2

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_2H_6	C_3H_8	C_4H_{10}	C_5H_{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).
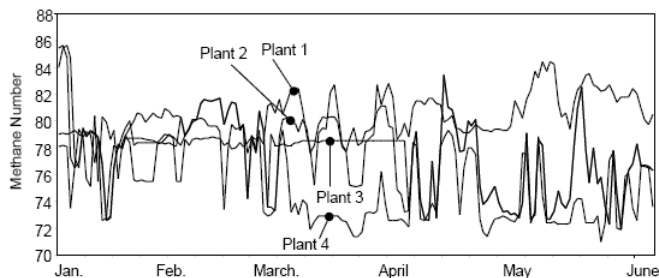
Fig. 1. Methane Number during 5 consecutive months (Saikaly et al., 2008)

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):

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

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:

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

With M the molar mass in [g mol^{-1}], T the absolute temperature in [K], σ a characteristic diameter of the molecules, often called "the collision diameter" in [1 $A°$], $\Omega^{(2,2)^*}$ 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:

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

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 $0.3 \le T_r \le 100$, 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:

$$\frac{\varepsilon}{k} = \frac{T_c}{1.2593} \tag{4}$$

$$\sigma = 0.809\,V_c^{1/3} \tag{5}$$

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

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

With $F_c = 1 - 0.2756\,\overline{\omega} + 0.059035\,\zeta_r^4 + \kappa$; $\overline{\omega}$ 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:

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

Dynamic viscosity is then expressed by:

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

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 υ components, gaseous blend viscosity is given by the expression:

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

Where

$$K_i = \frac{x_i\,\eta_i}{x_i + \eta_i \displaystyle\sum_{k=1,\neq i}^{\upsilon} x_k\,H_{ik}\left[3 + 2\,M_k/M_i\right]} \tag{10}$$

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

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

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

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

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

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

Coefficients C_i is obtained by:

$$C_i = \frac{M_i^{1/4}}{\left(\eta_i \, U_i\right)^{1/2}} \tag{14}$$

With:

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

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:

$$\eta_m = \sum_{i=1}^{\upsilon} \frac{x_i \, \eta_i}{\sum_{j=1}^{\upsilon} x_j \, \phi_{ij}} \tag{16}$$

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

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):

$$\eta_m = \eta_0(T) + \eta_1(T) \, \rho + \Delta\eta(\rho, T) \tag{17}$$

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:

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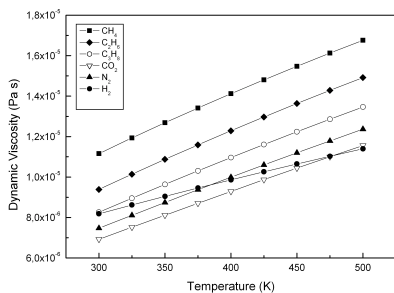

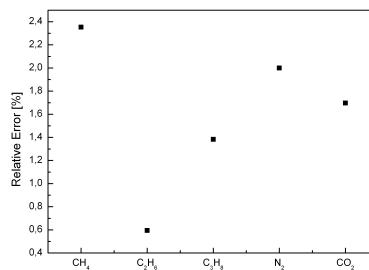Fig. 2. Dynamic viscosity for main constituents of natural gases

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.

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

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):

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

Where λ is in $[Wm^{-1}K^{-1}]$

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

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

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

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

Where C_v is the heat capacity at constant volume.

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

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

With C_{tr} in $[J\ mol^{-1}\ K^{-1}]$ 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) .

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

Where C_p is the heat capacity at constant pressure.

A modified Euken 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):

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

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:

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

With C_{rot} in $[J\ mol^{-1}\ K^{-1}]$ 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, Euken number is expressed in this case according to a coefficient of correction v as follows:

$$Eu = \frac{\lambda M}{\eta C_v} = 3.75\frac{v}{C_p/R - 1} \tag{28}$$

Coefficient V is given by the following formula:

$$v = 1 + \alpha \frac{0.215 + 0.28288\,\alpha - 1.061\,\beta + 0.26665\,\Gamma}{0.6366 + \beta\,\Gamma + 1.061\,\alpha\,\beta} \tag{29}$$

With $\alpha = \left(C_v / R\right) - 3/2$; $\beta = 0.7862 - 0.7109\overline{\omega} + 1.3168\overline{\omega}^2$ 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):

$$\lambda_m = \sum_{i=1}^{\upsilon} \frac{x_i\,\lambda_i}{\sum_{j=1}^{\upsilon} x_j\,A_{ij}} \tag{30}$$

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

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

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:

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

With $\Gamma_i = 210.0 \left(\dfrac{T_{c,i}\,M_i^3}{P_{c,i}^4}\right)^{1/6}$; $P_{c,i}$ is the critical pressure of the ith 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 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);
diocarbone = -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);
monocarbone = 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 diocarbone azote oxygene
hydrogene hydrosulf monocarbone];
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);
```
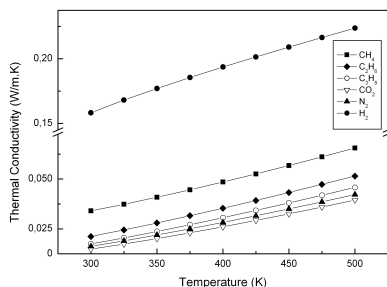
Fig. 4. Thermal conductivity for main
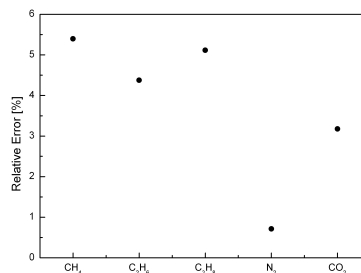constituents of natural gases

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.

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

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.
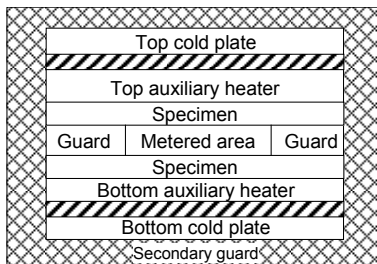

Fig. 6. Guarded hot plate method configuration.

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:

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

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:

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

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-Uribe et al. (2003, 2005) used another formulation for natural gas in the range $270 \leq T[K] \leq 330$ and $P \leq 12\ MPa$. This model presents compressibility factor according to the density by:

$$Z = 1 + B_m\ \rho + C_m\ \rho^2 \tag{39}$$

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:

$$B_m = \sum_i \sum_j x_i\ x_j\ B_{ij} \tag{40}$$

$$C_m = \sum_i \sum_j \sum_k x_i\ x_j\ x_k\ C_{ijk} \tag{41}$$

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

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

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

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

Speed of sound is written:

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

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

$$C_{v,m} = C_{v,m}^{IGL} + C_{v,m}^{res} \tag{45}$$

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

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

```
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);
diocarbone = -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);
monocarbone = 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 diocarbone azote oxygene hydrogene hydrosulf monocarbone];
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.

$$\forall T \in [300\ldots500]\ \max(\varepsilon_c) = \max\left|\frac{c_{hm}(T) - c_{CHEM}(T)}{c_{CHEM}(T)}\right| \tag{47}$$
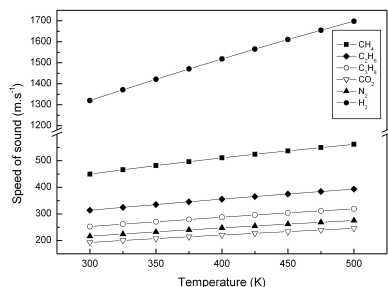
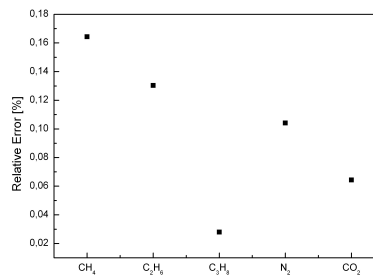Fig. 7. Speed of sound for main constituents of natural gases

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.
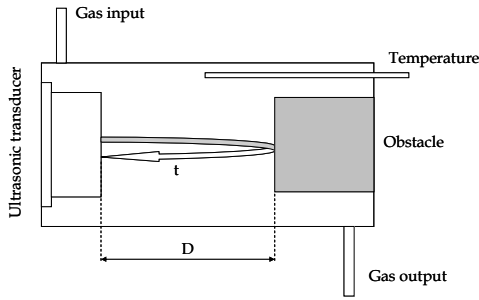
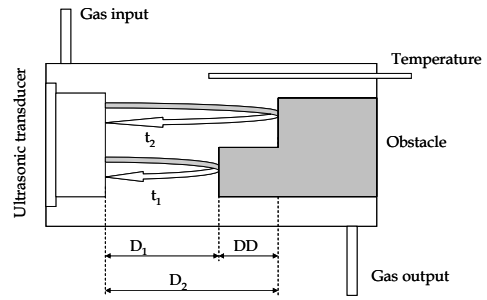Fig. 9. "Pulse echo" technique   Fig. 10. Modified "pulse echo" technique

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:

$$c_{gas} = \frac{2\,DD}{\Delta t} \tag{49}$$

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:

$$n_g^{\mu^0} - 1 = q\,\rho_g \stackrel{def}{=} IR \tag{50}$$

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:

$$RI = RI_0\,\frac{T_0}{T}\,\frac{P}{P_0} \tag{51}$$

Co-index of refraction has an additive property:

$$RI = \sum_{i=1}^{\upsilon} x_i\,RI_i \tag{52}$$

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