mathematical model to accurately predict the fueling emissions caused by the tank temperature change.

As shown in Figure 1, from the test data, the increase in the tank temperature would aggravate the refueling emission. Through the above analysis of the refueling process in section 2.3, it can be seen that there are two sources of refueling emissions. One is the evaporation of fuel in the tank before refueling. And the other one is the further evaporation of fuel due to fuel dispensing. The change in concentration gradient in the tank causes the fuel vapor to diffuse and form additional emissions. Since the fuel vapor outlet of the tank is connected to the atmosphere, the pressure in the tank is basically maintained at atmospheric pressure. As the temperature of the tank increases, the partial pressure of fuel vapor in the tank will increase. That is to say, the molar concentration of fuel vapor increases, so refueling emission should increase [11].

The trends obtained by different models were inconsistent. E1, E2, and E6 all got the same trend as the test result. The predicted value of E6 was the closest to the test result, and the maximum deviation was only 2.03%. The E1 and E2 models underestimated the effect of the tank temperature on refueling emission at high temperatures, and overestimated it at low temperatures. The E3, E4 and E5 models failed to predict the correct trend.

4.2. The influence of the RVP on refueling emission

Figure 2 showed the effect of the RVP on the refueling emissions. Maintaining the tank temperature at 293 K and the dispensed fuel temperature at 299 K, the RVP was changed to values of 56, 58, 61kPa, respectively. The RVP is one of the indicators that characterize the gasoline volatility, which is clearly stipulated in the standard of the gasoline for vehicles, so there was little change. However, the model can reflect the influence of the RVP change from different fuels (such as the addition of ethanol) on refuel emissions [8]. The higher the RVP, the higher the volatility of gasoline. This caused more fuel vapor accumulating in the top space of the fuel tank before the refueling, and more fuel vapor evaporating during the refueling.

As shown in Figure 2, the models all predicted the correct trend of the refueling emissions increasing with the increase of the RVP, which is consistent with the trend of the test results. However, the predicted value of the E3 model was nearly twice as high as the test result, which had no reference value. The prediction results of the E4 and E5 models were close but also significantly higher than the test result. The prediction results of the E1 and E2 models were close, although they are also higher.
than the test result, but the highest exceeds only about 8%. The prediction result of E6 model was lower than the test result -3.75% at lower RVP (56kPa), but the deviation was only 1.56% at higher RVP (61kPa). Generally speaking, the time-varying diffusion model was closest to the experimental data.

Figure 2. The influence of the RVP on the refueling emission

4.3. The influence of the dispensed fuel temperature on refueling emission

Figure 3 showed the effect of the dispensed fuel temperature on the refueling emissions. Maintaining the RVP to 61kPa and the tank temperature at 299 K, the dispensed fuel temperature was changed to values of 293, 295, 297, 299, 301, and 303 K, respectively.

The lower temperature of the dispensed fuel can further reduce the temperature of the fuel vapor in the fuel tank, resulting in the liquefaction of the fuel vapor, thereby reducing fuel emissions [9]. Since the fuel in the gas station is stored in the underground fuel tank, the temperature of the refueling fuel basically does not change much. The model prediction results can further indicate that one of the measures to reduce refueling emission is to reduce the fuel storage temperature in the gas station.

As shown in Figure 3, the higher the dispensed fuel temperature, the higher the refueling emissions. The models all predicted the correct trend. But the prediction result of the E3 model was much higher than the test value, about 91.5% when the dispensed fuel temperature was 303K, which had no
The prediction results of the E4 and E5 models were also significantly higher than the test values. The maximum deviation of E5 reaches 55% when the fuel temperature was 303K. The prediction results of the E1, E2 and E6 models were close to the test values, and the maximum deviation occurred when the fuel temperature was 303K, which was 9.8%, 13.8% and -4.1%, respectively.

5. Conclusion
In this paper, the predictions of the refueling vapor generation of gasoline vehicles under uncontrolled conditions were conducted by using the empirical models, the steady state model and the time-varying diffusion model, respectively, and the predicted results were verified with the test results. The main conclusions were as follows:

(1) The increase in the tank temperature would aggravate the refueling emission. The prediction result of the time-varying diffusion model (E6) was the best, with a maximum deviation of only 2.03%. While the empirical models (E3, E4) and the steady-state model (E5) failed to give the correct trend.

(2) The refueling emissions increased with the increase of the RVP and the dispensed fuel temperature. Each model obtained the correct trend. The prediction values of the empirical models (E3, E4) and the steady-state model (E5) deviated too much from the test data. The time-varying diffusion model (E6) gave more accurate prediction results. The maximum deviation for the RVP and the dispensed fuel temperature were -3.75% and -4.1% respectively, but lower than the test results.

(3) Although E1, E2, E3, and E4 models were all empirical models, E1 and E2 models had better adaptability, which depended on the amount of data used to fit the model. The lack of the universality was an inherent defect of the empirical of models. The steady-state model (E5) ignored the non-uniform distribution of fuel vapor concentration in the tank and the diffusion process of fuel vapor during refueling, resulting in a large deviation from the actual refueling process. The E6 model was derived based on the principle of the time-varying diffusion, which had better adaptability, but also required the further verification and correction with experimental data.

Acknowledgements
The study is financially supported by the National Natural Science Fund of China (No. 51706155) and The Open Fund of the National Engineering Laboratory for Mobile Source Emission Control Technology (No. NELMS2017B07).

References
[1] National Bureau of Statistics. (2020) 2019 National Economic and Social Development Statistical Bulletin. http://www.chinanews.com/auto/2020/02-28/9107518.shtml
[2] Ministry of Ecology and Environment of China. (2016) Limits and Measurement Methods for Emissions from Light-duty Vehicles (China 6). China Environmental Science Press, Beijing.
[3] Smith M. (1972) An Investigation of Passenger Car Refueling Losses. SAE Technical Paper 720931.
[4] Hochhauser, A.M., and Campion, R.J. (1976) An Experimental Study of Vehicle Refueling Emissions. SAE Technical Paper 760307.
[5] Rothman, D., and Johnson, R. (1985) Refueling Emissions from Uncontrolled Vehicles, U.S. Environmental Protection Agency. EPA Technical Report EPA-AASDSB-85-6.
[6] Cingle P, McClement D. (1988) Study of uncontrolled automotive refueling emissions. Final report. Automotive Testing Labs., Inc., East Liberty, OH (USA).
[7] Quigley CJ. (2007) Refueling and evaporative emissions of volatile organic compounds from gasoline powered motor vehicles. THE UNIVERSITY OF TEXAS AT AUSTIN.
[8] Reddy, S. (2010) Mathematical Models for Predicting Vehicle Refueling Vapor Generation. SAE Technical Paper 2010-01-1279.
[9] Huang, W., Zhong Q. (2004) NUMERICAL ANALYSIS OF PETROLEUM PRODUCTS EVAPORATION UNDER UNSTEADY CONDITIONS II. Numerical Analysis and
Application Examples. ACTA PETROLEI SINICA (PETROLEUM PROCESSING SECTION), 20(01):54-59.

[10] He, J., He, R. (2015) Mathematical model of refueling emission for gasoline vehicles and influencing factors analysis. Advanced Materials Research, 1070-1072, 1917-1924.

[11] He, R., Cai, J., He, J. et al. (2010) Experimental method of gasoline evaporation loss in refueling process of vehicle. JOURNAL OF TRAFFIC AND TRANSPORTATION ENGINEERING, 10(3): 57-61.

[12] Wei, H., He, R., Cai, J. (2010) Mathematical models of refueling emission for car with ORVR system. JOURNAL OF TRAFFIC AND TRANSPORTATION ENGINEERING, 10(1): 56-59.

[13] Yang, X., Liu, H., Cui, H., et al. (2015) Vehicular volatile organic compounds losses due to refueling and diurnal process in China:2010-2015. Journal of Environmental Sciences, 33:88-96.