TEP4170 HEAT AND COMBUSTION TECHNOLOGY Exam 19 May 2023 -Suggested solutions
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1)
"Oxy-combustion" is a technology used to capture CO_2 from combustion. Fuel is burned with pure oxygen (not air). To reduce the temperature to a feasible level, CO_2, water vapour or water (liquid) is added (this is usually the role of nitrogen and surplus air).

Methane CH_4 is burned with stoichiometric oxygen together with 7 mol H_2O per mol methane. Assume a simple, global and complete reaction. The products are all in gas phase.

- Put up the reaction balance.
- Determine the composition of the product mixture (mole fractions).

The flow of products is cooled to 40 °C at constant pressure 1 bar, and some water is condensed and removed.

- How much water is condensed (mol liquid H_2O per mol methane burned).

Data: the saturation pressure of water at 40 °C is 0.0738 bar.

Reaction balance: $CH_4 + 2O_2 + 7H_2O \longrightarrow CO_2 + (2+7)H_2O$
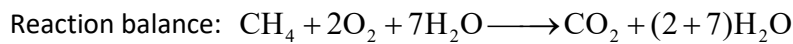
Product mixture, per mol of CH_4: n=1+2+7=10

Mole fractions: $X_{CO_2} = 1/10 = \underline{0.10}$; $X_{H_2O} = 9/10 = \underline{0.90}$

The saturation pressure at 40 °C of H_2O in the gas phase at 40 °C is $p_{sat}(40\ °C) = 0.0738$ bar 0.0738 bar, and the pas pressure is $p = 1$ bar.

The mole fraction after cooling will be $X_{H_2O(g)} = \dfrac{p_{sat}}{p} = 0.0738 = \dfrac{n_{H_2O(g)}}{n_{CO_2} + n_{H_2O(g)}}$

That is, $\dfrac{n_{H_2O(g)}}{n_{CO_2}} = \left(\dfrac{1}{X_{H_2O(g)}} - 1 \right)^{-1} = 0.080$

Condensed water: $\dfrac{n_{condensed}}{n_{CO_2}} = \dfrac{n_{H_2O}}{n_{CO_2}} - \dfrac{n_{H_2O(g)}}{n_{CO_2}} = 9 - 0.080 = \underline{8.92\ \text{mol/mol}}$

2) The species mass balance equation on "transport" form can be written as

$$\frac{\partial}{\partial t}(\rho Y_k) + \frac{\partial}{\partial x_j}(\rho Y_k u_j) = \frac{\partial}{\partial x_j}\left(\rho D \frac{\partial Y_k}{\partial x_j} \right) + R_k$$

-Introduce Reynolds' decomposition and develop the equation for the mean species mass.
For simplicity, you can assume that density and molecular transport properties do not fluctuate.
-Explain the meaning of each term of the resulting equation, and of the new quantities that appear.

Introduce the Reynolds decomposition, $u_i = \bar{u}_i + u_i'$; $Y_k = \bar{Y}_k + Y_k'$.

$$\frac{\partial}{\partial t}(\rho(\overline{Y}_k + Y'_k)) + \frac{\partial}{\partial x_j}(\rho(\overline{Y}_k\overline{u}_j + \overline{Y}_k u'_j + Y'_k\overline{u}_j + Y'_k u'_j)) = \frac{\partial}{\partial x_j}\left(\rho D\frac{\partial}{\partial x_j}(\overline{Y}_k + Y'_k)\right) + R_k$$

Assume (cf. problem) that density ρ and diffusivity D do not fluctuate.

Average the entire equation, that is, each term. Here $\overline{\overline{Y}_k} = \overline{Y}_k$; $\overline{Y'_k} = 0$; $\overline{\overline{Y}_k u'_j} = \overline{Y}_k \cdot \overline{u'_j} = 0$, $\overline{Y'_k\overline{u}_j} = \overline{Y'_k} \cdot \overline{u}_j = 0$ and we achieve the following equation (when the double-correlation term is moved over the the right-hand side):

$$\frac{\partial}{\partial t}(\rho\overline{Y}_k) + \frac{\partial}{\partial x_j}(\rho\overline{Y}_k\overline{u}_j) = \frac{\partial}{\partial x_j}\left(\rho D\frac{\partial\overline{Y}_k}{\partial x_j} - \rho\overline{Y'_k u'_j}\right) + \overline{R}_k$$

The terms are (enumerated from left): 1) change of mean species mass with time; 2) transfer of mean species mass with mean flow; 3) transport/exchange of mean species mass by molecular diffusion; 4) transport/exchange of mean species mass due to turbulent motions; 5) mean volumetric reaction (production) rate of the species.

New quantities are:

$\overline{Y}_k$ and $\overline{u}_j$ are the mean values of Y_k and u_j, i.e. mean species mass fraction of species k and mean velocity in x_j direction. $-\rho\overline{Y'_k u'_j}$ are the fluxes of mean species mass in x_j direction due to turbulent motions. $\overline{R}_k$ is the mean of the volumetric reaction (production) rate of species k.

3) Oxidation of "syngas" (a mixture of CO, H_2 and CO_2) is assumed described by the following set of reactions

$$CO + \tfrac{1}{2}O_2 \rightleftharpoons CO_2 \quad (1)$$
$$H_2 + \tfrac{1}{2}O_2 \rightleftharpoons H_2O \quad (2)$$
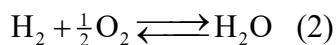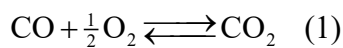
For this problem, all other reactions can be neglected. The forward rate coefficients $k_{1f}(T)$ and $k_{2f}(T)$ can be assumed as known as functions of temperature and a set of parameters (A,b,E) for each forward reaction. In principle, another set of parameters can be specified for each of the reverse rate coefficients $k_{1r}(T)$ and $k_{2r}(T)$, as well. However, this is (usually) not done.

-Explain how the reverse rate coefficients $k_{1r}(T)$ and $k_{2r}(T)$ can be determined, and why can this simplification be made.
-Express the reaction rate for O_2 based on this mechanism.
-Describe how to determine a time scale for Reaction (1).

The relation $K_c = k_f / k_r$ can be established at equilibrium. Since all three quantities are functions of the temperature alone, the ratio will be valid at other conditions at the same temperature. Hence
$$k_r(T) = k_f(T) / K_c(T)$$

$$\frac{d[O_2]}{dt} = -\tfrac{1}{2}k_{1f}[CO][O_2]^{1/2} + \tfrac{1}{2}k_{1r}[CO_2] - \tfrac{1}{2}k_{2f}[H_2][O_2]^{1/2} + \tfrac{1}{2}k_{2r}[H_2O]$$

A time scale can be expressed as $\tau = \dfrac{[CO]}{\left|\dfrac{d[CO]}{dt}\right|}$, where $\dfrac{d[CO]}{dt} = -k_{1f}[CO][O_2]^{1/2} + k_{1r}[CO_2]$

4)
A quantity is known as the "three-dimensional energy spectrum", $E(\kappa)$. Make a sketch of $E(\kappa)$. What is κ? What characterizes high values of κ, and low values of κ?

A range of the spectrum is called "dissipative", and Kolmogorov proposed quantities known as "Kolmogorov microscales" for length, velocity and time.

-Explain the basis for these quantities.
-Express the scales for length, velocity and time.

See sketch in Ertesvåg, Fig. 8.5

$\kappa = \left|\vec{\kappa}\right|$ is the wave number and $\vec{\kappa}$ is the wave number vector
The curve shows the kinetic energy of turbulent motions as distributed over wave numbers (reciprocal of length scales).

High values of κ: small eddies, large velocity gradients, large viscous forces, dissipation of kinetic energy to thermal energy. Low values of κ: large eddies few in number, much energy in each. Main contribution to mixing throughout the flow.

The "dissipative range" is the high-vavenumber range, where statistical quantities are independent of external geometries and forces. They are dependent on the energy transferred from bigger scales and the viscous forces (i.e. ε). A balance is established between the supply of energy from bigger scales, ε, and the work of the viscous forces to break down the kinetic energy to thermal energy (viscocity, length and velocity). The length and velocity (energy) are the quantities to be expressed. Thus scales representing length and velocity of the eddies in this range can then be expressed as $\eta = \eta(\varepsilon, v)$ and $\upsilon = \upsilon(\varepsilon, v)$.

Dimensional analysis gives $\eta = \left(v^3 / \varepsilon\right)^{1/4}$ and $\upsilon = \left(v\varepsilon\right)^{1/4}$.

A time scale can be expressed from length and velocity: $\tau = \eta / \upsilon = \left(v / \varepsilon\right)^{1/2}$

5)
-Define the mixture fraction (Norw: "blandingsfraksjon").
- Determine the stoichiometric mixture fraction for CO burning with (pure) O₂.
- For CO (as fuel) and O2 (as oxidizer): The mixture fraction has the value 0,2, and no fuel has reacted (i.e. pure mixing): - What is the mass fraction of CO? Explain.
Data, molar masses (kg/kmol): CO: 28, O₂: 32, CO₂: 44

The <u>mixture fraction</u> ξ is defined by $\xi = \dfrac{\varphi_{mix} - \varphi_2}{\varphi_1 - \varphi_2}$; or $\varphi_{mix} = \varphi_1 \xi + \varphi_2 (1 - \xi)$

where φ is a <u>conserved scalar</u> (quantity without source term), φ_1 and φ_2 are its values at two different inflows (1) and (2), and φ_{mix} its value in the mixture.

For a simple one-step, global reaction 1kg fu + r kg ox → (1+r) kg pr, the reaction rates will be

$R_{fu} = \frac{1}{r} R_{ox}$, and then $\left(Y_{fu} - \frac{1}{r} Y_{ox} \right)$ will be a conserved scalar (with source term $R_{fu} - \frac{1}{r} R_{ox} = 0$). r is the stoichiometric oxidizer on mass basis for the fuel.

If inlet (1) contains pure fuel ($Y_{fu,1} = Y_{CO,1} = 1, Y_{ox,1} = Y_{O_2,1} = 0$) and inlet (2) is pure oxidizer ($Y_{fu,2} = Y_{CO,2} = 0$, $Y_{ox,2} = Y_{O_2,2} = 1$), the compound function can be expressed as

$$\left(Y_{fu} - \frac{1}{r} Y_{ox} \right) = \left(Y_{fu} - \frac{1}{r} Y_{ox} \right)_1 \xi + \left(Y_{fu} - \frac{1}{r} Y_{ox} \right)_2 (1-\xi) = (1-0) \cdot \xi + (0 - \frac{1}{r} \cdot 1)(1-\xi) = \xi - \frac{1}{r}(1-\xi)$$

At stoichiometric conditions, that is when $Y_{ox} = rY_{fu}$, the mixture fraction is denoted $\xi = \xi_{st}$:

$$\left(Y_{fu} - \frac{1}{r} Y_{ox} \right) = 0 = \xi_{st} - \frac{1}{r}(1-\xi_{st}) \text{ or } \xi_{st} = \frac{1}{r+1}$$

CO reacting with pure O_2 , $CO + \frac{1}{2}O_2 \rightarrow CO_2$

$$r = \frac{0,5 \cdot M_{O_2}}{M_{CO}} = \frac{0,5 \cdot 32}{28} = 0,571 \text{ kg/kg, we obtain } \xi_{st} = 1/(1+0,571) = \underline{0,636} .$$

The mass fraction of CO can be calculated from the expressions above (keeping in mind that since there is only CO and O2, $Y_{CO} + Y_{O_2} = 1$. This will be correct (if correctly done).

However, since "no fuel has reacted", the simple way to answer is to remember what the mixture fraction is: The fraction of mass originating from Inlet 1. Thus, in a nonreacted mixture of CO and O2, $\underline{Y_{CO} = \xi = 0,2}$

6)
Premixed flames: -What is the laminar flame speed and how could you measure it using a Bunsen burner?

Flame speed is a central element in premixed flames combustion theory and is characteristic property for a given air/fuel mixture. It can be defined as the velocity at which the flame front moves with respect to the fresh gases in a one-dimensional geometry. If the appropriate coordinate system would be fixed to the propagating combustion wave then an observer riding with the flame would experience the unburned mixture approaching at the flame speed S_L. We assume that the flame is one-dimensional and unburned gas enters the flame in a direction normal to the flame sheet. Therefore, if we will use a Bunsen burner to measure S_L we need to know what is the fuel/air mixture mass flow rate to estimate fresh gas velocity Vu. Obtained premixed flame with triangle cross-section in order to remain stationary the flame speed must equal the speed of the normal component of the unburned gas at each location as illustrated below. Thus:

$$S_L = v_u \sin\alpha$$
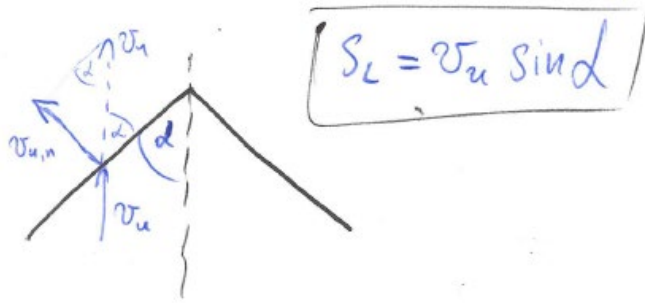
We need to know the fresh gas velocity v_u and the angle α.

7)
- Briefly explain what are turbulence-chemistry interactions: what is their physical meaning and what is the core problem of turbulence-chemistry interaction closure from the mathematical perspective?

Turbulent combustion results from the two-way interaction of chemistry and turbulence. When a flame interacts with a turbulent flow, turbulence is modified by combustion because of the strong flow accelerations through the flame front induced be heat release, and because of the large changes in kinematic viscosity associated with temperature changes. This mechanism may generate turbulence, called "flame-generated turbulence" or damp it (relaminarization due to combustion). On the other hand, turbulence alters the flame structure (e.g. flame wrinkling), which may enhance the chemical reaction but also, in extreme cases, completely inhibit it, leading to flame quenching.
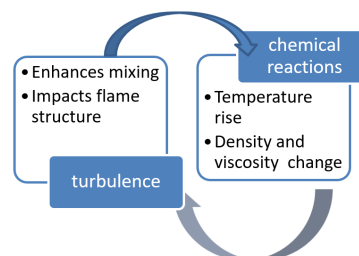
From the mathematical or modelling perspective, the problem of turbulence-chemistry interaction reveals in difficulty arising from the non-linear character of chemical source term in species transport equation, which is expressed from the Arrhenius law. As the reaction rate is highly non-linear, the averaged reaction rate cannot be easily expressed as a function of the mean mass fractions, the mean density and the mean temperature. The idea of expanding the mean reaction rate as a Taylor series of the temperature fluctuations, leads to additional difficulties because of unknown terms consisting of fluctuation quantities and in general cannot be used for realistic chemical schemes. Therefore, models developed from physical analysis, comparing chemical and turbulent time scales are needed.

- Describe the idea of presumed-PDF method for turbulent non-premixed combustion modelling,

In this approach the mixture fraction defined in Problem 5 is used. It is a conserved scalar bounded between 0 and 1, where 0 defines an oxidizer stream whereas 1 describes the fuel inlet stream. Instead of solving N species mass balance equations, only one transport equation for mixture fraction is solved, which has no source term. Then with the use of prescribed probability density function, mean mixture properties e.g. mass fraction can be obtained with the following formula

$$\bar{Y}_k = \int_0^1 Y_k(\xi) f(\xi) d\xi$$

where $f(\xi)$ is a probability density function and usually β-function is used for that purpose. Assuming infinitely fast chemistry ("mixed is burned") the relations $Y_k(\xi)$ can be obtained by assuming chemical equilibrium. Finding parameters to reproduce β-function requires knowing mean mixture fraction variance $\overline{\xi'}$. Therefore, in this approach on the top of continuity, momentum equations accompanied by turbulence model equations (e.g. k and ε) we need to solve two additional equations for the mean mixture fraction $\overline{\xi}$ and its variance $\overline{\xi'}$. It means this approach is potentially much less CPU demanding than computing for N species transport equations individually.

8)
-What is the main assumption behind the Eddy Dissipation Concept (EDC), which is shared with Eddy Dissipation Model?

The main assumption that is shared in the eddy type models is that the combustion occurs where the reactants are mixed molecularly. This happens in the smallest scales named the fine structures in the context of the EDC. In those scales most of the turbulence energy dissipates into heat, thus one can say that the chemical reactions occur where the energy dissipation takes place.

- Briefly describe what is a cascade model and why do we need it?

The energy cascade is a model of energy transfer from larger to smaller scales. It is used to find expressions for the characteristic scales of the fine structures such as velocity scale u^* or length scale L^* where as described above chemical reactions take place. The large scale level is related to the mean flow by a turbulence model e.g. k-ε model and thus the fine structure scales thanks to the cascade model can be obtained as a functions of k and ε.
(More details: The cascade is constructed so that each level is characterised by velocity u_n, length scale L_n and strain rate $\omega_n = u_n/L_n$, which is related to the next cascade level by $\omega_{n+1} = 2\omega_n$. At every level, the dissipation of energy q_n takes place and the sum over all the levels is equal to the dissipation rate of turbulence kinetic energy ε. With the assumption that for a large number of levels, when the flow is fully turbulent, the dissipation at the last level accounts for three quarters of the total dissipation, that is $q^*=3/4\varepsilon$. The feed to the first level of the cascade w'' is equal to the product of turbulence stress and strain rate in the mean flow, which is the production term in k equation)
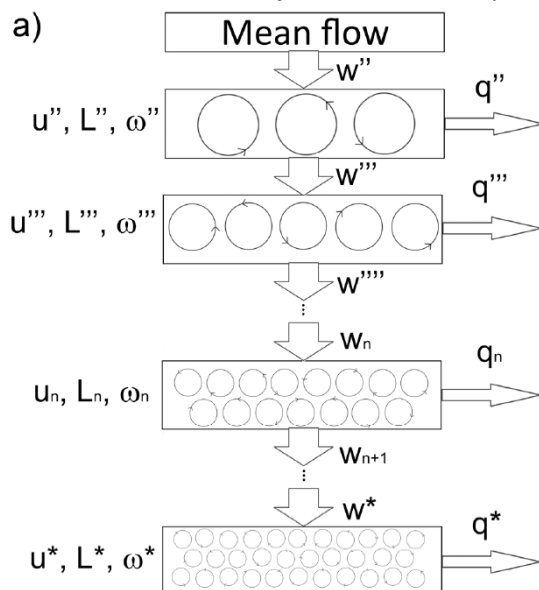
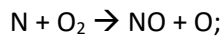**- How is the mean reaction rate formulated in EDC? Provide expression and explain each term.**
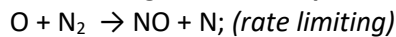
$$\bar{R}_k = \frac{\bar{\rho}\dot{m}^*\gamma^*}{1-\gamma^*}\left(Y_k^* - \tilde{Y}_k\right)$$

Where $\bar{R}_k$ is the mean reaction rate; $\tilde{Y}_k$ is the mean mass fraction of species k; Y_k^* mass fraction of species k in the fine structures (ODE of the Perfectly Stirred Reactor need to be solved for it); $\bar{\rho}$ is mean density; $\dot{m}^*$ is the mass exchange between fine structures and surroundings, divided by the mass of the fine structures, where $\frac{1}{\dot{m}^*} = \tau^*$ is the residence time of the fine structures; γ^* is the ratio between the mass in the fine structures and the total mass.
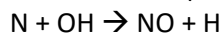
9)
- Describe what nitrogen oxides (NOx) are and what are their main formation paths.

Nitrogen oxides (NO$_x$ → NO and NO$_2$) are harmful for humans (e.g. respiratory problems) and environment (e.g. acid rains). During combustion mainly NO is formed which is a relatively less toxic gas compared to NO$_2$. Exposure to NO$_2$ can cause more severe health effects than exposure to NO, however both species are usually combined as NO$_x$ emissions because NO released to atmosphere quickly converts to NO$_2$. There are several formations paths of NO formation and usually the most contributing is a **thermal path known as Zeldovitch mechanism**:
O + N$_2$ → NO + N; *(rate limiting)*
N + O$_2$ → NO + O;
Third reaction (extended mechanism)
N + OH → NO + H
Therefore methods leading to combustion temperature reduction (EGR, water injection, combustion staging, diluting) have often huge impact on NO$_x$ emissions reduction. However, some fuels may contain nitrogen in its composition where so-called **Fuel-bound nitrogen mechanism plays an important role**. The amount of NO$_x$ formed depends on the type and amount of nitrogen compounds in the fuel and combustion conditions. E.g. very important in ammonia (NH$_3$) combustion. Hydrocarbon combustion chemistry activates another formation path: so-called **Feniomore mechanism (prompt NO)** which starts with CH radical. The other mechanisms are related to N$_2$O Intermediate route, NNH route and in combustion systems with high concentrations of OH or NH radicals (Superequilibrium concentrations of O and

10)
- The main component of particulate matter is soot. What are the main formation and destruction steps of soot? Describe the soot formation in a diffusion flame.

The main steps can be described as
-formation of precursor species (gaseous species, polycyclic aromatic hydrocarbons, e.g. benzene)
- Particle initiation, solid particles made by reactions and coagulation
- particle growth and agglomeration
-particle oxidation, more or less complete burnout

Important: soot is on the rich side of a non-premixed side

Surface Growth, Coagulation, Fragmentation, Oxidation

Coagulation

Surface Growth

Inception

Aromatic Formation