Research Paper

Dynamic simulation of liquefied petroleum gas vaporisation for burners

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HIGHLIGHTS

- A thermodynamic model is developed to investigate the vaporisation characteristics of LPG in a cylinder.
- Transient characteristics of LPG vaporisation are analysed under various conditions.
- The effects of various parameters on LPG vaporisation and the residues in LPG are analysed.
- A graphical procedure is proposed to determine the design value of Wobbe Index for burners.

ARTICLE INFO

ABSTRACT

This study numerically describes the transient behaviours of liquefied petroleum gas (LPG) natural vaporisation in a cylinder using an experimentally validated model. The model can be applied to easily predict transient compositions and thermophysical properties during the vaporisation process under various conditions. A simple graphical design procedure is presented to determine the Wobbe Index and the corresponding composition as design references for gas burners to avoid incomplete combustions. The effects of initial composition, surrounding temperature and discharge rate of LPG on both the LPG natural vaporisation and the residue amount in the cylinder are simulated and investigated. The results demonstrate that the present work may serve as a useful tool to evaluate the LPG behaviours throughout the vaporisation, design or retrofit gas burners, and predict the unburned residue.

1. Introduction

Liquefied petroleum gas (LPG) is mainly composed of propane (C_3H_8) and *n*-butane (C_4H_{10}) with some propylene (C_3H_6), butylene (C_4H_8), and other minor compositions of hydrocarbons. LPG is in gaseous form at ambient temperatures and pressures. Due to a dramatic reduction in the volume after being liquefied, LPG is commonly stored and transported in liquid form in pressurised steel cylinders. This makes LPG a popular domestic fuel in rural and remote areas, even in some urban regions away from natural gas transmission networks [1]. For instance, Chinese total LPG consumption for householders was 21.73 million tons in 2014 [2].

The common way for domestic and commercial burners to use LPG is to supply liquid LPG in commercially available cylinders without thermal insulation and then to use it in gaseous form. The liquid-to-vapour phase change occurring within the cylinder is called spontaneous (or natural) vaporisation in which process the heat for vaporisation comes from the liquid itself and/or from the surroundings and components with lower boiling points vaporise easier and earlier. The properties of both the liquid and the vapour vary continuously with the change in LPG compositions over time. The minimum inlet pressure of a gas regulator automatically modulates high-pressure gas to a safe pre-determined limit for gas burners, so the cylinder cannot be completely emptied and the remaining liquid is called as the residue. It means that if the vapour pressure in the cylinder is less than the required minimum value, the natural vaporisation process will be completed.

To estimate the physical properties of LPG and the residue amount, it is necessary to know the composition [3]. The chromatography method is usually applied to determine the composition of LPG after analysing its sample [4–7]. However, it is hard to adopt this method to continuously determine the composition that changes instantaneously through the vaporisation process. Some mathematical models were developed to predict the dynamic behaviours of LPG spontaneous

Nomenclature

A_A	antoine parameter
a	coefficient in SRK equation
B_A	antoine parameter
b	coefficient in SRK equation
C_A	antoine parameter
C_p	specific heat ($kJ\,kg^{-1}\,K^{-1}$)
D	Inner Diameter (m)
e	ratio of moles of gaseous LPG to total moles of LPG
$\hat{f}$	fugacity (Pa)
H	height of liquid level (m)
H_T	height of cylinder (m)
K	phase equilibrium constant
k	overall heat transfer coefficient ($kW\,m^{-2}\,K^{-1}$)
M	molecular mass ($kg\,mol^{-1}$)
m_g	mass of gaseous LPG (kg)
m_{go}	mass flow rate (i.e. discharge rate) ($kg\,s^{-1}$)
m_l	mass of liquid LPG (kg)
P	pressure (Pa)
P_{sat}	saturation pressure (Pa)
Q	heat (kJ)
R	universal gas constant ($J\,mol^{-1}\,K^{-1}$)
r	specific latent heat ($kJ\,kg^{-1}$)
T	temperature (K)
t	time (s)
V	mole volume ($m^3\,mol^{-1}$)
w	mass fraction (%)
x	mole fraction in liquid phase (%)
y	mole fraction in vapour phase (%)
Z	compressibility factor
z	total mole fraction (%)

Greek

ρ	density ($kg\,m^{-3}$)
$\hat{\phi}$	fugacity coefficient
ω	acentric factor

Subscripts

0	standard state
c	critical point
Cy	cylinder
Env	surroundings
g	gaseous phase
i	component i
j	component j
l	liquid phase

vaporisation in the cylinder [3,8,9]. However, such models are typically valid for specific and rigorous assumptions. The LPG within the cylinder was assumed to be ideal [3,8,9]. Furthermore, Yan [8] assumed that the change in LPG composition did not alter the values of some thermodynamic properties and the ratio of the pressure to the temperature of LPG kept constant. Tian and Jiang [3] treated the mass fraction of each component as an equivalent of its mole fraction and assumed that the LPG temperature remained unchanged throughout the vaporisation [3]. These above mentioned assumptions are in conflict with the practical natural vaporisation and may cause some limitations of the models.

This work emphasises the need to account for the non-ideal behaviour of both the liquid and the vapour phases in the pressurized steel cylinder and the importance of variable physical properties in investigating the real LPG spontaneous vaporisation process. The main objective of this study is to present a comprehensive model and explore the detailed transient characteristics of LPG natural vaporisation process for gas burners, which can provide a basis for designing or retrofitting burners to get good combustion performance and predicting the residue amount. First, a dynamic model is established which prediction accuracy is validated by using the previous experimental data. Further, the transient behaviours of LPG vaporisation are obtained and analysed, with special emphasis on variation of combustion properties of vapour LPG. Finally, the effects of initial composition, surrounding temperature and discharge rate on the natural vaporisation and the residue amount are discussed based on the simulation results.

2. Model development

2.1. Description

As shown in Fig. 1, when the user opens the reducing valve to use LPG, the vapour flows out. Then the vapour pressure in the cylinder reduces and the equilibrium no longer exists. The liquid LPG has to vaporise immediately to mitigate the drop in the pressure and to regain a vapour-liquid equilibrium (VLE) condition. Due to no temperature difference, the latent heat of vaporisation is only from the liquid itself at the beginning. The liquid temperature thus decreases, which generates the temperature difference between inside and outside of the cylinder.

The heat for vaporisation then comes from both the liquid and the surroundings.

2.2. Model assumptions

Five assumptions have been made concerning the simulation.

- The temperature is uniformly distributed in the cylinder and the vapour has the same temperature as the liquid.
- The cylinder wall and the LPG are in the same temperature.
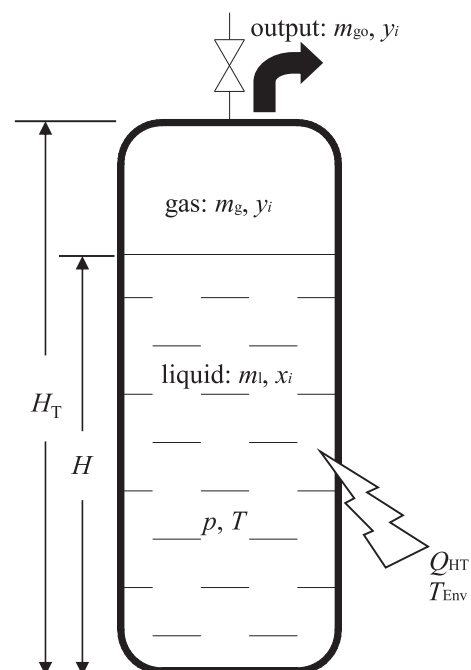- The cylinder's surrounding temperature is constant throughout the

Fig. 1. Spontaneous vaporisation of LPG in a cylinder.

vaporisation.

- Heat transfer by radiation to the cylinder is neglected.
- The discharge rate of the vapour is equal to the evaporation rate of the liquid.

2.3. Vapour-liquid equilibrium

For a multi-component mixture, a VLE condition requires that the fugacity of each component for vapour and liquid phases is identical [10]. The fugacity is defined by an equation related to both the chemical potential and the pressure of an ideal fluid. Both the LPG vapour and the liquid LPG in a real pressure cylinder are non-ideal. Based on the equation of state (EOS) approach, the VLE in the cylinder can be written as [10]:

$$\widehat{f}_{g,i} = \widehat{f}_{l,i} \quad i = 1,...,n \tag{1}$$

where

$$\widehat{f}_{g,i} = \widehat{\phi}_{g,i}(P,T)y_i P \tag{2}$$

$$\widehat{f}_{l,i} = \widehat{\phi}_{l,i}(P_{sat,i},T)x_i P \tag{3}$$

In this study, the SRK EOS (see Appendix A) is used to predict vapour-liquid coexistence of LPG due to its advantages in dealing with the VLE of hydrocarbon mixtures [10].

Then the VLE condition is described as:

$$\widehat{\phi}_{g,i} y_i = \widehat{\phi}_{l,i} x_i, \quad i = 1,...,n \tag{4}$$

The phase equilibrium constant for component i is:

$$K_i = \frac{y_i}{x_i} = \frac{\widehat{\phi}_{l,i}}{\widehat{\phi}_{g,i}}, \quad i = 1,...,n \tag{5}$$

As shown in Fig. 2, the convergence criterion is Eq. (6) in this work.

$$\left| \frac{\widehat{\phi}_{l,i} x_i}{\widehat{\phi}_{g,i} y_i} - 1 \right| < 10^{-7}, \quad i = 1,...,n \tag{6}$$

In general, only initial composition of liquid LPG inside the cylinder and the cylinder's surrounding temperature are available. When estimating the initial values of vapour pressure and equilibrium gas phase composition, we treat the vapour and the liquid as ideal fluids to reduce the computational time. The estimation procedures are shown in Appendix B.

2.4. Energy conservation

2.4.1. Latent heat of vaporisation
The heat needed to vaporise LPG in dt time interval is calculated as:

$$dQ = m_{go} r dt \tag{7}$$

where

$$r = \sum_{i=1}^{n} w_i r_i \tag{8}$$

$$w_i = \frac{x_i M_i}{\sum_{j=1}^{n} x_j M_j}, \quad i = 1,2,...,n \tag{9}$$

2.4.2. Heat from the liquid LPG itself
The released sensible heat caused by the liquid temperature drop is expressed as:

$$dQ_{TD} = -m_l C_p dT \tag{10}$$

where

$$m_l = \frac{\pi}{4} D_{Cy}^2 H \rho_l \tag{11}$$

$$C_p = \sum_{i=1}^{n} w_i C_{p,i} \tag{12}$$

2.4.3. Heat from the surroundings
There is a significant difference between the heat transfer from the surroundings to the liquid phase and to the vapour phase in the cylinder. For convenience, we use an overall heat transfer coefficient whose experimental values are available in [11]. The heat transferring from the surroundings to the cylinder in dt is given by:

$$dQ_{HT} = k_{Cy} \left(\pi D_{Cy} H_T + \frac{\pi}{2} D_{Cy}^2 \right) (T_{Env} - T) dt \tag{13}$$

2.4.4. Heat balance equation
The total heat for vaporisation is the sum of the convection heat from the surroundings and the sensible heat from the liquid LPG. One
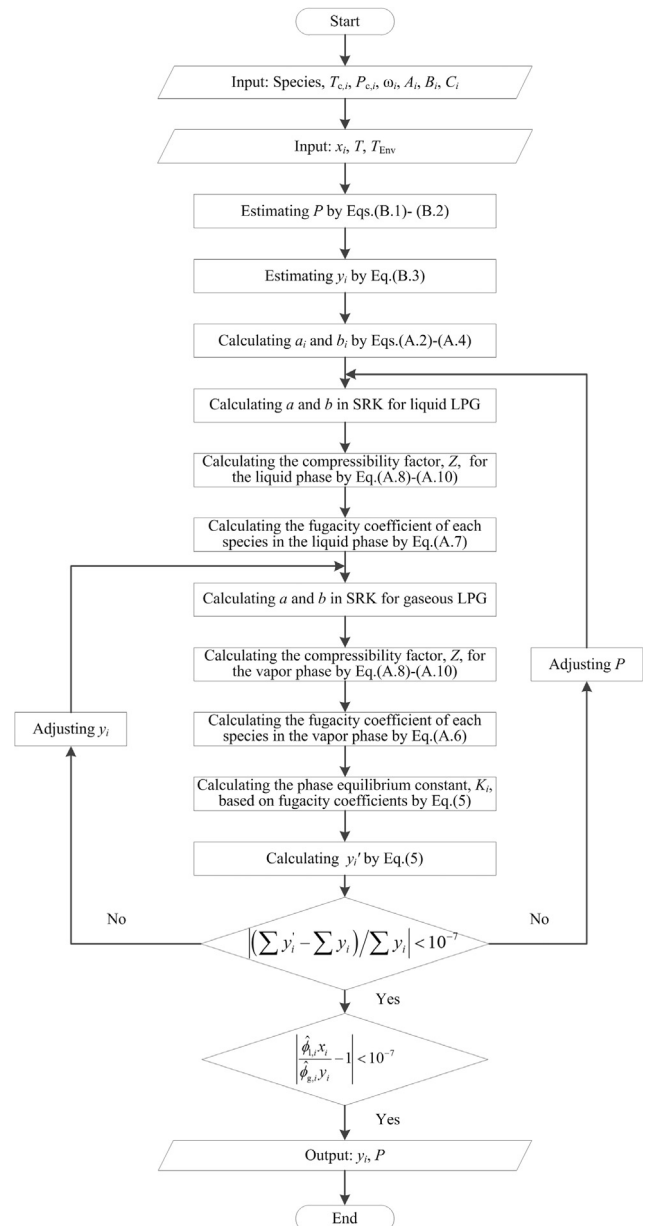

Fig. 2. Program flow diagram of VLE calculation of LPG.

obtains by the energy conservation:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{k_{Cy}}{\rho_1 C_p}\left(\frac{4H_T}{D_{Cy}H} + \frac{2}{H}\right)(T_{Env}-T)-\frac{4m_{go}r}{\pi D_{Cy}^2 H\rho_1 C_p} \tag{14}$$

2.5. Mass conservation

The discharging vapour causes the total mass of LPG to decrease over time. One of apparent response is the drop in liquid level in the cylinder. Therefore, one obtains by the mass conversation:

$$\frac{\mathrm{d}H}{\mathrm{d}t} = -\frac{4m_{go}}{\pi D_{Cy}^2(\rho_1-\rho_g)} \tag{15}$$

Similarly, one obtains the balance of the mass of each constituent:

$$\frac{\mathrm{d}z_i}{\mathrm{d}t} = \frac{4m_{go}(z_i-y_i)M_m}{\pi D^2[\rho_1 H + \rho_g(H_T-H)]M_{m,g}}, \quad i=1,2,...,n \tag{16}$$

For each component, there is a relation as follows:

$$x_i = (z_i-ey_i)/(1-e), \quad i=1,2,...,n \tag{17}$$

Moreover, the sum of each molar faction has to be equal to one at any time [10].

$$\sum_{i=1}^n x_i = \sum_{i=1}^n y_i = \sum_{i=1}^n z_i = 1 \tag{18}$$

2.6. Numerical solution procedure

The model for LPG spontaneous vaporisation consists of a coupled set of differential and algebraic equations (DAEs). To predict the evolutions of LPG properties over LPG mass residual ratio in the cylinder, Eqs. (14)–(16) can also be equivalently converted into the following forms:

$$\frac{\mathrm{d}T}{\mathrm{d}m} = \frac{k_{Cy}}{\rho_1 C_p m_{go}}\left(\frac{4H_T}{D_{Cy}H} + \frac{2}{H}\right)(T_{Env}-T)-\frac{4r}{\pi D_{Cy}^2 H\rho_1 C_p} \tag{19}$$

$$\frac{\mathrm{d}H}{\mathrm{d}m} = -\frac{4}{\pi D_{Cy}^2(\rho_1-\rho_g)} \tag{20}$$

$$\frac{\mathrm{d}z_i}{\mathrm{d}m} = \frac{4(z_i-y_i)M_m}{\pi D_{Cy}^2[\rho_1 H + \rho_g(H_T-H)]M_{m,g}}, \quad i=1,2,...,n \tag{21}$$

Fig. 3 represents the algorithm of the simulation program. The set of DAEs are numerically implemented by the 'ode15s solver' in Matlab®, because it solves DAEs fast and accurately [12]. As the composition, temperature, and pressure of LPG change with time, the VLE calculation should be called at each time step.

3. Simulation results and discussion

3.1. Model validation

In this study, the presented model was validated with the experimental data obtained by the chromatography method [11] under the same operating conditions listed in Table 2. For 'ysp118-I type' cylinders generally used as a group in commercial sectors, the minimum inlet pressure of the regulator is 0.17 MPa [11,13].

As shown in Figs. 4 and 5, more than 89% and 78% of the calculation results are with the ± 4% bandwidth of experimental results for compositions in vapour and liquid phases, respectively. The minimum relative error is 0.10% in Fig. 4 while 0.21% in Fig. 5. Apparently, the developed dynamic model can be expected to provide acceptable results of LPG spontaneous vaporisation in a cylinder.

3.2. Variation of compositions in LPG

Figs. 4 and 5 show that the propane mass fraction in the vapour is always higher than that in the liquid. This is because propane is easier to vaporise and it makes full use of its lower vaporisation point to maintain its pre-eminence in vapour phase at the early stage of natural vaporisation. With the more propane being discharged, its mass fraction in vapour drops dramatically at the late stage.

3.3. Variation of combustion properties of vapour LPG

Changes in gas composition alter combustion properties of fuels and make burners under unsteady combustion conditions such as yellow tipping, flame lifting, and flame flash-back [11,14,15]. Wobbe Index
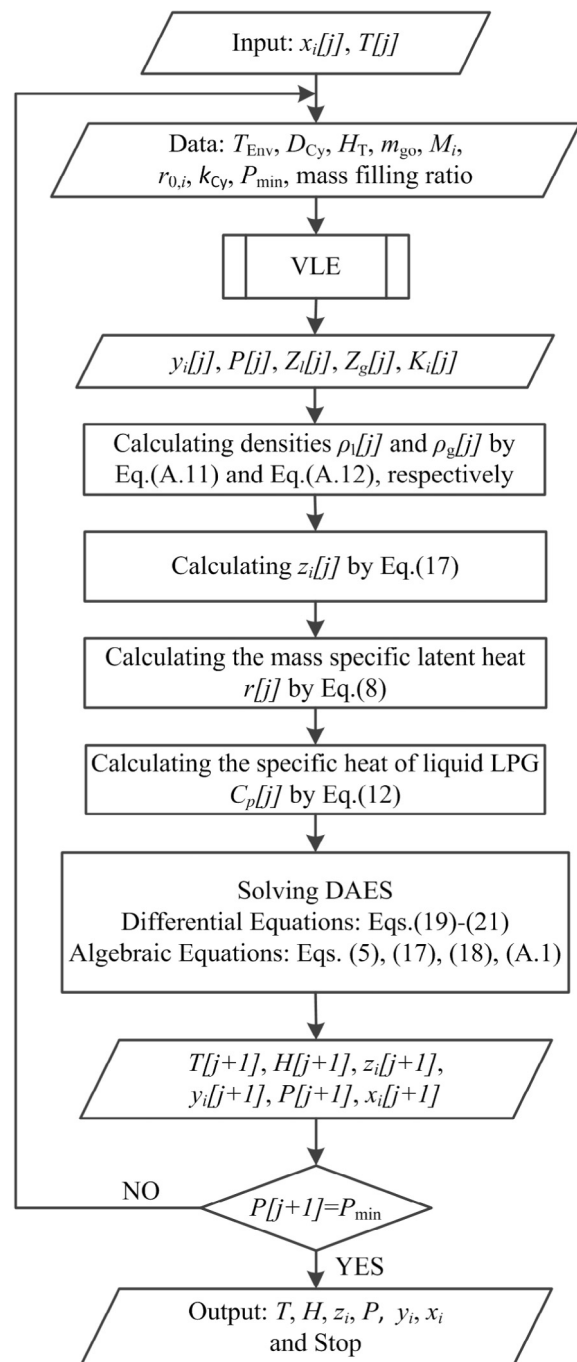

Fig. 3. Flow chart of the simulation program.

Table 1
Values of coefficients in Antoine equation for commercial LPG components.

Species	A_A	B_A	C_A
Propane	15.5406	1744.31	−36.99
Propylene	17.4343	2817.58	36.98
n-butane	15.8929	2274.46	−27.90
iso-butane	15.5622	2067.46	−30.86
butene-1	15.9230	2218.56	−28.92

Table 2
Specific operating conditions of LPG spontaneous vaporisation.

Parameter	Unit	Value
Type of the cylinder	–	ysp118-I
Height of cylinder	m	1.015
Inner cylinder diameter	m	0.4
Initial $C_3H_8 + 70$ $n\text{-}C_4H_{10}$	%	30
Initial $C_3H_8 + 50$ $n\text{-}C_4H_{10}$	%	50
Initial $C_3H_8 + 30$ $n\text{-}C_4H_{10}$	%	70
Capacity of cylinder	L	118
Heat transfer coefficient	$W\,m^{-2}\,K^{-1}$	17.5
Mass filling ratio	%	80
Discharge rate of vapour	$kg\,h^{-1}$	1.5
Surrounding temperature	°C	15

Fig. 4. Comparison of propane mass fraction in vapour phase between model calculated values and experimental data of [13].

Fig. 5. Comparison of propane mass fraction in liquid phase between model calculated values and experimental data of [13].
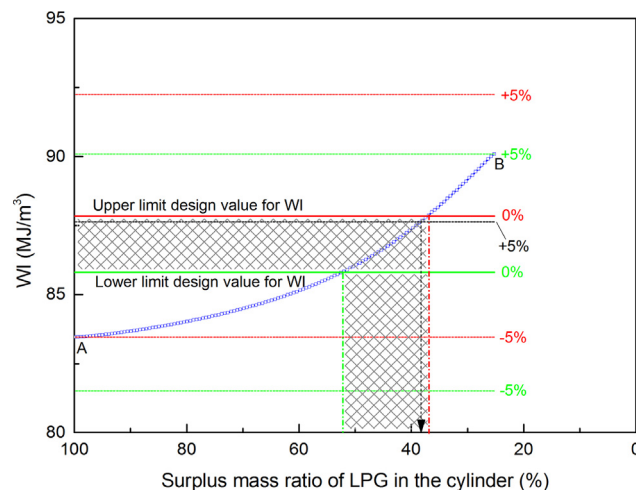

Fig. 6. Variation of WI at initial composition of (50/50 propane/n-butane), discharge rate of $1.5\,kg\,h^{-1}$ and surrounding temperature of 15 °C.

(WI) and combustion potential (CP) are two important parameters used to describe combustion characteristics of gas fuels. As is well known, the combustion conditions of gas appliances are stable for operation within a narrow permitted deviation in WI of ± 5% and a fluctuation range of ± 20% for CP [11,16].

The WI is calculated as the ratio of the gross heating value to the square root of the specific gravity [17]. The higher the value of WI, the higher is the heat input of a given burner per unit time [18]. The CP is related to the components and the specific gravity of a gas mixture [11,18] and the equation is presented in Appendix A.

The values of WI and CP for the LPG vapour can be obtained in light of the real-time gas composition. A polynomial relationship between the WI and the surplus mass ratio is shown in Fig. 6. For burners designed in terms of the initial vapour composition, the values of WI will exceed the maximum permitted deviation (5%) when the residue mass radio falls below 37.06%. In other words, after the point the gas with a higher WI will likely cause an increase in exhaust carbon monoxide, a decrease in combustion efficiency of burners, yellow-tipping flame and sooting due to the lower amount of excess air. This is in general agreement with the practical observations reported in [3,19]. Fig. 7 shows that the CP decreases gradually with the vaporisation and the percent deviation from start to end meets the fluctuating limits. Therefore, the WI is the serious factor for ensuring good combustion performances.
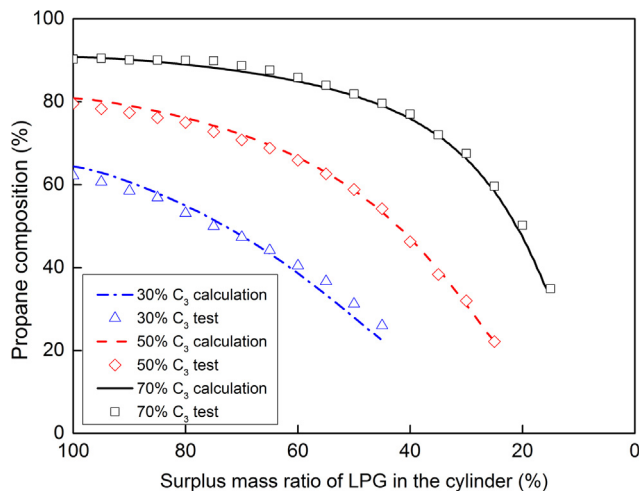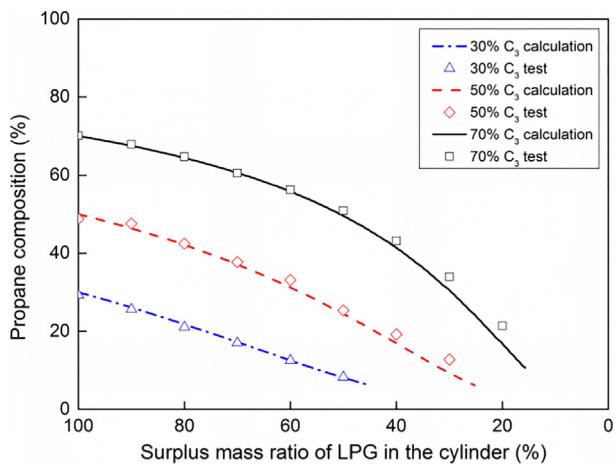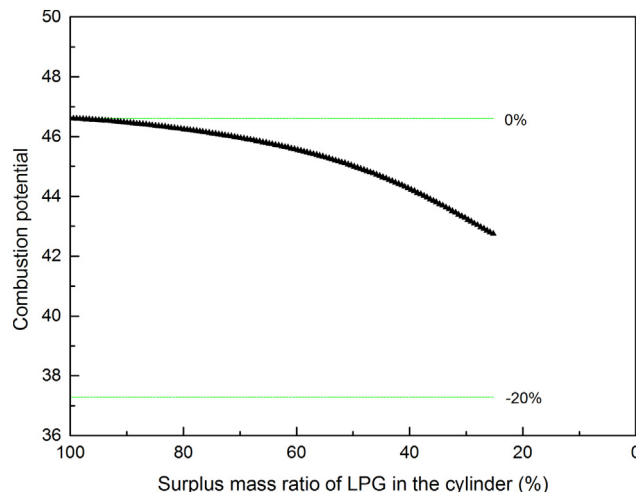

Fig. 7. Variation of CP at 50/50 propane/n-butane, $1.5\,kg\,h^{-1}$ and 15 °C.

However, many commercial end-users have no adequate knowledge to diagnose adverse combustion conditions and no special skills to address these issues. It is a good idea to design or retrofit burners on the grounds of the changes in WI. For example in Fig. 6, from the initial point (Point A), the upper limit design value for WI can be found ($WI_A/(1-5\%)$), while from the end point (Point B), the lower limit design value can be found ($WI_B/(1+5\%)$). Therefore, the appropriate range of WI [85.81, 87.85] is a design or retrofitting reference. Moreover, from Fig. 4, one can obtain corresponding propane and n-butane fractions in vapour phase that are from 60.85 to 42.78% and from 39.15 to 57.22%, respectively.

3.4. Effect of initial composition

Figs. 4 and 5 show that at the early stage, the more propane is contained in the initial LPG, the slower the decline speed of propane in vapour phase is. This results from the easier vaporisation of propane.

Fig. 8 illustrates that the temperature has a significant change and approximately linearly decreases at the beginning of the vaporisation due to no or little temperature difference between the cylinder and the surroundings. Then it decreases down gradually as the temperature difference increases. The tendency is consistent with the experimental phenomena in [11,13]. For different initial compositions, variation trends of LPG temperature are almost the same. Higher initial propane content results in less temperature drop, however, the temperature reduction is insensitive to the initial composition. The reason is that propane is near enough in specific latent heat to n-butane (for instance, the values for propane and n-butane are 359.9 and 375.3 kJ kg^{-1} respectively at 283 K). The LPG pressure drops as the vaporisation develops due to the continuous reduction in some components with higher saturated vapour pressure, the temperature reduction, and the increase of the vapour space. Fig. 8 shows that more propane in the mixture generates the higher LPG pressure.

Additionally, Figs. 4, 5 and 8 shows that the composition with the largest number of propane molecules has the least mass of LPG left in the cylinder. For example, the residue/total LPG mass ratios are 45.3%, 25.2% and 15.7% for initial compositions from 30/70 propane/n-butane to 70/30 propane/n-butane respectively. The composition of residue can be predicted rapidly by Fig. 5.

3.5. Effect of surrounding temperature

Fig. 9 presents that all surrounding temperatures show similar patterns of temperature or pressure variation. Molecules in liquid phase have higher kinetic energy to escape into the vapour phase and absorb more heat from the surroundings at a higher surrounding temperature, which results in an earlier end of the sharp fall in LPG temperature. A lower surrounding temperature leads to a lower LPG pressure. The steep reduction in LPG temperature leads to a larger fall in pressure at the early period.

Fig. 10 shows that a lower surrounding temperature results in a higher propane content in the liquid due to a more increase in the specific latent heat of vaporisation of propane compared with n-butane. For various surrounding temperatures, the composition difference in the remaining liquid is very small at the early period and enlarges quickly with the discharging process.

Figs. 9 and 10 illustrate that a higher surrounding temperature is favourable for alleviating the residue problem. For example, the residue/total LPG ratios are 34.1%, 25.2% and 6.8% at surrounding temperatures of 10 °C, 15 °C, and 20 °C, respectively. It is because that the surface tension of the liquid is smaller at a higher temperature [20] and molecules with more kinetic energy are easier to escape from the liquid into the vapour [21]. Fig. 10 can be used to explore what the composition of residue is. It is apparent that using LPG with more light-hydrocarbon components in colder climates is an effective measure for reducing the residue in the cylinder.

3.6. Effect of discharge rate

Fig. 11 shows a higher discharge rate causes a larger temperature drop and an earlier end of the sharp fall in temperature. This is because it takes a longer time to absorb more heat from the liquid itself for vaporisation. It also shows that a lower temperature at a higher discharge rate causes a more reduction in the pressure. There is a certain period in which the pressure at 1.0 kg h^{-1} is higher than that at 0.5 kg h^{-1} because the positive influence of the propane increase in vapour phase is greater than the negative effect of the temperature drop on the pressure.

Fig. 12 presents that the difference in propane composition among different discharge rates is very small in the early period and then becomes gradually larger. This is because a more significant fall in temperature happens at a higher discharge rate. As the consequence of such extreme cooling, more propane molecules are trapped and stayed in the liquid. The increase rate of propane composition is reduced with the flow rate increasing. The effect of discharge rate on the composition is more remarkable compared with that of surrounding temperature.

Figs. 11 and 12 also shows that using a lower discharge rate can minimize the residue. However, the difference in the residue is not very great for all flow rates. For example, there are 21.8%, 22.9%, 25.2% and 28.5% left over at rates of 0.5 kg h^{-1}, 1.0 kg h^{-1}, 1.5 kg h^{-1}, and 2.0 kg h^{-1}, respectively. One can conclude that connecting several cylinders in parallel to supply gas can decrease the discharge rate of vapour LPG from each one, which is a good option to lessen the residue.

4. Concluding remarks

The transient behaviours of LPG spontaneous vaporisation in the cylinder were clearly studied by the presented general model. Some conclusions are obtained by this investigation.

(1) The proposed model is proved to be applicable for determining real-time compositions and physical properties of LPG throughout the discharge process.
(2) From the beginning to the end of the natural vaporisation, the WI of vapour LPG increases by 8.0%. The WI obtained by the proposed graphical design procedure can ensure good combustion performances for burners.
(3) The order influence from high to low on the residue amount of LPG in the cylinder is surrounding temperature, initial composition and discharge rate. When surrounding temperature enhances from 10 °C to 20 °C, the unburned residue is reduced about five times.
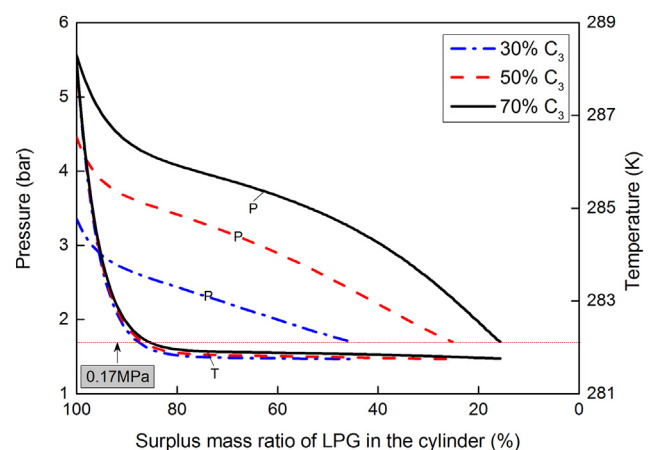

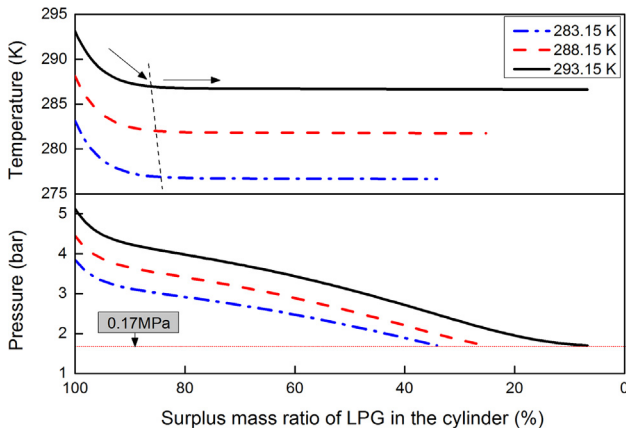**Fig. 8.** Effects of initial composition on LPG temperature and pressure at 1.5 kg h^{-1} and 15 °C.

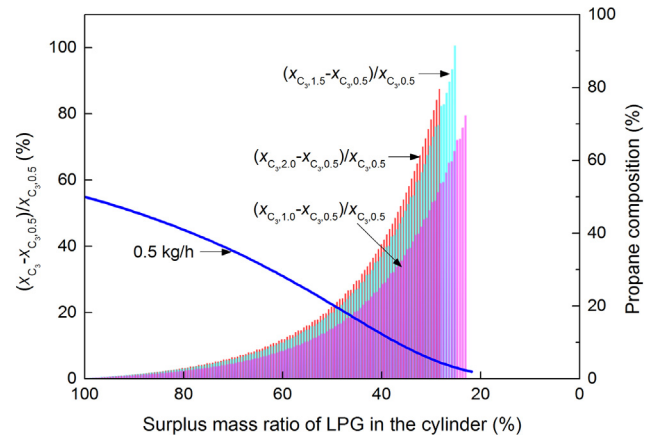**Fig. 9.** Effects of surrounding temperature on LPG temperature and pressure at 50/50 propane/n-butane and $1.5\,kg\,h^{-1}$.
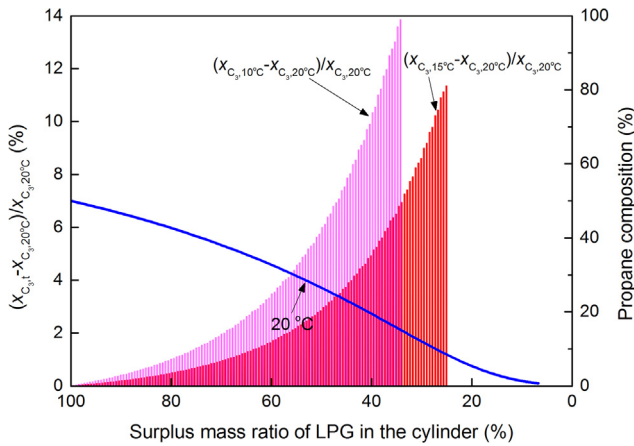

Fig. 10. Effect of surrounding temperature on propane composition in liquid phase at 50/50 propane/n-butane and $1.5\,kg\,h^{-1}$.
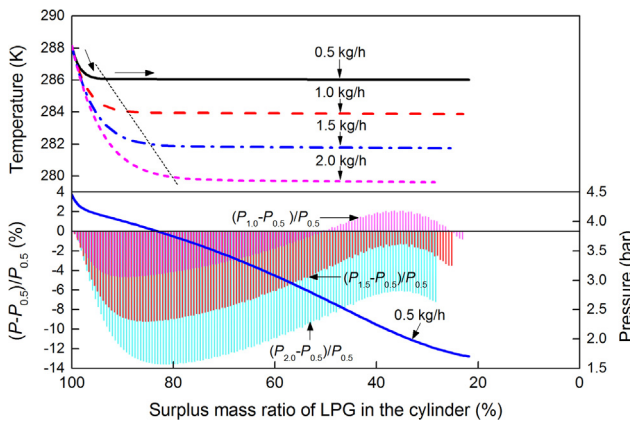

Fig. 11. Effects of discharge rate on LPG temperature and pressure at 50/50 propane/n-butane and 15 °C.

Fig. 12. Effect of discharge rate on propane composition in liquid phase at 50/50 propane/n-butane and 15 °C.

Appendix A. SRK EOS and formulas for physical properties

A.1. SRK EOS

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \tag{A.1}$$

where parameters a and b for a mixture, are related to the pure component parameters and determined by using the classic Van der Waals mixing rules [10]. For any pure species, a and b are defined as:

$$a(T) = 0.42748 \frac{R^2 T_c^2}{P_c} \alpha(T) \tag{A.2}$$

$$\alpha(T) = \left\{ 1 + m\left[1 - \left(\frac{T}{T_c}\right)^{0.5} \right] \right\}^2 \tag{A.3}$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \tag{A.4}$$

$$b = 0.08664 \frac{RT_c}{P_c} \tag{A.5}$$

The fugacity coefficients for component i in both phases are determined by:

$$\ln\phi_{g,i} = \frac{b_i}{b}(Z-1) - \ln(Z-B) + \frac{A}{B}\left(\frac{b_i}{b} - \frac{2}{a} \sum_{j=1}^{n} y_j a_{ij} \right)\ln\left(1 + \frac{b}{V}\right), \quad i = 1,2,...,n \tag{A.6}$$

$$\ln\phi_{l,i} = \frac{b_i}{b}(Z-1) - \ln(Z-B) + \frac{A}{B}\left(\frac{b_i}{b} - \frac{2}{a} \sum_{j=1}^{n} x_j a_{ij} \right)\ln\left(1 + \frac{b}{V}\right), \quad i = 1,2,...,n \tag{A.7}$$

where

$$A = \frac{aP}{R^2 T^2} \tag{A.8}$$

$$B = \frac{bP}{RT} \tag{A.9}$$

Substituting Eqs. (A.8) and (A.9) and $Z = PV/RT$ into Eq. (7), a cubic polynomial with the compressibility factor is obtained.

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \tag{A.10}$$

The largest and smallest real roots of Eq. (A.10) are the compressibility factors for vapour phase and liquid phase, respectively. Phase densities are obtained by:

$$\rho_l = \frac{PM_l}{Z_l RT} \tag{A.11}$$

$$\rho_g = \frac{PM_g}{Z_g RT} \tag{A.12}$$

A.2. Formulas for physical properties

The specific latent heat for component i is obtained by Watson's equation [13].

$$r_i = r_{i,0}\left(\frac{T_{c,i} - T}{T_{c,i} - 273.15}\right)^{0.38} \tag{A.13}$$

The specific heat for component i is calculated using an empirical formula derived by Jovanovi and Grozdani [22] specifically for hydrocarbons.

$$\ln(C_{p,i}) = 3.1731 - 0.081614\ln(1 - T/T_{c,i}) + 0.001758T_{c,i}^{1.16} - 0.0090872(T_{c,i} - T)^{0.7} \tag{A.14}$$

According to the Delbourg Interchangeability Index, it is calculated as follows [11,18]:

$$CP = 100\frac{u_{(D)}}{\sqrt{s}}[y_{H_2} + 0.7y_{CO} + 0.3y_{CH_4} + v_{(D)}(0.95y_{C_3H_8} + 1.1y_{C_4H_{10}} + 1.15y_{C_5H_{12}})] \tag{A.15}$$

where $u_{(D)}$ and $v_{(D)}$ are the gas type factors which values are both equal to 1 for the composition of LPG in our study.

Appendix B. Estimating initial values of vapour pressure and equilibrium gas phase composition

B.1. Estimation of pressure, P

The saturation pressure of each constituent of LPG is calculated by the Antoine equation [23]

$$\ln P_{\text{sat},i}^t = A_{A,i} - \frac{B_{A,i}}{T^t + C_{A,i}} - 8.9227, \quad i = 1,2,...,n \tag{B.1}$$

where $A_{A,i}$, $B_{A,i}$ and $C_{A,i}$ are constant for component i and their values are listed in Table 1. For common components of LPG, the maximum mean relative error between predicted values and experimental values is 1.20% in the temperature range of -40 to $40\,^\circ$C [23].

The vapour pressure in the cylinder is obtained:

$$P = \sum_{i=1}^{n} x_i P_{\text{sat},i} \tag{B.2}$$

B.2. Estimation of gas phase composition, y_i

The gas phase composition is estimated by using Raoult's Law.

$$y_i = x_i \frac{P_{\text{sat},i}}{P}, \quad i = 1,...,n \tag{B.3}$$

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