We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Natural gas: physical properties and combustion features

Le Corre Olivier and Loubar Khaled

GEPEA, Ecole des Mines de Nantes, CNRS, UMR 6144

Ecole des Mines de Nantes, NAtech, GEM, PRES UNAM

La Chantrerie, 4, rue Alfred Kastler, B.P. 20722,

F-44307, Nantes, Cedex 3, France

1. Introduction

One calls combustible natural gas or simply natural gas, any combustible gas fluid coming from the basement. The concept of a unique “natural gas” is incorrect. It is more exact to speak about natural gases. In fact, the chemical composition of available natural gas (at the final customer) depends on its geographic origin and various mixtures carried out by networks operators.

The majority of natural gases are mixtures of saturated hydrocarbons where methane prevails; they come from underground accumulations of gases alone or gases associated with oil. There are thus as many compositions of natural gases as exploited hydrocarbon layers. Apart from the methane which is the prevailing element, the crude natural gas usually contains decreasing volumetric percentages of ethane, propane, butane, pentane, etc. The ultimate analysis of a natural gas thus includes/understands the molar fraction of hydrocarbons in CH_4 , C_2H_6 , C_3H_8 , C_4H_{10} and the remainder of heavier hydrocarbons is generally indicated under the term C_{5+} . Table 1 gives typical compositions. Apart from these hydrocarbons, one often finds one or more minor elements, or impurities, quoted hereafter:

- nitrogen N_2 : it has as a disadvantage its inert character which decreases the commercial value of gas,
- carbon dioxide CO_2 : it is harmful by its corrosive properties,
- hydrogen sulfide H_2S : it is harmful by its corrosive properties,
- helium He : it can be developed commercially,
- water H_2O : the natural gas of a layer is generally saturated with steam. To be exploited, it undergoes a partial dehydration.

In this chapter, the characteristics of natural gas in term of composition and physical properties and combustion features are presented. The physical models for the calculation of the physical properties are developed and a synthesis of the models selected is carried out.

Fuel	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	N ₂	CO ₂	MN
No.1	87.1	8.8	2.5	0.8	0	0.8	0	70.7
No.2	97.3	2.1	0.2	0.1	0	0.3	0	90.6
No. 3	87.0	9.4	2.6	0.6	0	0.4	0	70.9
No.4	91.2	6.5	1.1	0.2	0	1.0	0	79.3
No.5	88.6	4.6	1.1	0.3	0.1	3.9	1.4	82.2
No.6	82.9	3.2	0.6	0.2	0.1	12	1	87.9
No.7	92.3	3.2	0.6	0.2	0.1	3	0.4	85.7
No.8	89.5	3.1	3.6	0.2	0.1	2.9	0.4	76.3
No.9	87.7	3.0	5.6	0.2	0.1	2.9	0.4	71.8
No10	84.9	2.9	8.5	0.2	0.1	2.7	0.3	66.5

Table 1. Sample group of fuel gases (Saikaly et al., 2008).

Various techniques of determination of combustion features such as equivalence ratio, the low heating value and Wobbe index are exposed. These techniques are based on direct or indirect methods. The section “Physical Properties” is a toolbox to calculate transport properties (dynamic viscosity and thermal conductivity) and other important properties such as speed of sound, refractive index and density. Regards time, the ultimate consumer burns a fuel whose chemical composition varies, see Figure 1. These variations bring problems for plant operation, whatever is the prime mover (Internal Combustion engine, gas turbine or boiler).

The section “Combustion features” details:

- Air-fuel ratio is the ratio of air to fuel in stoichiometric conditions.
- Network operator sells natural gas volume but final customer needs heat. Low heating value *LHV* is the link and is very important. By contract, network operator takes obligations on the *LHV* minimum value.
- Wobbe index (*W*) is an important criterion of inter-changeability of gases in the industrial applications (engines, boilers, burners, etc). Gas composition variation does not involve any notable change of the factor of air and the velocity burning when the index of Wobbe remains almost constant.
- Methane number (*MN*) characterizes gaseous fuel tendency to auto-ignition. By convention, this index has a value 100 for methane and 0 for hydrogen (Leiker et al., 1972). The gaseous fuels are thus compared with a methane-hydrogen binary mixture. Two gases with same value *MN* have the same resistance against the spontaneous combustion.

2. Physical Properties

2.1 Introduction

Physical models of transport properties relating to the gases (viscosity, conductivity) result from the kinetic theory of gases, see (Hirschfelder et al., 1954) and (Chapman & Cowling, 1970).

Fig. 1. Methane Number during 5 consecutive months (Saikaly et al., 2008)

The assumptions with regards to the kinetic theory of gases are:

1. The average distance between the molecules is sufficiently important so that the molecular interactions (other than shocks) are negligible,
2. The number of molecules per unit volume is large and constant (gas homogeneity on a macroscopic scale).

The following assumptions are relating to kinematics:

1. Between two shocks, presumed elastic, the movement of each molecule is rectilinear and uniform,
2. The direction of the Speed Vectors of the various molecules obeys a uniform space distribution,
3. The module of the Speed Vectors varies according to a law of distribution which does not depend on time when the macroscopic variables of state are fixed.

Natural gases are a mixture of ν components. Their physical properties such as dynamic viscosity and thermal conductivity, evaluated on the basis of kinetics of gases, are obtained starting from the properties of pure gases and corrective factors (related on the mixtures, the polar moments, etc).

2.2 Dynamic viscosity

Natural gas viscosity is required to carry out flow calculations at the various stages of the production and in particular to determine pressure network losses. Natural gas generally behaves as a Newtonian fluid, see (Rojey et al., 2000) and, in this case, dynamic viscosity η in unit [Pa.s] is defined by Equation (1):

$$\tau = \eta \frac{du}{dy} \quad (1)$$

With τ the shear stress and $\frac{du}{dy}$ the shear rate.

2.2.1 Pure gases

Considering brownian motion of the molecules regards to the intermolecular forces, Chapman and Enskog theory can be applied. This approach considers in detail the interactions between molecules which enter in collision and is based on equation of Maxwell-Boltzmann function distribution, see (Chapman & Cowling, 1970).

For mono-atomic gases, analytic solution of this equation gives the viscosity depending of a two double integrals $\Omega^{(2,2)}$, corresponding to molecules binary collisions, often called "collision integral for viscosity". However, this theoretical approach is only applicable to mono-atomic gases under low pressures and high temperatures. To apply this model to polyatomic gases, a correction for energy storage and transfer are required, see (Le Neindre, 1998). In general terms, the solution obtained for the dynamic viscosity of the mono-atomic gases which do not have degree of freedom of rotation or vibration is written:

$$\eta = 2.6693 \cdot 10^{-6} \frac{\sqrt{M T}}{\sigma^2 \Omega^{(2,2)*}} \quad (2)$$

With M the molar mass in $[\text{g mol}^{-1}]$, T the absolute temperature in $[\text{K}]$, σ a characteristic diameter of the molecules, often called "the collision diameter" in $[1 \text{ \AA}]$, $\Omega^{(2,2)*}$ the collision integral depending on the reduced temperature T^* defined as $T^* = kT / \varepsilon$, where k is the Boltzmann constant and ε is the maximum energy of attraction. Correlations exist to approximate the collision integral.

- For nonpolar gases, Neufeld et al. (1972) have proposed the expression:

$$\Omega^{(2,2)*} = A (T^*)^{-B} + C e^{(-D T^*)} + E e^{(-F T^*)} \quad (3)$$

Where $A=1.16145$, $B=0.14874$, $C=0.52487$, $D=0.77320$, $E=2.16178$ and $F=2.43787$. Equation (3) is valuable in the range $0.3 \leq T_r \leq 100$, where $T_r = T / T_c$, T_c being the critical temperature, with a standard deviation of 0.064%.

Chung et al. (1984) and (1988) have experimentally obtained:

$$\frac{\varepsilon}{k} = \frac{T_c}{1.2593} \quad (4)$$

$$\sigma = 0.809 V_c^{1/3} \quad (5)$$

To take into account molecule shapes, Chung et al. have introduced a corrective factor F_c :

$$\eta = 4.0785 \cdot 10^{-6} F_c \frac{\sqrt{M T}}{V_c^{2/3} \Omega^{(2,2)*}} \quad (6)$$

With $F_c = 1 - 0.2756 \bar{\omega} + 0.059035 \zeta_r^4 + \kappa$; $\bar{\omega}$ is the acentric factor, κ is a correction for gases being strongly polar; the dimensionless dipole moment ζ_r being given by $\zeta_r = 131.3 \zeta / (V_c T_c)^{1/2}$

- Reichenberg (1974) have chosen a linear dependence:

$$\Omega^{(2,2)*} = a (T^*)^{-n} \quad (7)$$

Dynamic viscosity is then expressed by:

$$\eta = 4.0785 \cdot 10^{-6} M^{1/2} T^{1/2-n} a^{-1} \frac{(T_c / 1.2593)^n}{V_c^{2/3}} \quad (8)$$

2.2.2 Gaseous blends

At low pressure, dynamic viscosity of gases blend, noted η_m , can be estimated from the viscosity of pure gases. For a mixture of ν components, gaseous blend viscosity is given by the expression:

$$\eta_m = \sum_{i=1}^{\nu} K_i \left(1 + 2 \sum_{j=1}^{i-1} H_{ij} K_i + \sum_{j=1, \neq i}^{\nu} \sum_{k=1, \neq i}^{\nu} H_{ij} H_{ik} K_j K_k \right) \quad (9)$$

Where

$$K_i = \frac{x_i \eta_i}{x_i + \eta_i \sum_{k=1, \neq i}^{\nu} x_k H_{ik} [3 + 2 M_k / M_i]} \quad (10)$$

Where η_i is the dynamic viscosity of i^{th} pure gas, M_i its molar mass, x_i its molar fraction and coefficients H_{ij} are obtained by

$$H_{ij} = \left[\frac{M_i M_j}{32(M_i + M_j)^3} \right]^{1/2} (C_i + C_j)^2 \frac{[1 + 0.36 T_{r,ij} (T_{r,ij} - 1)]^{1/6} F_{R,ij}}{T_{r,ij}^{1/2}} \quad (11)$$

Reduced temperature $T_{r,ij}$ is based on critical temperature of pure gases i and j :

$$T_{r,ij} = \frac{T}{(T_{c,i} T_{c,j})^{1/2}} \quad (12)$$

Correction coefficients $F_{R,ij}$ is given by:

$$F_{R,ij} = \frac{T_{r,ij}^{7/2} + \left[10 \left(\zeta_{r,i} \zeta_{r,j}\right)^{1/2}\right]^7}{T_{r,ij}^{7/2} \left[1 + \left(10 \left(\zeta_{r,i} \zeta_{r,j}\right)^{1/2}\right)^7\right]} \quad (13)$$

Coefficients C_i is obtained by:

$$C_i = \frac{M_i^{1/4}}{(\eta_i U_i)^{1/2}} \quad (14)$$

With:

$$U_i = \frac{F_{R,ii} \left[1 + 0.36 T_{r,ii} (T_{r,ii} - 1)\right]^{1/6}}{T_{r,ii}^{1/2}} \quad (15)$$

Wilke (1950) have introduced simplifications into equation (9) by neglecting the term of the second order. The expression of dynamic viscosity obtained makes easier the application:

$$\eta_m = \frac{\sum_{i=1}^v \frac{x_i \eta_i}{\sum_{j=1}^v x_j \phi_{ij}}}{\sum_{j=1}^v x_j \phi_{ij}} \quad (16)$$

$$\text{With } \phi_{ij} = \frac{\left[1 + \left(\eta_i / \eta_j\right)^{1/2} \left(M_i / M_j\right)^{1/4}\right]^2}{\left[8 \left(1 + M_i / M_j\right)\right]^{1/2}}$$

In the literature, specific correlations were established to calculate the viscosity of gas hydrocarbons. In particular, to calculate the viscosity of methane, an equation of the following general form was proposed by Hanley et al (1975) and included by Vogel et al. (2000):

$$\eta_m = \eta_0(T) + \eta_1(T) \rho + \Delta\eta(\rho, T) \quad (17)$$

where $\eta_0(T)$ represents dynamic viscosity in extreme cases of $\rho = 0$. The sum $\eta_1(T) \rho + \Delta\eta(\rho, T)$ is the residual dynamic viscosity which takes account of the increase in viscosity from $\eta_0(T)$.

```
function viscosity = func_viscosity(compo)
% compo is a vector in volume fraction
% [CH4 C2H6 C3H8 i-C4H10 n-C4H10 C5H12 CO2 N2 O2 H2 H2S CO]
P = 101325; % current gas pressure in Pa
T = 273.15; % current gas temperature in K
M = [16.043 30.069 44.096 58.123 58.123 72.151 44.01 28.013 32 2.016 34 28.01]; % molar
mass in g mol-1
Tc = [190.58 305.42 369.82 408.14 425.18 469.65 304.19 126.1 154.58 33.18 373.53
132.92]; % Critical temperature
Vc = [99.2 148.3 203 263 255 304 93.9 89.8 73.4 64.3 98.6 93.2]; %Critical Volume
cm3/mol
Dip = [0 0 0 0.1 0 0 0 0 0 0 0.9 0.1]; % Dipolar Moment
omega = [0.011 0.099 0.1518 0.1770 0.1993 0.2486 0.2276 0.0403 0.0218 -0.215 0.0827
0.0663];
T_et = 1.2593*T/Tc; %
omegaV = 1.16145*T_et^(-0.14874)+0.52487*(exp(-0.77320*T_et))+ 2.16178*(exp(-2.43787*T_et));
mu_r = 131.3*Dip./sqrt(Vc.*Tc);
Fc = ones(1,12)-0.2756*omega+0.05903*mu_r.^4;
eta = 40.785*(Fc.*sqrt(T.*M))./(Vc.^(2/3).*omegaV)/10000000;
for i = 1:12
    for j = 1:12
        A(i,j) = (1 + sqrt(eta(i)/eta(j)))*(M(i)/M(j))^(1/4))^2/sqrt(8*(1+M(i)/M(j))); %
    end
end
p1 = compo.*eta;
for i = 1:12
    p2(i) = p1(i)/sum(compo.*A(i,:)); %
end
viscosity = sum(p2); %Pa s-1
```

Sandia National Laboratory (www.sandia.gov) has developed CHEMKIN, a reference tool for chemical. The Gas Research Group (www.me.berkeley.edu/gri_mech/overview.html), carried out by the University of California at Berkeley, Stanford University, The University of Texas at Austin, and SRI International, has set up the description of methane and its co-products. The hand-made **Matlab**® function is compared to this reference code. Error is defined as:

$$\forall T \in [300...500] \max(\varepsilon_{\eta}) = \max \left| \frac{\eta_{hm}(T) - \eta_{CHEM}(T)}{\eta_{CHEM}(T)} \right| \tag{19}$$

Fig. 2. Dynamic viscosity for main constituents of natural gases

Fig. 3. Relative error between hand-made function and CHEMKIN for dynamic viscosity

The variation of the viscosity of the various components of natural gas according to the temperature is presented on Figure 2 at atmospheric pressure. Good agreement is obtained for the 5 major gases constituting a natural gas, see Figure 3.

2.2.3 Viscometer

Various methods exist to measure the dynamic viscosity of a gas (Guérin, 1981):

- U-tubes of Fagelson (1929) are an extension of Rankine apparatus (1910)
- Double-Helmholtz resonator is first conceived (Greenspan and Wimenitz, 1953). The precision have been extended (Wilhem et al, 2000).
- Rotational viscometers are available products.

2.3 Thermal conductivity

Fourier law characterizes heat conduction: the heat conduction flux φ crossing surface S in a given direction is proportional to the gradient of temperature $\partial T / \partial y$. This factor of proportionality is called thermal conductivity λ .

$$\varphi = \lambda S \frac{\partial T}{\partial y} \quad (20)$$

2.3.1 Pure gases

Thermal conductivity of a mono-atomic gas, for which only the energy of translation acts, is given by the traditional expression (Reid et al., 1987):

$$\lambda = 2.63 \cdot 10^{-23} \frac{\sqrt{T/M}}{\sigma^2 \Omega^{(2,2)*}} \quad (21)$$

Where λ is in $[Wm^{-1}K^{-1}]$

Using Equation (2), thermal conductivity is expressed from dynamic viscosity by:

$$\lambda = \frac{15}{4} \frac{R}{M} \eta \quad (22)$$

For polyatomic gases (constituents of natural gases), Eucken number Eu is introduced:

$$Eu = \frac{\lambda M}{\eta C_v} \quad (23)$$

Where C_v is the heat capacity at constant volume.

For mono-atomic gases, Eucken Number is close to 5/2. For polyatomic gases, Eucken Number is modified by separating the contributions due to translation energy from those due to internal energy (Reid et al., 1987):

$$Eu = \frac{\lambda M}{\eta C_v} = f_{tr} \left(\frac{C_{tr}}{C_v} \right) + f_{in} \left(\frac{C_{in}}{C_v} \right) \quad (24)$$

With C_{tr} in $[J \text{ mol}^{-1} K^{-1}]$ the part of the heat capacity due to translation modes $C_{tr} = 3/2 R$ and C_{in} , related to internal modes, is defined as: $C_{in} = C_v - C_{tr}$, see (Reid et al., 1987).

$$Eu = \frac{\lambda M}{\eta C_v} = 1 + \frac{\frac{9}{4}}{\frac{C_p}{R} - 1} \quad (25)$$

Where C_p is the heat capacity at constant pressure.

A modified Eucken relation was proposed for which f_{in} is related to a coefficient of molecular diffusion too. This new relation is written as, see (Reid et al., 1987):

$$Eu = \frac{\lambda M}{\eta C_v} = 1.32 + \frac{1.77}{\frac{C_p}{R} - 1} \quad (26)$$

Mason and Monchick (1962) worked out a theory based on a dynamic formalism to calculate the conductivity of polyatomic gases. They obtained for non-polar gases, by supposing the contributions of the negligible modes of vibrations, the following expression:

$$Eu = \frac{\lambda M}{\eta C_v} = 1.32 + \frac{1.77}{\frac{C_p}{R} - 1} - 0.886 \frac{(C_{rot}/C_v)}{Z_{rot}} \quad (27)$$

With C_{rot} in $[J \text{ mol}^{-1} K^{-1}]$ the part of the heat capacity due to rotation modes and Z_{rot} the number of collisions necessary to change a quantum of rotation energy into translation energy.

Equation (27) was applied to hydrogen, nitrogen and carbon dioxide, but the main problem for their use remains the precise determination of the number of collisions of rotation Z_{rot} which is function of the temperature.

Chung and al. (1984) used similar method to Mason and Monchick (1962) and obtained the relation of thermal conductivity. Indeed, Eucken number is expressed in this case according to a coefficient of correction ν as follows:

$$Eu = \frac{\lambda M}{\eta C_v} = 3.75 \frac{\nu}{C_p/R - 1} \quad (28)$$

Coefficient V is given by the following formula:

$$v = 1 + \alpha \frac{0.215 + 0.28288 \alpha - 1.061 \beta + 0.26665 \Gamma}{0.6366 + \beta \Gamma + 1.061 \alpha \beta} \quad (29)$$

With $\alpha = (C_v/R) - 3/2$; $\beta = 0.7862 - 0.7109\bar{\omega} + 1.3168\bar{\omega}^2$ and $\Gamma = 2.0 + 10.50 T_r^2$.

Term β is given by an empirical correlation for the contribution of translation energy of the molecules to thermal conductivity for polyatomic gases and applies for the non-polar molecules. As the two main components of the natural gas (methane and ethane) are non-polar and that the other components have weak dipole moment, this correlation represents well the behaviour of natural gases. In the case of the polar molecules, a default value of 0,758 should be used. Term α corresponds to the heat-storage capacity due to the internal degrees of freedom. Thus, term V can be included/understood as being a shape factor pointing out the deviations of the polyatomic molecules with respect to the model of the rigid sphere.

2.3.2 Gaseous blends

Thermal conductivity of blends is estimated in the same manner as for viscosity. The thermal conductivity of a gas mixture λ_m can be thus calculated starting from a standard formula in the same way than Equation (16), see (Reid et al., 1987):

$$\lambda_m = \sum_{i=1}^v \frac{x_i \lambda_i}{\sum_{j=1}^v x_j A_{ij}} \quad (30)$$

Mason and Saxena (1958) proposed the following expression for coefficient A_{ij} :

$$A_{ij} = \frac{\varepsilon \left[1 + (\lambda_{tr,i} / \lambda_{tr,j})^{1/2} (M_i / M_j)^{1/4} \right]^2}{\left[8 (1 + M_i / M_j) \right]^{1/2}} \quad (31)$$

Where λ_{tr} represents thermal conductivity of monoatomic gas and ε is a constant close to 1.0; Mason and Saxena (1958) proposed $\varepsilon = 1.065$. Heat conductivities ratio due to the energy of translation of the molecules can be obtained in a purely empirical way:

$$\lambda_{tr,i} / \lambda_{tr,j} = \frac{\Gamma_j \left[e^{0.0464 T_{r,i}} - e^{0.2412 T_{r,i}} \right]}{\Gamma_i \left[e^{0.0464 T_{r,j}} - e^{0.2412 T_{r,j}} \right]} \quad (32)$$

With $\Gamma_i = 210.0 \left(\frac{T_{c,i} M_i^3}{P_{c,i}^4} \right)^{1/6}$; $P_{c,i}$ is the critical pressure of the i^{th} component.

```

function thermal_conductivity = func_conductivity(compo)

P = 101325; % current gas pressure in Pa
T = 273.15; % current gas temperature in K
R = 8.314; %ideal gas constant J/K/mol
M = [16.043 30.069 44.096 58.123 58.123 72.151 44.01 28.013 32 2.016 34 28.01]; % molar
mass in g mol-1
Tc = [190.58 305.42 369.82 408.14 425.18 469.65 304.19 126.1 154.58 33.18 373.53
132.92]; % Critical temperature
Vc = [99.2 148.3 203 263 255 304 93.9 89.8 73.4 64.3 98.6 93.2]; %Critical Volume
cm3/mol
Pc = [4.604 4.88 4.249 3.648 3.797 3.369 7.382 3.394 5.043 1.313 8.963 3.499]; %
Critical pressure
Dip = [0 0 0 0.1 0 0 0 0 0.9 0.1]; % Dipolar Moment
omega = [0.011 0.099 0.1518 0.1770 0.1993 0.2486 0.2276 0.0403 0.0218 -0.215 0.0827
0.0663];

methane = -672.87+439.74*(T/100)^0.25-24.875*(T/100)^0.75+323.88*(T/100)^(-0.5);
ethane = 6.895+17.26*(T/100)-0.6402*(T/100)^2+0.00728*(T/100)^3;
propane = -4.092+30.46*(T/100)-1.571*(T/100)^2+0.03171*(T/100)^3;
ibutane = 3.954+37.12*(T/100)-1.833*(T/100)^2+0.03498*(T/100)^3;
nbutane = 3.954+37.12*(T/100)-1.833*(T/100)^2+0.03498*(T/100)^3;
pentane = R*(1.878+4.1216*(T/100)+0.12532*(T/100)^2-0.037*(T/100)^3+0.001525*(T/100)^4);
diocarbene = -3.7357+30.529*(T/100)^0.5-4.1034*(T/100)+0.024198*(T/100)^2;
azote = 39.060-512.79*(T/100)^(-1.5)+1072.7*(T/100)^(-2)-820.4*(T/100)^(-3);
oxygene = 37.432+0.020102*(T/100)^1.5-178.57*(T/100)^(-1.5)+236.88*(T/100)^(-2);
hydrogene = 56.505-702.74*(T/100)^(-0.75)+1165*(T/100)^(-1)-560.7*(T/100)^(-1.5);
hydrosulf = R*(3.071029+0.5578*(T/100)-0.1031*(T/100)^2+0.01202*(T/100)^3-0.0004838*(T/100)^4);
monocarbene = 69.145-0.70463*(T/100)^0.75-200.77*(T/100)^(-0.5)+176.76*(T/100)^(-0.75);

Cpmol = [methane ethane propane ibutane nbutane pentane diocarbene azote oxygene
hydrogene hydrosulf monocarbene];
cp=Cpmol.*1000./M;

alpha = (cp.*M*1e-3-R*ones(1,12))./(R*ones(1,12))-1.5*ones(1,12);
beta = 0.7862*ones(1,12)-0.7109*omega+1.3168*omega.^2;
zed = 2*ones(1,12)+10.5*(T./Tc).^2;
psi = ones(1,12)+alpha.*(0.215*ones(1,12)+0.28288*alpha-1.061*beta+0.26665*zed)./ ...
(0.6366*ones(1,12)+beta.*zed+1.061*alpha.*beta);
%*****Dynamic Viscosity*****
T_et = 1.2593*T./Tc;
omegaV = 1.16145.*T_et.^(-0.14874)+0.52487*(exp(-0.77320*T_et))+ ...
2.16178*(exp(-2.43787*T_et));
mu_r = 131.3*Dip./sqrt(Vc.*Tc);
Fc = ones(1,12)-0.2756*omega+0.05903*mu_r.^4;
eta = 40.785*(Fc.*sqrt(T.*M))./(Vc.^(2/3).*omegaV)/10000000;
%*****
lambda = 3.75*R*eta.*psi./M*1000;

%for mixture
temp = 210*(Tc.*M.^3./(Pc*10).^4).^(1/6);
lambda_tr = temp.*(exp(0.0464.*(T./Tc))-exp(-0.2412.*(T./Tc)));

for i = 1:12
    for j = 1:12
        A(i,j) = (1 + sqrt(lambda_tr(i)/lambda_tr(j)))*(M(i)/M(j))^(1/4))^2/ ...
            sqrt(8*(1+M(i)/M(j)));
    end
end
p1 = lambda.*compo;

for i = 1:12
    p2(i) = p1(i)/sum(compo.*A(i,:));
end
thermal_conductivity = sum(p2);

```

Fig. 4. Thermal conductivity for main constituents of natural gases

Fig. 5. Relative error between hand-made function and CHEMKIN for thermal conductivity

The variation of the thermal conductivity of the various components of natural gas according to the temperature is presented on Figure 4 at atmospheric pressure. Good agreement is obtained for the 5 major gases constituting a natural gas, see Figure 5.

$$\forall T \in [300 \dots 500] \max(\varepsilon_{\lambda}) = \max \left| \frac{\lambda_{hm}(T) - \lambda_{CHEM}(T)}{\lambda_{CHEM}(T)} \right| \tag{33}$$

2.3.3 Thermal conductivity measurement

Different techniques can be used to measure the thermal conductivity:

Katharometer: Thermal conductivity determination of a gas is commonly based on the method of hot wires (Guérin, 1981). A wire is tended in the axis of a metal cylindrical room whose walls are maintained at constant temperature and traversed by a gas, constituting a cell. If one applies a constant electromotive force at the ends of this wire, its temperature rises until the energy spent by Joule effect is, at each time, compensated by the energy dissipated by radiation, convection and thermal conduction. By choosing conditions such as the losses other than the last are negligible (temperature of the wire lower than 400°C, diameter maximum of the tube of 1 cm, rather slow gas flow: 6 to 12 l/h), the temperature of the wire depends primarily on the nature of the gas which surrounds it. If the wire has a resistivity whose temperature coefficient is raised, resistance is function of the thermal conductivity of this gas.

Guarded Hot Plate Method: Guarded hot plate is a widely used and versatile method for measuring the thermal conductivity. A flat, electrically heated metering section surrounded on all lateral sides by a guard heater section controlled through differential thermocouples, supplies the planar heat source introduced over the hot face of the specimens (gas). The most common measurement configuration is the conventional, symmetrically arranged guarded hot plate where the heater assembly is sandwiched between two specimens, see Figure 6. It is an absolute method of measurement and its applicability requires: (a) the establishment of steady-state conditions, and (b) the measurement of the unidirectional heat flux in the metered

region, the temperatures of the hot and cold surfaces, the thickness of the specimens and other parameters which may affect the unidirectional heat flux through the metered area of the specimen.

Fig. 6. Guarded hot plate method configuration.

2.4 Speed of sound

Speed of sound is connected to thermodynamic scale of the fluid by the relation:

$$c = \left(\frac{\partial P}{\partial \rho} \right)_S \tag{34}$$

where P and ρ represent the pressure and the density respectively, and S the entropy. The previous relation shows the direct link between the speed of sound and state equation of gas.

2.4.1 Speed of sound for ideal gas

For ideal gas, speed of sound is:

$$c = \sqrt{\gamma R T / M} \tag{35}$$

For a mixture of ideal gases, speed of sound is:

$$c_m^2 = \frac{\gamma_m R T}{M_m} = \frac{\left(\frac{\sum_{i=1}^v x_i C_{p,i}}{\sum_{i=1}^v x_i C_{v,i}} \right) \frac{R T}{\sum_{i=1}^v x_i M_i}}{\tag{36}}$$

Ideal gas law is a good approximation for low pressure. However, in order to take into account the real behavior of gases, several state laws were proposed. Van Der Waals equation thus introduces two corrective terms:

$$P = \frac{R T}{(V - b)} + \frac{a}{V^2} \tag{37}$$

Then, in this case, speed of sound is:

$$c^2 = \gamma_r \left(\frac{R T}{\left(1 - \frac{b}{V}\right)^2} + \frac{2 a}{V} \right) \quad (38)$$

Thermodynamic properties models based on state equation provide value of compressibility factor. It is useful, in the field of gas industry, to have specific methods of calculation for natural gas of commercial type. The equation derived from virial equation, established by Groups European of Gas Research - GEGR (Jaescheke et al., 2003), gives calculation for the compressibility factor of commercial gas with an average error of about 0.06% for a pressure up to 12 MPa. However, one of the methods most used in this field is based on the model AGA8-DC92 developed by American Gas Association (Starling & Savidge, 1992). This model makes it possible to estimate the density with an average absolute deviation (AAD) of 0.04% and the speed of sound with AAD of 0.08%. In addition, Estela-Urbe et al. (2003, 2005) used another formulation for natural gas in the range $270 \leq T[K] \leq 330$ and $P \leq 12 \text{ MPa}$. This model presents compressibility factor according to the density by:

$$Z = 1 + B_m \rho + C_m \rho^2 \quad (39)$$

Coefficients B_m and C_m respectively represents the second and the third coefficient of the virial development of the gas mixture. They are given according to temperature and composition of natural gas by the relations:

$$B_m = \sum_i \sum_j x_i x_j B_{ij} \quad (40)$$

$$C_m = \sum_i \sum_j \sum_k x_i x_j x_k C_{ijk} \quad (41)$$

Where B_{ij} and C_{ijk} are given by:

$$B_{ij} = b_{ij,0} + \frac{b_{ij,1}}{T} + \frac{b_{ij,2}}{T^2} \quad (42)$$

$$C_{ij} = c_{ijk,0} + \frac{c_{ijk,1}}{T} + \frac{c_{ijk,2}}{T^2} \quad (43)$$

Reader is referred to Estela-Urbe et al. (2003, 2005) for coefficients b_{ij} and c_{ijk} .

Speed of sound is written:

$$c_m^2 = \left(\frac{R T}{M_m} \right) \left[Z + \rho \left(\frac{\partial Z}{\partial \rho} \right)_T + \frac{R}{C_{v,m}} \left(Z + T \left(\frac{\partial Z}{\partial T} \right)_\rho \right)^2 \right] \quad (44)$$

Where $C_{v,m}$ is heat capacity at constant volume of the mixture calculated by:

$$C_{v,m} = C_{v,m}^{IGL} + C_{v,m}^{res} \quad (45)$$

$C_{v,m}^{IGL}$ is heat capacity calculated by ideal gas law, see (Jaeschke & Schley, 1995), and $C_{v,m}^{res}$ is residual correction, calculated by:

$$C_{v,m}^{res} = - \left[2T \frac{dB_m}{dT} + T^2 \frac{d^2 B_m}{dT^2} \right] \rho - \left[T \frac{dC_m}{dT} + \frac{T^2}{2} \frac{d^2 C_m}{dT^2} \right] \rho^2 \quad (46)$$

```
function speedofsound = func_speedofsound(compo)
P = 101325; % current gas pressure in Pa
T = 273.15; % current gas temperature in K
R = 8.314; %ideal gas constant J/K/mol
M = [16.043 30.069 44.096 58.123 58.123 72.151 44.01 28.013 32 2.016 34 28.01];
methane = -672.87+439.74*(T/100)^0.25-24.875*(T/100)^0.75+323.88*(T/100)^(-0.5);
ethane = 6.895+17.26*(T/100)-0.6402*(T/100)^2+0.00728*(T/100)^3;
propane = -4.092+30.46*(T/100)-1.571*(T/100)^2+0.03171*(T/100)^3;
ibutane = 3.954+37.12*(T/100)-1.833*(T/100)^2+0.03498*(T/100)^3;
nbutane = 3.954+37.12*(T/100)-1.833*(T/100)^2+0.03498*(T/100)^3;
pentane = R*(1.878+4.1216*(T/100)+0.12532*(T/100)^2-0.037*(T/100)^3+0.001525*(T/100)^4);
diocarbhone = -3.7357+30.529*(T/100)^0.5-4.1034*(T/100)+0.024198*(T/100)^2;
azote = 39.060-512.79*(T/100)^(-1.5)+1072.7*(T/100)^(-2)-820.4*(T/100)^(-3);
oxygenne = 37.432+0.020102*(T/100)^1.5-178.57*(T/100)^(-1.5)+236.88*(T/100)^(-2);
hydrogene = 56.505-702.74*(T/100)^(-0.75)+1165*(T/100)^(-1)-560.7*(T/100)^(-1.5);
hydrosulf = R*(3.071029+0.5578*(T/100)-0.1031*(T/100)^2+0.01202*(T/100)^3-0.0004838*(T/100)^4);
monocarbhone = 69.145-0.70463*(T/100)^0.75-200.77*(T/100)^(-0.5)+176.76*(T/100)^(-0.75);
Cpmol = [methane ethane propane ibutane nbutane pentane diocarbhone azote oxygenne
hydrogene hydrosulf monocarbhone];
MassMol = 1/100*sum(M.*compo);
HeatCapacity = 1/100*sum(Cpmol.*compo)*1000./MassMol;
speedofsound = sqrt(HeatCapacity / ( HeatCapacity -1000*R/MassMol)*R*T/MassMol*1000
```

The variation of the speed of sound of the various components of natural gas according to the temperature is presented on Figure 7 at atmospheric pressure. Good agreement is obtained for the 5 major gases constituting a natural gas, see figure 8.

$$\forall T \in [300 \dots 500] \max(\varepsilon_c) = \max \left| \frac{c_{hm}(T) - c_{CHEM}(T)}{c_{CHEM}(T)} \right| \quad (47)$$

Fig. 7. Speed of sound for main constituents of natural gases

Fig. 8. Relative error between hand-made function and CHEMKIN for speed of sound

2.4.2 Sound velocity sensor

Acoustic wave propagation is characterized by the speed of sound c in the propagation medium. Several techniques allow the measurement of this characteristic in gases. Three methods of measurement can be distinguished such as:

- the acoustic waves dephasing,
- the acoustic resonator,
- the time of transit.

The last method is largely used in industrial applications such as level measurement, flow metering, etc... (Hauptmann et al., 2002). It involves measurement of the transit time of an ultrasonic pulse travelling over a known propagation distance in the gas. This technique typically employs one or more piezoelectric transducers to generate and detect sound waves in the frequency range of about 20 kHz to 1 MHz and higher. A particular technique known as a “pulse echo” technique uses a single transducer as both the transmitter and the receiver see Figure 9. The generated sound wave is reflected back to the source transducer from a target located at a known distance from the transducer, and is received by the same transducer. If the distance between the transducer and the reflecting target is D , and the measured two-way travel time is t , then the speed of sound is represented by:

$$c = \frac{2 D}{t} \tag{48}$$

This method is advantageous because it uses only one transducer. However, in applications requiring high precision speed of sound measurements, the method has the disadvantage of introducing time delay errors associated with imperfectly defined and variable distance, D , and an imperfect ability to determine the exact time delay with respect to the time of the transmitted pulse and the time instant when the reflected sound wave is received at the transducer.

Fig. 9. “Pulse echo” technique

Fig. 10. Modified “pulse echo” technique

To reduce the time delay error, the pulse echo method may be modified to measure a time difference between two received signals (Kelner et al., 2004). A transmitted wave is reflected from two different targets rather than a single target, see Figure 10. The distance, DD , between the two targets is known. Using this method, the speed of sound is represented by:

$$c_{gas} = \frac{2\,DD}{\Delta t}$$

(49)

where Δt is the time difference between the two received signals.

2.5 Refractive index

Guérin (1981) expressed refractive index n_g of a gas, for radiation of wavelength μ , according to the density:

$$n_g^{\mu_0} - 1 = q \rho_g^{def} = IR$$

(50)

Where q is a constant.

Noting RI_0 the value of RI corresponding to the normal conditions (273,15 K, 1 atm) and assuming that the gases follow ideal gas law, the value of RI (called co-index of refraction, but named improperly refractive index too) relates to temperature T (in Kelvin) and pressure P (in atmosphere) is given by:

$$RI = RI_0 \frac{T_0}{T} \frac{P}{P_0}$$

(51)

Co-index of refraction has an additive property:

$$RI = \sum_{i=1}^{\nu} x_i \, RI_i$$

(52)

Equations (51-52) are enough to calculate with precision the co-index of refraction of natural gases.

2.6 Density and specific density

In the case of a gas mixture, the expression of the specific density d_m is written:

$$d_m = d_m^{IGL} \frac{Z_{air}(T, P)}{Z_m(T, P)} \quad (53)$$

with

$$Z_m = 1 - \left(\sum_{i=1}^v x_i \sqrt{1 - Z_i} \right)^2 + 0.0005 (2 x_H - x_H^2) \quad (54)$$

With Z_i compressibility factor of component i , x_H molar fraction of hydrogen.

Specific density d_m^{IGL} is independent of any state of reference and is calculated starting from the equation:

$$d_m^{IGL} = \sum_{i=1}^v x_i \frac{M_i}{M_{air}} \quad (55)$$

In the same way, the density is obtained by:

$$\rho(T, P) = \frac{\rho_m^{IGL}(T, P)}{Z_m(T, P)} \quad (56)$$

$$\rho_m^{IGL} = \left(\frac{P}{R T} \right) \sum_{i=1}^v x_i M_i \quad (57)$$

2.7 Synthesis

Quality of natural gas, mainly composed of methane, varies according to the various sources of supply (layers). Consequently, physical properties and energy content are subject to variations. As a result, one of the important information required for natural gas exploitation relates to its physical properties. Besides the properties of transport (viscosity, thermal conductivity), various models of determination speed of sound, index of refraction and density were presented.

3. Combustion features

Combustion features of a gas such as the low heating value, Wobbe index and air-fuel equivalence ratio are of a great industrial interest. These properties interest both engine manufacturers and business activities of CHP installations and boilers. The commercial transactions on natural gas are generally based on the energy content of gas, obtained by multiplying the volumes measured by the higher heating value.

3.1 Air Fuel Ratio

Air Fuel ratio ε is defined as the ratio of air volume (or mass) V_a (at normal conditions of temperature and pressure) required to the theoretical complete combustion per fuel volume unit (or mass). Complete combustion of generic fuel $C_xH_yO_zN_u$ under stoichiometric conditions gives equivalence ratio [Nm³/Nm³]:

$$\begin{cases} x = \frac{x_{CH_4} + 2x_{C_2H_6} + 3x_{C_3H_8} + 4x_{C_4H_{10}} + 5x_{C_5H_{12}} + x_{CO_2}}{x_{CH_4} + x_{C_2H_6} + x_{C_3H_8} + x_{C_4H_{10}} + x_{C_5H_{12}} + x_{CO_2} + x_{O_2} + x_{N_2}} \\ y = \frac{4x_{CH_4} + 6x_{C_2H_6} + 8x_{C_3H_8} + 10x_{C_4H_{10}} + 12x_{C_5H_{12}} + x_{CO_2}}{x_{CH_4} + x_{C_2H_6} + x_{C_3H_8} + x_{C_4H_{10}} + x_{C_5H_{12}} + x_{CO_2} + x_{O_2} + x_{N_2}} \\ z = \frac{2x_{CO_2}}{x_{CH_4} + x_{C_2H_6} + x_{C_3H_8} + x_{C_4H_{10}} + x_{C_5H_{12}} + x_{CO_2} + x_{O_2} + x_{N_2}} \\ u = \frac{2x_{N_2}}{x_{CH_4} + x_{C_2H_6} + x_{C_3H_8} + x_{C_4H_{10}} + x_{C_5H_{12}} + x_{CO_2} + x_{O_2} + x_{N_2}} \end{cases} \quad (59)$$

$$\varepsilon = \frac{1}{21\%} \left(x + \frac{y}{4} - \frac{z}{2} \right) \quad (60)$$

$$\varepsilon = \sum_{i=1}^v x_i \varepsilon_i \quad (61)$$

Industrial combustion is never complete, dissociations/recombinations occurred.

Where λ is the relative air fuel ratio.

3.2 Heating value

Low heating value is the energy released during fuel combustion (of unit of mass or volume) under stoichiometric condition and thermodynamic conditions (P , T) giving CO_2 and H_2O products. Through the world, different thermodynamic reference conditions are considered as reference conditions.

$$LHV = \sum_{i=1}^v x_i LHV_i \quad (63)$$

High heating value HHV is deduced from low heating value LHV and is defined as the heat that can be obtained by condensing the water vapor produced by combustion.

3.3 Wobbe index

Wobbe index (W) is an important criterion of inter-changeability of gases in the industrial applications (engines, boilers, burners, etc). Gas composition variation does not involve any notable change of air factor and of flame speed when Wobbe index remains almost constant. Wobbe index can be calculated starting from the high heating value (HHV) and specific gas density (d) by:

$$W = \frac{HHV}{\sqrt{d}} \quad (64)$$

This parameter is usually used to characterize gas quality. Indeed, two gases with the same Wobbe index deliver the same quantity of heat for the same supply pressure. Thus, for an industrial burner for example, one maintains heat flow with a constant value by the output control of gas according to the index of Wobbe.

In DOE report (2007), a modified Wobbe index is used in real applications:

$$W_r = \frac{LHV}{\sqrt{d T}} \quad (65)$$

This modified Wobbe index takes account for heating of the fuel and the uncovered heat from water vapour formed during combustion.

3.4 Methane number

Methane number (MN) characterizes gaseous fuel tendency to auto-ignition. By convention, this index has the value 100 for methane and 0 for hydrogen (Leiker et al., 1972). The gaseous fuels are thus compared with a methane-hydrogen binary mixture. Two gases with same value of MN have the same resistance against the spontaneous combustion

4. Measuring instruments

Combustion features can be determined according to two types of methods: direct or indirect. Direct methods are based on calorimetric measures where the energy released by the combustion of a gas sample is measured. Indirect methods are issued of either calculation from gas composition, or of measurements of gas physical properties.

4.1 Calorimeter

This direct method is based on calorimetric measures. Ulbig & Hoburg (2002) synthesized measurement of heat value by:

- combustion of a gas sample inside a calorimetric bomb (isochoric combustion),
- combustion of a gas with a gas-burner (isobar combustion),
- catalytic combustion (isobar combustion without flame) by oxidation of a gas on a catalyst.

Combustion technique with a gas-burner is largely used. Various types of calorimeters, based on this technique, are employed: Junkers, Reinke, Thomas--Cambridge and Culter--Hammer. Operation principle, presented on Figure 11, is identical. Specific quantity of gas is measured then burned completely. In a heat exchanger, energy released by combustion heats a coolant (water or air). Consequently, coolant temperature increase makes it possible to measure gas heating value. Apparatus calibration is done using reference gas which its specific heating value is known (in general pure methane).

Fig. 11. Calorimeter operation principle

Catalytic combustion is safe way (flameless) to measure high heating value of gases (Hornemann, 1995), (Heyden & Berg, 1998). This batch method is based on the following principle: gas mixture and air are introduced on a noble metal (platinum). Air quantity introduced is sufficient for gas mixture oxidation. Hydrocarbons are oxidized over noble metal being a catalyst. The procedure is renewed thereafter with an unknown gas mixture. Heat released can be measured either starting from temperature changes related to the catalytic reaction, or starting from electric output changes required to keep catalyst at

constant temperature. This method can however be subject at two errors: incomplete gas oxidation or catalyst poisoning.

4.2 Stoichiometric combustion

For saturated linear hydrocarbons (alkanes), there exists a linear relation between air fuel ratio and low heating value of gas mixtures, see Figure 12. This measurement principle is thus issued on air volume knowledge per unit of gas volume under stoichiometric combustion. Consequently, that makes it possible to reach the calorific value of gas starting from the following relation see (Ingrain, 1990):

$$LHV = K \left(\frac{V_a}{V_m} \right) \quad (66)$$

Fig. 12. Linear relation between LHV and Stoichiometric Air-to-gas ratio

4.3 Gas composition

Gas chromatography and mass spectroscopy are the most commonly employed laboratory techniques. These two techniques are based upon the separation of gas species followed detection.

4.3.1 Gas chromatography

Gas chromatography is a partition method. It is based on components distribution of a sample between mobile phase (the gas) and stationary phase (liquid or solid), see Figure 13 upon a column. The column provides a pathway, which aims to separate the species based upon molecular size, charge, polarizability, and other physical parameters which limit interactions between the gas species and the column materials. If the components of the sample have different partition coefficients between the two phases, they migrate with different speeds. An inert carrier gas (e.g. nitrogen or helium) is used to transport the gas sample through the columns.

Fig. 13. Gas chromatography principle

Gas chromatography is considered accurate and reliable. However, it is usually slow and the columns require maintenance. It is not considered practical for a continuous on-line application.

Calculation of heating value and Wobbe index of gas are obtained regards to the standard procedure ISO 6976. For a natural gas, the higher heating value is written see (Ingrain, 1990):

$$HHV = \frac{\sum_{i=1}^v x_i HHV_i}{Z_m} \quad (67)$$

Where Z_m is the compressibility factor, see Equation (54).

4.3.2 Mass Spectrometer

Mass spectrometer is based mainly upon the mass-to-charge ratio of ionized species. The mass spectrum is generated by first ionizing natural gas and the accelerating it with an electric field. The ions are separated by their momentum distribution.

Most mass spectrometers have software that determines gas concentrations from peak intensities and allows real time calculations

4.4 Gas composition by Infrared spectroscopy

Infrared spectroscopy method exploits the property that natural gas components absorb light in a given wavelength of the infra-red spectrum. Only the hydrogen, which do not absorb the infrared radiation, and the carbon monoxide, which absorbs in another area of the spectrum, do not take part in this phenomenon. The general diagram is represented on the figure 14.

From calibration, using the absorption band of the methane and the band of hydrocarbons higher than methane, the measurement of radiation absorption lead to the determination of the heating value of natural gas. However, the components higher than the C_4 , as well as hydrogen, do not absorb the infra-red radiation. Consequently, those components are not taken into account for the calculation of the calorific value

Fig. 14. Infrared spectroscopy principle

5. Physical properties methods

Besides the combustion or analysis of fuel gases, it is also possible to correlate and, respectively, calculate the calorific value by measuring the physical properties of the gas mixture. Correlations have to be determined, allowing the calorific value to be reliably calculated as a function of one or several different physical properties.

- For gases distributed in the United Kingdom, British Gas (Thurston et al., 2002) established correlation to estimate low heating value *LHV* regards to speed of sound measurement and thermal conductivity of natural gas. Low heating value is thus given by the expression :

$$LHV = a_1 \lambda_{T_H} + a_2 \lambda_{T_L} + a_3 c + a_4 T_a + a_5 T_a^2 + a_6 \quad (68)$$

Where λ_{T_H} is the thermal conductivity of natural gas at temperature T_H , respectively λ_{T_L} the thermal conductivity at temperature T_L , c is the speed of sound, T_a the ambient temperature, a_1 to a_6 are the fitted coefficients.

Thurston et al. (2002) proposed : $a_1 = 36.25649$, $a_2 = -45.5768$, $a_3 = 0.047029$, $a_4 = 0.091067$, $a_5 = 0.00074$ and $a_6 = 24.18731$ under conditions $T_H - T_a = 70\text{ K}$ and $T_L - T_a = 50\text{ K}$.

- In partnership with the department of energy of the United States, Morrow and Behring (1999), of Southwest Research Institute, have developed a correlation based on speed of sound, nitrogen and carbon dioxide contents. *HHV* is evaluated by:

$$HHV = \frac{54343.048 + B M_{CH}}{M} \quad (69)$$

$$B = 20442.406 + (0.04552871 - 0.02523803 x_{N_2} - 0.02568212 x_{CO_2})c \quad (70)$$

Where x_{N_2} is the volume fraction of N_2 , respectively x_{CO_2} the volume fraction of CO_2 , and c is the speed of sound, M is the mass molar of the mixture, evaluated by:

$$M = \sum_{i=0}^2 (a_0^i + a_1^i x_{N_2} + a_2^i x_{CO_2}) c^i \quad (71)$$

- Bonne (1996) proposed a general expression :

$$HHV = 3643.53 + 1050.71 \left(\frac{102}{\eta} \right)^3 - 7.60221 \lambda_{T_H} - 2294.2 \left(\frac{\lambda_{T_L}}{\lambda_{T_H}} \right) \quad (72)$$

Where λ is the thermal conductivity (cal/s m °C) and T_L , T_H are the low and high temperatures respectively (°C). η is the gas viscosity (μpoise). This HHV estimation has a maximal error of 0.067 MJ.m^{-3} with a standard error of $0.01831 \text{ MJ.m}^{-3}$.

$$HHV = -1287.7 + 808700 C_p^{0.73846} - 1048800 \lambda^{-1.742} - 9.0189 \cdot 10^{-4} (\eta M)^{1.7514} \quad (73)$$

- Pinvidic et al. (2000), of Gaz de France, developed a correlation of high heating value regards to light beam optical absorption by gas components. Light beam defines three bands of wave length measure, located to the near infrared, with a width of 10 to 20 10^{-9} m . HHV is deduced from the measurement of temperature T , pressure P and transmission coefficients τ_i , $i \in \{1, 2, 3\}$ of natural gas in three bands. HHV is expressed thus by the following relation:

$$HHV = \sum_{i=1}^3 \left(a_{0,i} + a_{1,i} \frac{T}{P} \right) \ln(\tau_i) + \left(a_0 + a_1 \frac{T}{P} \right) \quad (74)$$

Where $a_{0,i}$, $a_{1,i}$, a_0 and a_1 are obtained from reference gases. This fitting has a maximum error of 1%.

- Tacke and Kastner (2003) developed measure device of HHV , in particular, for natural gas. The apparatus set up uses infrared radiation dispersion regards to wavelengths getting a spectrum. This spectrum is detected by a system to be analyzed thereafter. HHV is deduced through the correlation:

$$HHV = \sum_i \alpha_{\mu_i} HHV_{\mu_i} \tag{75}$$

Where α_{μ_i} is the absorption coefficient for wavelength μ_i and HHV_{μ_i} is the high heating value of the component which has its wavelength μ_i .

- Florisson and Burrie (1989) determined Wobbe index based on density estimation and nitrogen and carbon dioxide contents. The correlation is valid only for gases whose Wobbe index is in the range 43.4 and 44.4 MJ m⁻³.

$$W = \frac{5.671 + 61.36 d - 98.97 x_{CO_2} - 64.57 x_{N_2}}{\sqrt{d}} \tag{76}$$

- Pickenäcker et al. (2000) showed that Wobbe index can also be given by a technique based on measurements of dynamic viscosity. They obtained the following correlation:

$$W = -28.486 \ln \left[\eta \left(\frac{T_{ref}}{T} \right)^{0.8405} \right] + 311.10 \tag{77}$$

- Rahmouni et al. (2003-2004)

Fig. 15. Determination of the ternary composition by using a mixture diagram.

A non-correlative method was proposed by Rahmouni et al. (2004). Combustion properties of natural gas were calculated from a ternary composition that has the same physical properties as the tested gas. As illustrated on Figure 15, when measured physical properties of natural gas are represented in a ternary diagram mixture, an 'equivalent' ternary composition is determined. That pseudo-composition has no connection to the composition of the real gas (natural gas of five or more constituents). The term 'equivalent' means that the three compounds – gas, has the same two physical properties than the real gas (same refraction index and same thermal conductivity for instance). Then, the combustion properties are evaluated using the 'equivalent' ternary composition (or pseudo-composition) and match the real gas combustion properties.

The choice of these properties was based on a statistical analysis (numerical experiment plan, principal component analysis) of a natural gas base distributed in Europe. The basic assumption is that if the measurement of two physical properties corresponds to the description of a ternary gas, then the properties of combustion of this ternary gas will be also those of the real gas which models the ternary gas, with the help of a reasonable error.

The statistical analysis concluded that methane and ethane, then comes propane and nitrogen, are the most influent component of natural gas. Thus, two ternary mixtures can be considered: CH₄-C₂H₆-C₃H₈ or CH₄-C₂H₆-N₂.

Three combinations Ternary diagram / physical properties were used:

- The measurement of thermal conductivity and co-index of refraction for T = 293 K and using CH₄-C₂H₆-C₃H₈ diagram,
- Combination of the precedent measurements with the CH₄-C₂H₆-N₂ diagram,
- The measurement of thermal conductivity for two temperature levels 293 K and 343 K.

The relations below describe the intersection of two physical properties in a ternary diagram which give the ternary pseudo-composition:

$$x_1 = x_{10} + \left(1 - \frac{a_1(\phi_1)}{\sqrt{3}}\right) \cdot \left(\frac{b_1(\phi_1) - b_2(\phi_2)}{a_2(\phi_2) - a_1(\phi_1)}\right) + \frac{b_1(\phi_1)}{\sqrt{3}} \quad (78)$$

$$x_2 = x_{20} + \frac{2 a_1(\phi_1)}{\sqrt{3}} \cdot \left(\frac{b_2(\phi_2) - b_1(\phi_1)}{a_1(\phi_1) - a_2(\phi_2)}\right) + \frac{2 b_1(\phi_1)}{\sqrt{3}} \quad (79)$$

$$x_3 = 1 - x_1 - x_2 \quad (80)$$

Where ϕ_i : Physical property i , x_1, x_2 and x_3 : Ternary gas composition, x_{10} : Lower limit of x_1 axis, x_{20} : Lower limit of x_2 axis, a_1, b_1, a_2 and b_2 : Coefficients depending on physical properties and temperature. Once the composition of the ternary mixture is determined, the combustion properties can be calculated using Equations 63, 64 and 65.

Fig. 16. Relative error between pseudo-composition and direct GC analysis for high heating value

Based on the work of Rahmouni et al. (2003-a and 2003-b), Loubar et al. (2007) have used a quaternary pseudo-composition in order to improve the accuracy of combustion properties determination. However, with a pseudo-composition of five components, it is impossible to use the previous graphical method involving mixture diagrams. So, they determined the compositions by solving a nonlinear system of equations expressing, for quaternary gases, the thermal conductivity (Equation 30), at two fixed temperatures ($T_1 = 333$ K and $T_2 = 383$ K), the speed of sound determined at $T_3 = 303$ K (Equation 36) and the carbon dioxide content. Figure 16 shows the percentage of the relative error of high heating value, calculated from pseudo-composition and the GC analysis. The mean absolute deviation (MAD) is about 0.01%.

6. Summary

The actual composition of natural gas depends primarily on the production field from which it is extracted and limited variations in composition must therefore be accepted. Moreover, at a local distribution level, seasonal adjustments by the local gas distributor may cause significant variations in the gas composition. Consequently, physical properties and energy content are subject to variations and their calculation / estimation is of great importance for technical and economical aspects.

In this chapter, physical models for the calculation of physical properties of natural gas are presented. Physical models of transport properties (viscosity, conductivity) result from the kinetic theory of gases. Viscosity and thermal conductivity of gases mixture (like natural

gas) can be estimated from the properties of pure gases and requiring some correction factors. These physical models offer a good tool for industrial calculations and applications. Speed of sound can be easily determined from the composition of natural gas. Besides, different methods and devices are developed to measure this property with a good accuracy. A particular technique known as a “pulse echo” was presented. This technique uses a single ultrasonic transducer as both the transmitter and the receiver and two obstacles separated by a known distance. The speed of sound of natural gas is then determined from the transit time and the distance between the targets.

In addition, properties such as refractive index and the specific density were presented. These properties can be used in correlations in order to estimate other properties that are difficult to measure or need expensive instruments.

Various techniques of determination of combustion features such as air-fuel ratio, the low heating value and Wobbe index are exposed. These techniques are based on direct or indirect methods. Besides the combustion or analysis of fuel gases, it is possible to correlate and, respectively, calculate the combustion features by measuring the physical properties of the gas mixture. Some correlations can be limited to a region, a quality of natural gas or a specified range of combustion properties variation. So, it is important to consider those correlations according to their specified conditions. Researchers and industrials continue their efforts in developing methods and devices to reach rapid and accurate measurement / determination of natural gas properties regarding the stakes.

7. References

- Bonne U. (1996). Sensing fuel properties with thermal microsensors. Proc. SPIE Vol. 2722, p. 165-176, Smart Structures and Materials 1996: Smart Electronics and MEMS, Vijay K. Varadan; Paul J. McWhorter; Eds.
- Chapman C. & Cowling T.G. (1970). *The mathematical theory of non-uniform gases*, Press Syndicate of the University of Cambridge, ISBN 0 521 40844.
- Chung T.H., Lee L.L. & Starling K.E. (1984). Applications of Kinetic Gas Theories and Multiparameter Correlation for Prediction of Dilute Gas Viscosity and Thermal Conductivity, *Industrial & engineering chemistry fundamentals*, Vol. 23, No. 1, p 8-13, ISSN 0196-4313
- Chung T.H., Ajlan M., Lee L.L. & Starling K.E. (1988). Generalized Multiparameter Correlation for Nonpolar and Polar Fluid Transport Properties, *Industrial & engineering chemistry research*, Vol. 27, No. 4, p 671-679, ISSN 0888-5885.
- DOE (2007) LNG Interchangeability/Gas Quality: Results of the National Energy Technology Laboratory's Research for the FERC on Natural Gas Quality and Interchangeability, DOE/NETL-207/1290, prepared by U.S. Department of Energy, National Energy Technology Laboratory
- Estela-Urbe J.F., Jaramillo J., Salazar M.A. & Trusler J.P.M. (2003). Viriel equation of state for natural gas systems. *Fluid Phase Equilibria*, Vol. 204, No. 2, pp. 169--182. ISSN 0378-3812
- Estela-Urbe J.F. and Jaramillo J. (2005). Generalised viriel equation of state for natural gas systems. *Fluid Phase Equilibria* Vol. 231, No.1, pp. 84--98, ISSN 0378-3812.

- Florisson O. & Burrie P.H. (1989). Rapid determination of the Wobbe index of natural gas. *Journal of physics. Part E. Scientific instruments* ISSN 0022-3735, Vol. 22, No.2, p. 123-128.
- Guérin H. (1981) *Traité de manipulation et d'analyse des gaz*. Ed. Masson 2nd édition.
- Greenspan M. and Wimenitz F.N. (1953). *An acoustic viscometer for gases- Part I*. National Bureau of Standard Report No. 2658. pages 25. OSTI ID: 4379711.
- Hanley H.J., McCarty R.D. & Haynes W.N. (1975). Equation for the viscosity and thermal conductivity coefficients of methane, *Cryogenics*, Vol. 15, No. 7, p413-417
- Hauptmann P., Hoppe N. and Püttmer A. (2002). Application of ultrasonic sensors in the process industry. *Meas. Sci. Technol.* 13 R73 – R83, ISSN 0957-0233
- Heyden W.H.V. & Berg R.A. (1998) Measuring heating value using catalytic combustion. *United States Patent*, US 0 575 986 2A, pp. 1--14, 1998.
- Hirschfelder J.O., Curtiss C.F. & Bird R.B. (1954). *Molecular theory of gases and liquids*, Ed. John Wiley, ISBN 978-0-471-40065-3.
- Hornemann J.A.T. (1995) *Method for determining the calorific value of a gas and/or the Wobbe index of natural gas*. European Patent, EP 0 665 953 B1, pp. 1--9.
- Ingrain D. (1990). Caloric value of gases (in french). *Technique de l'ingénieur*, ISSN 0399-4147 Vol. RC3, No. R 2980, pp. 1--10.
- Jaescheke M., Benito A., Fredheim A., Henault J. M., Viglietti B., van Wesenbeeck P., Klimeck R., Kunz O. & Wagner W. (2003), GERG Project : Wide-range reference equation of state for natural gases. *Gas- und Wasserfach. Gas Erdgas*, Vol. 144, No. 7, p. 430 – 435, ISSN 0016-4909.
- Jaeschke M. and Schley P. (1995). Ideal gas thermodynamic properties for natural gas applications. *International Journal of Thermophysics*, Vol. 16, No. 6, p. 1381 – 1392, ISSN 0195-928X, DOI 10.1007/BF02083547.
- Kelner E., Minachi A., Owen T. E, Burzynski JR. M. and Petullo S. P. (2004). Device for precision measurement of speed of sound in a gas. *United States Patent*, US 2004/0093948 A1.
- Leiker M., Christoph K., Rankl M., Cartellieri W. & Pleifer U. (1972). Evaluation of anti-knocking property of gaseous fuels by means of methane number and its practical application to gas engines, *ASME paperNo. 72-DGP-4*, Vol. 94, Issue 7, p55
- Le Neindre B. (1998). *Heat conductivity of gases and liquids* (in french), Ed. Technique de l'ingénieur, K 427, p1-43.
- Loubar K., Rahmouni C., Le Corre O. and Tazerout M. (2007). A combustionless determination method for combustion properties of natural gases, *Fuel*, Vol. 86, No. 16, p 2535-2544, ISSN 0016-2361, DOI: 10.1016/j.fuel.2007.02.024.
- Morrow T.B. and Behring K.A. (1999). Energy flow measurement technology, and the promise of reduced operating costs. *4th International Symposium on Fluid Flow Measurement*, Denver, CO. June 28--30, pp. 1--12, 1999.
- Mason E.A. and Monchick I. (1962). Heat Conductivity of Polyatomic and Polar Gases, *The journal of Chemical Physics*, Vol. 36, p. 1622- 1962. ISSN 0021-9606 doi:10.1063/1.1732790
- Mason E.A. and Saxena S.C. Approximate formula for the thermal conductivity of gas mixtures, *The Physics of Fluids*, Vol.1, No. 5, p. 361-369, ISSN 0031- 9171 doi:10.1063/1.1724352.

- Neufeld P.D., Jansen A.R. & Aziz R.A. (1972). Empirical equations to calculate 16 of the transport collision integrals $\Omega^{(l,s)*}$ for the (12-6) potential, *Journal of Chemical Physics*, Vol. 57, p 1100-1102, ISSN 0021-9606
- Pickenäcker K., Trimis D. & Wawrzinek K. (2000). Excess air controlled operation of boilers and furnaces by means of Wobbe number measurement. *5th European Conference on Industrial Furnaces and Boilers (INFUB5)*, ISBN 972-8034-04-0, Espinho-Porto, Portugal (11/04/2000)
- Pinvidic J.J., Juen G.L. & Pelous G.P. (2000). Method and apparatus for determining the calorific value of a natural gas optically and in real time. *United States Patent*, US S6157455A.
- Saikaly K., Rousseau S., Rahmouni C., Le Corre O. & Truffet L. (2008). Safe operating conditions determination for stationary SI gas engines, *Fuel Processing Technology*, Vol. 89, No. 11, 1p169-1179, ISSN 0378-3820
- Rahmouni C., Le Corre O. and Tazerout M. (2003-a). Online determination of natural gas properties, *Comptes Rendus Mecanique*, Vol. 331, No. 8, Pages 545-550, ISSN 1631-0721, DOI: 10.1016/S1631-0721(03)00126-8.
- Rahmouni C., Tazerout M. and O. Le Corre (2003-b)., Determination of the combustion properties of natural gases by pseudo-constituents*, *Fuel*, Vol. 82, No. 11, Pages 1399-1409, ISSN 0016-2361, DOI: 10.1016/S0016-2361(03)00029-2.
- Rahmouni C., Tazerout M. and Le Corre O. (2004). Method for determining at least one energetic property of a gas fuel mixture by measuring physical properties of the gas mixture, *Patent US2004195531*, 2004-10-07, Also published as US7091509, FR2827961, RU2004102387, WO03012435, EP1412742
- Reid R.C., Prausnitz J.M. and Poling B.E. (1987). *The properties of gases & liquids*. Ed. McGraw Hill Book Company, Fourth Edition, ISBN 978-0-07-118971-2.
- Rojey A., Durand B., Jaffret C., Jullian S. & Valais M. (2000). *Natural gas : Production – processing – transport (translate by N. Marshall)*, Eds Technip, ISBN-13 978-2710806936
- Starling K. E. and Savidge J. L. (1992), *Compressibility factors of natural gas and other related hydrocarbon gases*. AGA Transmission Measurement Committee. Report 8, American Gas Association.
- Tacke M. & Kastner J. (2003). Photometric device and photometric method for determining the gross calorific value of a test gas. *United States Patent*, US 6555820B1.
- Thurston R.R., Hammond P.S. and Price B.L. (2002). Method and apparatus for measuring the calorific value of a gas. *United States Patent*, US 6442996B1.
- Ulbig P. & Hoburg D. (2002). Determination of the calorific value of natural gas by different methods. *Thermochimica acta*. Vol. 382, No.1-2, pp. 27 – 35, ISSN 0040-6031.
- Vogel E., Wilhelm J., Küchenmeister C. & Jaeschke M. (2000). High-precision viscosity measurements on methane, *High temperatures-high pressures*, Vol. 32, No. 1, p. 73-81, doi:10.1068/htwu359.
- Wilhem J., Gillis K.A., Mehl J.B. and Moldover M.R. (2000). An improved Greenspan acoustic viscometer. *International Journal of Thermophysics*, Vol .21, No. 5, p. 983-997, ISSN 0195-928X, DOI: 10.1023/A:1026471901657
- Wilke C.R. (1950). A viscosity for gas mixtures, *Journal of Chemical Physics*, Vol. 18, p517-519, ISSN 0021-9606

IntechOpen

IntechOpen

Natural Gas

Edited by Primož Potočnik

ISBN 978-953-307-112-1

Hard cover, 606 pages

Publisher Sciyo

Published online 18, August, 2010

Published in print edition August, 2010

The contributions in this book present an overview of cutting edge research on natural gas which is a vital component of world's supply of energy. Natural gas is a combustible mixture of hydrocarbon gases, primarily methane but also heavier gaseous hydrocarbons such as ethane, propane and butane. Unlike other fossil fuels, natural gas is clean burning and emits lower levels of potentially harmful by-products into the air. Therefore, it is considered as one of the cleanest, safest, and most useful of all energy sources applied in variety of residential, commercial and industrial fields. The book is organized in 25 chapters that cover various aspects of natural gas research: technology, applications, forecasting, numerical simulations, transport and risk assessment.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Olivier Le Corre and Khaled Loubar (2010). Natural Gas : Physical Properties and Combustion Features, Natural Gas, Primož Potočnik (Ed.), ISBN: 978-953-307-112-1, InTech, Available from: <http://www.intechopen.com/books/natural-gas/natural-gas-physical-properties-and-combustion-features>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2010 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](https://creativecommons.org/licenses/by-nc-sa/3.0/), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen