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Reaction Mechanisms of Methane for Modelling Combustion and Suppression

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Recent studies on combustion chemistry of methane is reported in this paper. Detailed combustion mechanisms has been described by identifying the key intermediate reactions. Some reduction mechanisms under different conditions are also discussed. The inhibiting effect of some fire suppressing agents on the combustion of methane and the oxidation mechanisms of methane in supercritical water are introduced. The calculation of heat of combustion indicates that the value of 13.1 MJ/kg of oxygen consumed is applicable for estimating the heat release of burning methane in air.

Key Words: Methane, Combustion mechanisms, Suppression.

INTRODUCTION

Methane (CH_4) is a colourless, odourless and tasteless gas. It is a major component of natural gas commonly used for cooking. In places with cold climates, this is also used for space heating in dense urban areas[1]. Although it has a simple chemical structure, the intermediate combustion reactions are very complex. Methane is also an important raw material for the production of hydrogen, alcohols and many other products of the chemical industry. As methane is the first member of the alkane group, it is often used as a reference fluid. Because of its almost spherical shape, it is widely used in validating numerical combustion models[2]. In addition, it is an intermediate product in the oxidation of many organic compounds of higher molecular weight. It is the rate-limiting step in the overall oxidation to give final products such as carbon dioxide and water.

With the considerable growth in recent years of the natural gas industry throughout the world, fire safety appliances associated with methane combustion should be watched carefully. Therefore, its properties and chemical reactions were studied extensively in literature[3–8]. The greatest hazards caused by methane are those of fire and/or explosion. Methane forms an explosive mixture with air when the concentration is in between 5 and 15% by volume. The 5% volume is the lower explosive limit (LEL) and 5% concentration by volume is equivalent to

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100% LEL. 15% volume is the upper explosive limit (UEL)[9]. An increase in the initial temperature of the methane/air mixture will extend the limit of flammability from 3.25 volume % to 29.1 volume % in the temperature range of 370–427°C.

A good understanding of the combustion mechanisms of methane under different conditions is important for improving the combustion efficiency and reducing environmental pollution. It will be helpful for selecting chemical agents for suppressing methane fire with more efficient fire extinguishers. As methane is the simplest organic compound, a good understanding of its combustion kinetics will be useful for extending the theory to studying the combustion of other organic compounds of higher molecular weight.

Recent studies on the mechanisms and kinetics of methane combustion will be reported in this paper. These include the detailed combustion mechanism, identification of the main reactions and some reduced mechanisms under different conditions. The heat release of burning methane per unit mass of oxygen consumed will be calculated to verify whether this gives the universal constant of 13.1 MJ/kg of oxygen consumed. In addition, the inhibiting effect of some fire suppressing agents on methane combustion and the oxidation mechanisms of methane in supercritical water will also be introduced.

Reaction mechanism of methane combustion

The chemical reactions of methane with oxygen are very complicated and can be described in different levels. The simplest level is the global reaction, which is mainly a description of the species consumed and produced or mass balancing:

$$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$$

In fact, methane oxidation does not take place only through a simultaneous collision of one methane molecule with two oxygen molecules. A more detailed description of the reactions is required for modelling the reaction[10].

Currently, the most detailed chemical reaction mechanism best representing the natural gas flames and ignition is the GRI-Mech developed by the Gas Research Institute. The systematic optimization procedure used to produce the GRI-Mech mechanism is shown in the website http://www.me.berkeley.edu/gri_mech/. The study is still ongoing and the database of GRI-Mech is constantly updated, improved and expanded. The current version is GRI-Mech 3.0 with 325 elementary chemical reactions for the 53 species. The associated rate coefficient expressions and thermochemical parameters are also presented. It is the most detailed and accepted mechanism for describing methane combustion at present. Propane and C_2 oxidation products have also been added. Formaldehyde, NO formation and reburn targets are included in the GRI-Mech 3.0 mechanism. The conditions for GRI-Mech 3.0 optimization are from temperature 1000–2500 K, pressure 10 torr to 10 atm and equivalence ratio from 0.1 to 5 for premixed systems. The use of GRI-Mech 3.0 outside the optimization and validation ranges is still reasonable. It is because the elementary reactions in natural gas ignition and flame propagation (including NO formation and reduc-

tion) are described by rate parameters reflecting the current good understanding of elementary reaction rate theory.

However, there are some suggested improvements. Soot formation and the chemistry involved in selective non-catalytic reduction of NO, which may be important in natural gas reburning at lower temperatures, cannot be described by GRI-Mech 3.0. In addition, reactions involved in the combustion of other hydrocarbon constituents of natural gas (*e.g.*, ethane and propane) are included, it is not yet applicable to model the combustion of pure fuels such as methanol, propane, ethylene and acetylene. These compounds are on the species list of GRI-Mech, but the optimization processes are not extended for these fuels.

A detailed mechanism for methane combustion over a wide range of operating conditions (900–1300 K, 6–10 atm) with 207 reactions and 40 species was reported by Hunter *et al.*[3] Not only detailed species profiles can be reproduced from the flow reactor in the intermediate temperature range at elevated pressures, the ignition delay data observed in shock tubes and the laminar speed of an atmospheric, laminar, premixed methane/air flame can also be predicted. HO_2 provided the major route for CH_3 oxidation and CH_2O was found to be a vital intermediate for all of the CH_4 oxidation paths.

Other accepted detailed mechanisms of methane combustion were developed by Stahi *et al.*[11] and Borisov *et al.*[12].

Identification of main reactions in a complex mechanism

As described in the previous section, the oxidation process of methane includes many elementary reactions. A complicated analysis is required to understand the thermodynamic and kinetic behaviour. Many such reactions were neglected in specified treatment. The main chemical reactions were identified in a complex combustion reaction[13–15].

The fastest and slowest reactions: In the reduction of complex mechanism, the identification of the fastest and slowest reactions for a particular chemical species is important. Very fast reactions with high reaction rates can reach a steady state rapidly. These are assumed under partial equilibrium conditions to determine the concentration of atomic species which are difficult to measure. The entire reaction is limited by the slowest reactions[16]. The rate of chemical reaction can be estimated by the rate coefficients K_r, expressed in Arrhenius form as:

$$K_r = AT^b \exp\left(-\frac{E}{RT}\right) \tag{1}$$

where, E = activation energy (kJ mol^{-1}),
R = gas particular constant (kJ mol^{-1} K^{-1}),
T = temperature at which the reaction is developed (K),
A = (cm mol s) empirical constant, and
b = nondimensional empirical constant.

The highest and lowest rate values of K_r and the corresponding reactions from a detailed methane combustion mechanism can be identified as shown in Table-1[17].

TABLE-1
THE HIGHEST AND LOWEST RATE COEFFICIENTS K_r AND THE CORRESPONDING REACTIONS IDENTIFIED FROM METHANE COMBUSTION MECHANISM

Reaction species	Kinetic K_r^a		Reactions	
	Lowest	Highest	Lowest K_r	Highest K_r
H-O	9.67×10^{12}	4.55×10^{15}	$OH + OH = H_2O + O$	$H + OH = H_2O$
$H\text{-}O_2$	1.82×10^{13}	1.47×10^{14}	$HO_2 + O = OH + O_2$	$H + O_2 = HO_2$
H_2O_2	2.57×10^{11}	2.42×10^{13}	$HO_2 + HO_2 = H_2O_2 + O_2$	$H_2O_2 + O = HO_2 + OH$
CO	6.30×10^{11}	8.74×10^{13}	$CO + OH = CO_2 + H$	$CO + HO_2 = CO_2 + OH$
CH	1.42×0^{12}	6.00×10^{13}	$CH + H_2O = CH_2 + OH$	$CH + O_2 = CHO + O$
CHO	3.96×10^{12}	1.00×10^{14}	$CHO + O_2 = CO + HO_2$	$CHO + OH = H_2O + CO$
CH_2	6.25×10^{12}	1.08×10^{14}	$CH_2 + H = CH + H_2$	$CH_2 + H_2 = CH_3 + H$ $CH_2 + CH_2 = C_2H_2 + H + H$
CH_2O	8.70×10^{10}	6.90×10^{13}	$CH_2O + CH_3 = CHO + CH_4$	$CH_2O + H = CHO + H_2$
CH_3	2.69×10^{11}	1.08×10^{16}	$O_2 + CH_3 = CH_2O + OH$	$CH_3O + H = CH_3 + OH$
CH_3O	4.75×10^{9}	3.00×10^{13}	$CH_3OH + CHO =$ $CH_2O + CH_3O$	$CH_2OH + H = CH_2O + H_2$
CH_3O_2	1.98×10^{10}	3.91×10^{12}	$CH_3O_2 + CHO =$ $CH_3O + CH_2O$	$CH_3O_2 + CH_3 =$ $CH_3O + CH_3O$
CH_4	6.26×10^{12}	1.15×10^{14}	$CH_4 + HO_2 = H_2O_2 + CH_3$	$CH_4 + H = H_2 + CH_3$
CH_3OH	8.26×10^{9}	4.43×10^{14}	$CH_2OH + CH_3OH =$ $CH_3O + CH_3OH$	$CH_3OH = CH_3 + OH$
CH_3O_2H	2.60×10^{12}	1.50×10^{15}	$OH + CH_3O_2H = H_2O + CH_3O_2$	$OH + CH_3O_2H = H_2O + CH_3O_2$
C_2H	3.00×10^{12}	1.00×10^{13}	$C_2H + O_2 = HCCO + O$	$C_2H + O = CH_2 + CO$
HCCO	3.00×10^{12}	1.50×10^{14}	$CH_2 + HCCO = C_2H_3 + CO$	$H + HCCO = CH_2 + CO$
C_2H_2	1.04×10^{13}	3.88×10^{14}	$C_2H_2 + O_2 = HCCO + OH$	$C_2H_2 + O = CH_2 + CO$
CH_2CO	2.23×10^{12}	3.33×10^{13}	$CH_2CO + O = CHO + CHO$	$CH_2CO + H = CH_3 + CO$
C_2H_3	6.32×10^{10}	5.00×10^{13}	$C_2H_3 = C_2H_2 + H$	$C_2H_3 + OH = C_2H_2 + H_2O$
CH_3CO	2.99×10^{9}	2.00×10^{13}	$CH_3CO = CH_3 + CO$	$CH_3CO + H = CH_2CO + H_2$
C_2H_4	4.66×10^{12}	1.21×10^{15}	$C_2H_4 + O_2 = OCHO + CH_3$	$C_2H_4 + H = C_2H_3 + H_2$
CH_3CHO	7.67×10^{11}	1.63×10^{13}	$CH_3CHO + O = OH + CH_2CHO$	$CH_3CHO + O_2 = HO_2 + CH_3CO$
C_2H_5	1.14×10^{10}	5.00×10^{13}	$C_2H_5 + O_2 = C_2H_4 + HO_2$	$C_2H_5 + O = H + CH_3CHO$
C_2H_6	1.06×10^{13}	1.22×10^{14}	$C_2H_6 + HO_2 = C_2H_5 + H_2O_2$	$C_2H_6 + H = C_2H_5 + H_2$

[a]Rate constants are given as $K_r = AT^b \exp(-E/RT)$ and expressed in cm, kJ, K, mol, s units.

The rate-limiting reactions: The rate-limiting reactions in a complex chemical mechanism can be identified by sensitivity analysis[18].

Expressing the rate law for a reaction mechanism with R reactions on S species as a system of first-order ordinary differential equations:

$$\frac{dc_i}{dt} = F_i\,(c_1, \ldots, c_s; k_1, \ldots, k_R) \tag{2}$$

where, c_i is the concentration of species i at time t,
k_r is the parameter of the system, and
c_i^0 is the initial conditions at t_0.

$$c_i\,(t = t_0) = c_i^0 \qquad i = 1, 2, \ldots, S$$

The solution of the differential equation system depends on the initial conditions as well as on the parameters.

When the initial conditions of the reactants are changed, such as increasing or decreasing the species concentration, the system temperature or pressure, the system can be analyzed.

The dependence of the solution c_i on the parameters k_r is called sensitivity. Absolute sensitivity $E_{i,r}$ and relative sensitivity are defined as:

$$E_{i,r} = \frac{\partial c_i}{\partial k_r} \tag{3}$$

and

$$E_{i,r}^{(rel)} = \frac{k_r}{c_i}\frac{\partial c_i}{\partial k_r} = \frac{\partial \ln c_i}{\partial \ln k_r} \tag{4}$$

By calculating the sensitivity coefficients, the rate-determining steps or rate-limiting steps can be identified. Sensitivity analysis is a useful tool for studying the complex reaction mechanisms.

The results of sensitivity analysis for NO emission in a methane/air flame are shown in Table-2[19]. It is observed that the formation of the small CH_i-species is a controlling step in the prompt-NO formation. The important rate-determining reactions are:

$$CH_3 + OH \rightleftharpoons CH_2 + H_2O$$
$$CH_3 + H \rightleftharpoons CH_2 + H_2$$
$$CH_2 + OH \rightleftharpoons CH + H_2O$$
$$CH_2 + H \rightleftharpoons CH + H_2$$
$$CH + H \rightleftharpoons C + H_2$$

The following reaction is the only important initiating step in the prompt-NO formation:

$$CH + N_2 \rightleftharpoons HCN + N$$

The characteristic reaction paths: The characteristic reaction paths in a complex mechanism can be determined by using a reaction flow analysis. Software packages such as MIXFLA (http://reaflow.iwr.uniheidelberg.de/software/mixflame/mixflame.htm) for performing this analysis are available. This method is used to identify the contribution of different reactions to the formation (or consumption) of particular chemical species. If the percentage of contribution of a reaction is equal to or greater than one arbitrarily assigned limit, the reaction is included as part of the reduced mechanism[17].

TABLE-2
RESULTS OF SENSITIVITY ANALYSIS FOR NO EMISSION IN METHANE/AIR FLAME

Reactions	Fuel/Air equivalence ratio								
	0.70	0.80	0.90	1.00	1.10	1.20	1.30	1.40	1.50
$H + O_2 \rightleftharpoons O + OH$	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.27	0.38
$H + OH + M \rightleftharpoons H_2O + M$	–0.02	0.01	0.05	0.09	0.12	0.16	0.05	–0.05	–0.01
$H + O_2 + M \rightleftharpoons HO_2 + M$	–0.09	0.02	0.09	0.10	0.08	0.06	0.02	–0.06	–0.06
$CO + OH \rightleftharpoons CO_2 + H$	0.11	0.08	0.05	0.03	0.01	0.01	0.00	–0.04	–0.04
$CH_4 + M \rightleftharpoons CH_3 + H + M$	0.00	0.00	0.00	0.00	0.01	0.03	0.04	–0.40	–0.42
$CH_3 + H \rightleftharpoons CH_2 + H_2$	0.02	0.02	0.03	0.05	0.08	0.14	0.10	0.02	0.00
$CH_3 + O \rightleftharpoons CH_2O + H$	–0.19	–0.18	–0.18	–0.22	–0.31	–0.44	–0.29	0.12	0.02
$CH_3 + OH \rightleftharpoons CH_2 + H_2O$	0.14	0.13	0.12	0.14	0.17	0.19	0.09	0.02	0.00
$HCO + M \rightleftharpoons CO + H + M$	0.02	–0.01	–0.02	–0.03	–0.03	–0.05	–0.02	0.06	0.03
$HCO + H \rightleftharpoons CO + H_2$	0.00	0.00	0.01	0.01	0.02	0.04	0.02	–0.06	–0.03
$CH_2 + H \rightleftharpoons CH + H_2$	0.02	0.01	0.02	0.02	0.05	0.10	0.11	0.04	0.04
$CH_2 + OH \rightleftharpoons CH_2O + H$	–0.05	–0.06	–0.07	–0.09	–0.15	–0.23	–0.18	0.05	0.00
$CH_2 + OH \rightleftharpoons CH + H_2O$	0.17	0.15	0.14	0.16	0.22	0.29	0.21	0.05	0.03
$CH + H \rightleftharpoons C + H_2$	–0.02	–0.03	–0.05	–0.10	–0.19	–0.33	–0.35	–0.35	–0.24
$CH + OH \rightleftharpoons HCO + H$	–0.01	–0.02	–0.02	–0.03	–0.04	–0.07	–0.07	–0.01	–0.03
$CH + O_2 \rightleftharpoons HCO + O$	–0.17	–0.13	–0.10	–0.08	–0.06	–0.05	–0.03	0.00	–0.03
$CH + CO_2 \rightleftharpoons HCO + CO$	–0.01	–0.02	–0.02	–0.03	–0.04	–0.07	–0.07	–0.01	–0.03
$C + O_2 \rightleftharpoons CO + O$	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.05	0.06
$2CH_3 \rightleftharpoons C_2H_4 + H_2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.07
$C_2H_6 + H \rightleftharpoons C_2H_5 + H_2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.11
$C_2H_3 + M \rightleftharpoons C_2H_2 + H + M$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.25
$C_2H_3 + H \rightleftharpoons C_2H_2 + H_2$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	–0.15	–0.26
$C_2H_2 + O \rightleftharpoons CH_2 + CO$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	–0.06	–0.15
$C_2H_2 + O \rightleftharpoons HCCO + H$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	–0.04	–0.10
$NH + H \rightleftharpoons N + H_2$	0.00	0.00	0.00	0.00	0.00	–0.01	–0.01	–0.03	–0.06
$NH + OH \rightleftharpoons HNO + H$	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.06	0.08
$NH + NO \rightleftharpoons N_2O + H$	0.26	0.15	0.09	0.06	0.04	0.02	0.00	–0.01	0.00
$N + O_2 \rightleftharpoons NO + O$	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.04	0.14
$N + OH \rightleftharpoons NO + H$	0.00	0.00	0.01	0.01	0.02	0.05	0.14	0.21	0.21
$N + NO \rightleftharpoons N_2 + O$	0.35	0.53	0.60	0.58	0.44	0.16	–0.11	–0.08	–0.02

Reactions	Fuel/Air equivalence ratio								
	0.70	0.80	0.90	1.00	1.10	1.20	1.30	1.40	1.50
$N_2O + M \rightleftharpoons N_2 + O + M$	0.39	0.23	0.14	0.09	0.06	0.03	0.01	0.00	0.00
$N_2O + H \rightleftharpoons N_2 + OH$	–0.27	–0.15	–0.09	–0.06	–0.04	–0.02	–0.01	–0.01	0.00
$HCN + O \rightleftharpoons NCO + H$	0.00	0.00	0.00	0.00	0.00	0.01	0.06	0.18	0.23
$HCN + O \rightleftharpoons NH + CO$	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.06	0.07
$HCN + OH \rightleftharpoons HNCO + H$	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.05	0.06
$CN + OH \rightleftharpoons NCO + H$	0.00	0.00	0.00	0.00	0.00	0.01	0.06	0.15	0.08
$CN + O_2 \rightleftharpoons NCO + O$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.10
$C + NO \rightleftharpoons CN + O$	0.00	0.00	0.00	0.00	–0.01	–0.05	–0.19	–0.34	–0.24
$CH + NO \rightleftharpoons HCN + O$	0.00	0.00	0.00	–0.01	–0.01	–0.03	–0.09	–0.25	–0.33
$CH_2 + NO \longrightarrow HCNO + H$	0.00	0.00	0.00	0.00	0.00	–0.01	–0.02	–0.07	–0.15
$CH + N_2 \rightleftharpoons HCN + N$	0.23	0.22	0.23	0.28	0.42	0.67	0.78	0.89	0.97
$CH_3 + N \rightleftharpoons HCN + 2H$	0.00	0.00	0.00	0.00	0.00	0.00	–0.01	–0.19	–0.38

In considering the percentage of contribution of different reactions r ($r = 1, \ldots, R$) to the formation (or consumption) of the chemical species s ($s = 1, \ldots, S$), a scheme of the form given in Table-3 can be identified[18]:

TABLE-3
SCHEMATIC ILLUSTRATION OF THE OUTPUT OF A REACTION FLOW ANALYSIS

Reaction ⇓	Species ⇒					
	1	2	3	...	S-1	S
1	20%	3%	0	...	0	0
2	0	0	0	...	0	0
3	2%	5%	0	...	100%	90%
.	.	.	.		.	.
.	.	.	.		.	.
.	.	.	.		.	.
R-1	78%	90%	100%	...	0	50%
R	0	2%	0	...	0	0

About 20% of the formation of species 1 can be attributed to reaction 1, 2% to reaction 3 and 78% to reaction R-1. The percentages in the columns have to add to 100%. By using the method, the characteristic reaction paths in a complex mechanism can be determined.

By using reaction flow analysis, the characteristic reaction paths for premixed stoichiometric methane/air flames were studied[18]. The different reaction paths depend on mixing ratio even for same mechanism. In the stoichiometric flame, methane is mainly oxidized directly. Methyl radicals formed in the rich flame would be recombined to C_2H_6 and then oxidized.

Some reduced mechanisms for methane combustion under different conditions

As it is very complicated and difficult in dealing with the detailed combustion mechanism, some reduced chemical mechanisms were developed for describing the methane combustion under different conditions by using the above-mentioned methods.

Low temperature: Since methane contains only one carbon atom which does not form acetaldehyde, it will readily give chain branching even under low temperature combustion conditions. However, formaldehyde formed will provide the chain branching step necessary for explosion. The reduced mechanism which explains the low temperature results of combustion is shown in Table-4[20].

TABLE-4
REACTION MECHANISM OF METHANE COMBUSTION AT LOW TEMPERATURE

S.No.	Reactions	
1.	$CH_4 + O_2 \longrightarrow CH_3 + HO_2$	Chain initiation
2.	$CH_3 + O_2 \longrightarrow CH_2O + OH$	
3.	$OH + CH_4 \longrightarrow H_2O + CH_3$	Chain propagation
4.	$OH + CH_2O \longrightarrow H_2O + HCO$	
5.	$CH_2O + O_2 \longrightarrow HO_2 + HCO$	Chain branching
6.	$HCO + O_2 \longrightarrow CO + HO_2$	
7.	$HO_2 + CH_4 \longrightarrow H_2O_2 + CH_3$	Chain propagation
8.	$HO_2 + CH_2O \longrightarrow H_2O_2 + HCO$	
9.	$OH \longrightarrow$ wall	Chain termination
10.	$CH_2O \longrightarrow$ wall	

Reaction (1) is slow. Reactions (2) and (3) are fast since they involve a radical and one of the initial reactions. The same is true for reactions (5) to (7). Reaction (5) represents the necessary chain branching step. Reactions (4) and (8) introduce the formyl radical known to exist in the low-temperature combustion conditions.

High temperature: The combustion of methane at high temperature involves the further oxidation of CO to form CO_2. At high temperature, certain high activation energy steps become feasible, particularly the pyrolysis reactions. Higher concentrations of O and H radicals are present as well. The reduced mechanism and the approximate rate constants are shown in Table-5[20, 21]. Reaction (1) is the only one of the first three radical initiation reactions fast enough to explain the ignition results by shockwaves. The attacks of CH_4 by various radicals formed later in the system are shown in reactions (4) to (6). For methane and all other hydrocarbon systems at high temperature, the primary initiation step is most likely the pyrolysis of the hydrocarbon molecule to give alkyl radicals.

TABLE-5
REACTION MECHANISM OF METHANE COMBUSTION AT HIGH TEMPERATURE

S.No.	Reaction	k_f, rate constant[a]
1.	$CH_4 + M \longrightarrow CH_3 + H + M$	1.5×10^{19} exp(–100600/RT)
2.	$CH_4 + O_2 \longrightarrow CH_3 + HO_2$	1.0×10^{14} exp(–45400/RT)
3.	$O_2 + M \longrightarrow 2O + M$	$3.6 \times 10^{18}\ T^{-1.0}$exp(–118800/RT)
4.	$CH_4 + O \longrightarrow CH_3 + H_2$	1.7×10^{13} exp(–8760/RT)
5.	$CH_4 + H \longrightarrow CH_3 + H_2$	6.3×10^{13} exp(–12700/RT)
6.	$CH_4 + OH \longrightarrow CH_3 + H_2O$	2.8×10^{13} exp(–5000/RT)
7.	$CH_3 + O \longrightarrow H_2CO + H$	10^{13}–10^{15}
8.	$CH_3 + O_2 \longrightarrow H_2CO + OH$	10^{11}–10^{14}
9.	$H_2CO + OH \longrightarrow CO + H_2O$	10^{13}–10^{15}
10.	$HCO + OH \longrightarrow CO + H_2O$	10^{12}–10^{15}
11.	$CO + OH \longrightarrow CO_2 + H$	3.1×10^{11} exp(–600/RT)
12.	$H + O_2 \longrightarrow OH + O$	2.2×10^{14} exp(–16600/RT)
13.	$O + H_2 \longrightarrow OH + H$	4.0×10^{14} exp(–9460/RT)
14.	$O + H_2O \longrightarrow 2OH$	8.4×10^{14} exp(–18240/RT)
15.	$H + H_2O \longrightarrow H_2 + OH$	1.0×10^{14} exp(–20400/RT)
16.	$H + OH + M \longrightarrow H_2O + M$	$2.0 \times 10^{1}\ T^{-1.0}$
17.	$CH_3 + O_2 \longrightarrow HCO + H_2O$	10^{11}–10^{12}
18.	$HCO + M \longrightarrow H + CO + M$	$2.0 \times 10^{13}\ T^{1/2}$exp(–28800/RT)

[a]Units: cm, cal, K, mol, s.

A skeletal mechanism that can describe the combustion process of methane including the nitrogen chemistry at high temperature ($T \geq 1500K$) and under not too fuel-rich conditions ($\Phi \geq 1.4$) was reported by Glarborg *et al.*[2] The mechanism, as shown in Table-6, is derived from the full reaction mechanism by using sensitivity analysis and rate of production analysis. The skeletal mechanism is the result of a trade-off between model complexity, model accuracy and range of applicability. In comparing with the full mechanism, the most important simplification of the skeletal model is that the C_2-hydrocarbon chemistry has been excluded. A number of nitrogen species and reactions are left out in the skeletal model. Except near blowout, only a small part of the oxidation process for methane occurs through the C_2-species in stirred reactors[19]. However, at lower temperature or at very fuel-rich conditions, CH_3-recombination reactions become competitive. Omitting the C_2-chemistry would decrease the accuracy of the model predictions.

TABLE-6
SKELETAL MECHANISM FOR METHANE OXIDATION INCLUDING THE NITROGEN CHEMISTRY AT HIGH TEMPERATURE ($T \geq 1500K$) AND UNDER NOT TOO FUEL-RICH CONDITIONS ($\Phi \leq 1.4$)

(1)	$H + O_2 \longrightarrow O + OH$	(40)	$CH_2(S) + O_2 \longrightarrow CO + OH + H$
(2)	$O + H_2 \longrightarrow H + OH$	(41)	$CH_2(S) + CO_2 \longrightarrow CH_2O + CO$
(3)	$OH + H_2 \longrightarrow H_2O + H$	(42)	$CH + H \longrightarrow C + H_2$
(4)	$OH + OH \longrightarrow H_2O + O$	(43)	$CH + O \longrightarrow CO + H$
(5)	$H + OH + M \longrightarrow H_2O + M$	(44)	$CH + OH \longrightarrow HCO + H$
(6)	$H + O_2 + M \longrightarrow H_2O + M$	(45)	$CH + OH \longrightarrow C + H_2O$
(7)	$HO_2 + H \longrightarrow OH + OH$	(46)	$CH + O_2 \longrightarrow HCO + O$
(8)	$HO_2 + OH \longrightarrow H_2O + O_2$	(47)	$CH + H_2O \longrightarrow CH_2O + H$
(9)	$CO + OH \longrightarrow CO_2 + H$	(48)	$CH + CO_2 \longrightarrow HCO + CO$
(10)	$CH_4 + H \longrightarrow CH_3 + H_2$	(49)	$C + OH \longrightarrow CO + H$
(11)	$CH_4 + O \longrightarrow CH_3 + OH$	(50)	$C + O_2 \longrightarrow CO + O$
(12)	$CH_4 + OH \longrightarrow CH_3 + H_2O$	(51)	$NH + H \longrightarrow N + H_2$
(13)	$CH_3 + H \longrightarrow CH_4$	(52)	$NH + O \longrightarrow NO + H$
(14)	$CH_3 + H \longrightarrow CH_2 + H_2$	(53)	$NH + O \longrightarrow N + OH$
(15)	$CH_3 + H\ CH_2(S) + H_2$	(54)	$NH + NO \longrightarrow N_2O + H$
(16)	$CH_3 + O \longrightarrow CH_2O + H$	(55)	$N + OH \longrightarrow NO + H$
(17)	$CH_3 + OH \longrightarrow CH_2 + H_2O$	(56)	$N + O_2 \longrightarrow NO + O$
(18)	$CH_3 + OH \longrightarrow CH_2(S) + H_2O$	(57)	$N + NO \longrightarrow N_2 + O$
(19)	$CH_3 + OH \longrightarrow CH_2OH + H$	(58)	$O + N_2 + M \longrightarrow N_2O + M$
(20)	$CH_3 + O_2 \longrightarrow CH_2OH + O$	(59)	$N_2O + H \longrightarrow N_2 + OH$
(21)	$CH_3 + HO_2 \longrightarrow CH_2OH + OH$	(60)	$HCN + O \longrightarrow NCO + H$
(22)	$CH_3 + HCO \longrightarrow CH_4 + CO$	(61)	$HCN + O \longrightarrow NH + CO$
(23)	$CH_2OH + M \longrightarrow CH_2O + H + M$	(62)	$HCN + OH \longrightarrow CN + H_2O$
(24)	$CH_2OH + O_2 \longrightarrow CH_2O + HO_2$	(63)	$HCN + OH \longrightarrow NCO + H_2$
(25)	$CH_2O + H \longrightarrow HCO + H_2$	(64)	$CN + OH \longrightarrow NCO + H$
(26)	$CH_2O + OH \longrightarrow HCO + H_2O$	(65)	$CN + O_2 \longrightarrow NCO + O$
(27)	$HCO + M \longrightarrow CO + H + M$	(66)	$NCO + H \longrightarrow NH + CO$
(28)	$HCO + H \longrightarrow CO + H_2$	(67)	$NCO + OH \longrightarrow NO + CO + H$
(29)	$HCO + OH \longrightarrow CO + H_2O$	(68)	$NCO + NO \longrightarrow N_2O + CO$
(30)	$HCO + O_2 \longrightarrow CO + HO_2$	(69)	$CH + N_2 \longrightarrow HCN + N$
(31)	$CH_2 + H + M \longrightarrow CH_3 + M$	(70)	$C + N_2 \longrightarrow CN + N$
(32)	$CH_2 + H \longrightarrow CH + H_2$	(71)	$CH_2 + NO \longrightarrow NCO + H_2$
(33)	$CH_2 + O \longrightarrow CO + H + H$	(72)	$CH_2(S) + NO \longrightarrow OH + HCN$
(34)	$CH_2 + O \longrightarrow CO + H_2$	(73)	$CH + NO \longrightarrow HCN + O$
(35)	$CH_2 + OH \longrightarrow CH_2O + H$	(74)	$C + NO \longrightarrow CN + O$
(36)	$CH_2 + OH \longrightarrow CH + H_2O$	(75)	$C + NO \longrightarrow N + CO$
(37)	$CH_2 + O_2 \longrightarrow CH_2O + O$	(76)	$N + CO_2 \longrightarrow NO + CO$
(38)	$CH_2 + O_2 \longrightarrow CO_2 + H_2$	(77)	$N + CH_2 \longrightarrow HCN + 2H$
(39)	$CH_2(S) + M \longrightarrow CH_2 + M$		

Premixed laminar flames: The reduced methane combustion mechanism for the simulation of premixed laminar flames is shown in Table-7[17].

TABLE-7
REACTION MECHANISM OF METHANE COMBUSTION IN PREMIXED LAMINAR FLAMES[a]

Reactions	A	b	E
1. $O_2 + H \longrightarrow OH + O$	2.00×10^{14}	0.00	70.30
2. $H_2 + O \longrightarrow OH + H$	5.06×10^{04}	2.67	26.30
3. $H_2 + OH \longrightarrow H_2O + H$	1.00×10^{08}	1.60	13.80
4. $OH + OH \longrightarrow H_2O + O$	1.50×10^{09}	1.14	0.42
5. $HO_2 + H \longrightarrow OH + OH$	1.50×10^{14}	0.00	4.20
6. $HO_2 + H \longrightarrow H_2 + O_2$	2.50×10^{13}	0.00	2.90
7. $HO_2 + H \longrightarrow H_2O + O$	3.00×10^{13}	0.00	7.20
8. $HO_2 + O \longrightarrow OH + O_2$	1.80×10^{13}	0.00	–1.70
9. $OH_2 + OH \longrightarrow H_2O + O_2$	6.00×10^{13}	0.00	0.00
10. $HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$	2.50×10^{11}	0.00	–5.20
11. $H_2O_2 + H \longrightarrow H_2 + HO_2$	1.70×10^{12}	0.00	15.70
12. $H_2O_2 + H \longrightarrow H_2O + OH$	1.00×10^{13}	0.00	15.00
13. $CH_2 + OH_2 \longrightarrow CH_3 + H$	1.08×10^{14}	0.00	0.00
14. $H_2O_2 + OH \longrightarrow H_2O + HO_2$	5.40×10^{12}	0.00	4.20
15. $CO + OH \longrightarrow CO_2 + H$	6.00×10^{06}	1.50	–3.10
16. $CO + HO_2 \longrightarrow CO_2 + OH$	1.50×10^{14}	0.00	98.70
17. $CO + O_2 \longrightarrow CO_2 + O$	2.50×10^{12}	0.00	200.00
18. $CH_2O + OH \longrightarrow HCO + H_2O$	3.40×10^{09}	1.20	–1.90
19. $CH_2O + H \longrightarrow HCO + H_2$	2.30×10^{10}	1.05	13.70
20. $HCO + OH \longrightarrow CO + H_2O$	1.00×10^{14}	0.00	0.00
21. $CH_3 + O \longrightarrow CH_2O + H$	8.43×10^{13}	0.00	0.00
22. $CH_3 + O_2 \longrightarrow CH_2O + OH$	3.30×10^{11}	0.00	37.40
23. $CH_3 + CH_3 \longrightarrow C_2H_4 + H_2$	1.00×10^{16}	0.00	134.00
24. $CH_3 + CH_3 \longrightarrow C_2H_6$	1.69×10^{53}	–12.00	81.20
25. $CH_4 + O \longrightarrow OH + CH_3$	6.92×10^{08}	1.56	35.50
26. $C_2H_2 + O \longrightarrow CH_2 + CO$	1.72×10^{05}	2.80	2.10
27. $C_2H_3 + OH \longrightarrow C_2H_2 + H_2O$	5.00×10^{13}	0.00	0.00
28. $C_2H_4 + OH \longrightarrow C_2H_3 + H_2O$	6.50×10^{13}	0.00	24.90
29. $C_2H_5 + O_2 \longrightarrow C_2H_4 + HO_2$	1.10×10^{10}	0.00	–6.30
30. $C_2H_6 + O \longrightarrow C_2H_5 + OH$	1.00×10^{09}	1.50	24.40
31. $C_2H_6 + OH \longrightarrow C_2H_5 + H_2O$	7.20×10^{06}	2.00	3.60

[a]Rate constants are given as $k = AT^b \exp(-E/RT)$ and expressed in cm, kJ, K, mol, s units.

The mechanism was simplified from an existing complex methane combustion mechanism[11] by using a three-step procedure. Firstly, the main elementary reactions transforming the reactants into the basic products are identified; Secondly, the reactions with the higher and lower kinetic constants are selected from the detailed mechanism and, finally, the higher equilibrium compositions are selected. The reduced methane combustion mechanism including 31 elementary reactions and 19 species can simulate the species concentration, velocity and temperature profiles of a premixed methane combustion flame in steady state.

Non-premixed laminar flames: A four-step mechanism involving 8 species for the combustion of methane in air in nonpremixed flames is shown in Table-8[23]. The mechanism is obtained by making steady-state and partial equilibrium approximations. The model gives good predictions of laminar flame structure including steady-state minor species for a wide range of flame stretch and across the whole breadth of the reaction zone including rich mixtures. A good prediction of extinction is also obtained.

TABLE-8
REACTION MECHANISM OF METHANE COMBUSTION IN NON-PREMIXED LAMINAR FLAMES

1.	$CH_4 + H_2O + 2H \rightleftharpoons CO + 4H_2$
2.	$CO + H_2O \rightleftharpoons CO_2 + H_2$
3.	$2H + M \rightleftharpoons H_2 + M$
4.	$3H_2 + O_2 \rightleftharpoons 2H_2O + 2H$

Heat of combustion: Heat release rate (HRR) is the most important parameter for deciding the burning behaviour of materials for fire hazard assessment[24]. Heat release rates for small samples can be measured easily by using bench-scale apparatus. These devices can be grouped into two classes based on the principle: (i) direct measurement of the heat released by the flame and (ii) calculation from the amount of oxygen consumed. The results obtained from the two methods are very similar, as suggested by Moussan *et al.*[25]. However, there is heat loss and the response is slow due to low thermal inertia in the first method; therefore, the oxygen consumption method is considered as well.

Oxygen consumption method is based on the principle that the heat released per unit mass of oxygen consumed is taken as approximately the same, about 13.1 MJ/kg, for a wide range of common organic compounds[26]. The accuracy of the flow measurements and the assumption of constant heat release of oxygen consumption will affect the heat release rate measurement. The latter is based on the enthalpy of combustion of pure chemical compounds burning completely to carbon dioxide, water and other fully oxidized products[26]. As the oxygen supply is limited in real fires and in many larger scale experiments, the combustion is incomplete and results in the formation of partially oxidized products. It is

worthwhile to investigate whether the value of 13.1 MJ/kg can be applied to calculate the heat release of methane burning in air.

The heat of combustion per g of oxygen consumed for methane can be calculated according to the reaction of methane combustion. According to Hess's law, the heat of combustion of a chemical reaction is equal to the summation of formation enthalpy of products subtracting the summation of formation enthalpy of reactants.

The equation of complete combustion of methane to carbon dioxide and water is described as:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \tag{5}$$

The heat of combustion can be calculated as (The standard molar enthalpy of formation of CO_2 and H_2O are shown in Table-9):

$$\Delta H_{\text{combustion heat}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}} = \Delta H_{CO_2} + 2 \times \Delta H_{H_2O} - \Delta H_{CH_4}$$

$$= -393.51 + 2 \times (-241.83) - (-74.85) = -802.32 \text{ kJ/mol}$$

The heat of combustion per g of oxygen consumed is:

$$\frac{802.32}{2 \times 32} = 12.54 \text{ kJ/g}$$

This value is close to the value of 13.1 kJ/g.

TABLE-9
STANDARD MOLAR ENTHALPY OF FORMATION OF VARIOUS SUBSTANCES

Enthalpy (kJ/mol)	CO_2	CO	$H_2O(g)$	CH_4	O_2
ΔH	–393.51	–110.52	–241.83	–74.85	0

For incomplete combustion of methane, the reaction can be described as:

$$CH_4 + aO_2 \longrightarrow bCO_2 + cCO + dH_2O \tag{6}$$

The heat of reaction (6) is calculated as:

$$\Delta H_{\text{combustion heat}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$

$$= b \times \Delta H_{CO_2} + c \times \Delta H_{CO} + d \times \Delta H_{H_2O} - \Delta H_{CH_4}$$

$$= b \times (-393.51) + c \times (-110.52) + d \times (-241.83) - (-74.85) \tag{7}$$

For reaction (6), mass conservation gives:

$$\text{O:} \quad 2a = 2b + c + d$$

$$\text{C:} \quad b + c = 1$$

$$\text{H:} \quad d = 2$$

According to the above relationship, the following values can be obtained:

$$b = 2a-3$$

$$c = 4-2a$$

$$d = 2$$

Substituting these values into equn. (7) gives:

$$\Delta H_{\text{combustion heat}} = (2a-3) \times (-393.51) + (4-2a) \times (-110.52) + 2 \times (-241.83) - (-74.85) = -565.98a + 329.64$$

The heat of reaction can be calculated if the molar ratio of CO_2/CO produced in the burning of methane is known.

In actual fires, the concentration of CO among the combustion products is usually low and rarely exceeds 10% of the concentration of CO_2,[25] *i.e.*, b/c is larger than 9. Assuming that b/c = 9, so a = 39/20.

Then, the heat released by burning 1 kg of O_2 is:

$$[-565.98 \times (39/20) + 329.64]/[(39/20) \times 32] = 12.4 \text{ kJ/g}$$

From the above results, it can be seen that the value 13.1 kJ/g is applicable for methane burning in air.

Inhibition effects of retardant on methane combustion: With the wide use of methane, there will be higher fire and explosion risks of methane which are very dangerous to people's daily life. Therefore, the suppression of methane combustion has been investigated[27–29], with the focus mainly on the use of halogen flame-retardants. Since halogenated organic compounds are basically flame suppressants, their presence in flames may lead to reduced burning intensity and increased extinction tendency[30–32], which in turn may reduce the destructive power and increase the emission of by-products.

Effect of CH_3Cl: Chlorinated hydrocarbons (CHCs) are widely used as fire suppressants. Their inhibiting effects on regular hydrocarbon flames are two-fold: the flame temperature is lowered due to the reduction of the heat content of the unburnt reactant mixture and chlorine removes the key flame radicals such as H and OH by HCl[27].

In the past, detailed reaction mechanisms had been developed and tested individually for CH_3Cl laminar premixed flames[33–35], pyrolysis and oxidation in flow reactors[27, 36, 37] and counterflow diffusion flames[38].

The detailed oxidation kinetics and the flame inhibition effects of chloromethane on methane combustion had been studied[39]. The experimental results indicated that temperature reduction due to increased CH_3Cl substitution is a significant factor for the reduction in the laminar burning intensity. Furthermore, when the experimental results were examined on the basis of the mass-burning rate at a fixed flame temperature, the response was found to be insensitive to the chloromethane concentration in the mixture. The reaction mechanism including chlorinated species is shown in Table-10. The results of numerical simulation by using the reaction mechanism were found to be in close agreement with the experimental findings.

TABLE-10
THE REACTION MECHANISM INCLUDING CHLORINATED SPECIES

	Reactions	$k = AT^n \exp(-E/RT)^a$		
		A	n	E
1.	$H + Cl + M \rightleftharpoons HCl + M$	5.30×10^{21}	−2.0	−2000
2.	$Cl + Cl + M \rightleftharpoons Cl_2 + M$	3.34×10^{14}		−1800
3.	$Cl + HO_2 \rightleftharpoons HCl + O_2$	1.08×10^{13}		−338
4.	$Cl + HO_2 \rightleftharpoons ClO + OH$	2.47×10^{13}		894
5.	$Cl + H_2O_2 \rightleftharpoons HCl + HO_2$	6.62×10^{12}		1950
6.	$Cl + HOCl \rightleftharpoons Cl_2 + OH$	1.81×10^{12}		260
7.	$Cl + HOCl \rightleftharpoons HCl + ClO$	7.28×10^{12}		100
8.	$Cl + CH_4 \rightleftharpoons CH_3 + HCl$	3.09×10^{13}		3600
9.	$Cl + CH_3O \rightleftharpoons HCl + CH_2O$	4.00×10^{14}		
10.	$Cl + CH_2OH \rightleftharpoons HCl + CH_2O$	4.00×10^{14}		
11.	$Cl + CH_2O \rightleftharpoons HCO + HCl$	5.00×10^{13}		500
12.	$Cl + C_2H_6 \rightleftharpoons C_2H_5 + HCl$	4.37×10^{13}		100
13.	$Cl + C_2H_4 \rightleftharpoons C_2H_3 + HCl$	2.39×10^{13}		2600
14.	$Cl + C_2H_2 \rightleftharpoons C_2H + HCl$	1.58×10^{14}		16900
15.	$ClO + O \rightleftharpoons Cl + O_2$	9.70×10^{12}		507
16.	$ClO + H_2 \rightleftharpoons HOCl + H$	6.03×10^{11}		14100
17.	$ClO + C_2H_4 \rightleftharpoons CH_3 + HOCl$	6.03×10^{11}		15000
18.	$ClO + CH_3 \rightleftharpoons CH_3O + Cl$	3.33×10^{11}	0.46	30
19.	$ClO + CH_3 \rightleftharpoons CH_2O + HCl$	3.47×10^{18}	−1.80	2070
20.	$ClO + CH_3O \rightleftharpoons HOCl + CH_2O$	2.41×10^{13}		
21.	$ClO + CH_2O \rightleftharpoons HCO + HOCl$	5.50×10^{3}	2.81	5860
22.	$ClO + CO \rightleftharpoons Cl + CO_2$	6.03×10^{11}		17400
23.	$HOCl \rightleftharpoons Cl + OH$	1.76×10^{20}		56720
24.	$HOCl \rightleftharpoons H + ClO$	8.12×10^{14}	−2.09	93690
25.	$HOCl + H \rightleftharpoons HCl + OH$	9.55×10^{13}		7620
26.	$HOCl + O \rightleftharpoons OH + ClO$	6.03×10^{12}		4370
27.	$HOCl + OH \rightleftharpoons H_2O + ClO$	1.81×10^{12}		990
28.	$HOCl + Cl \rightleftharpoons HCl + ClO$	7.28×10^{12}		100
29.	$HOCl + Cl \rightleftharpoons Cl_2 + OH$	1.81×10^{12}		260
30.	$HCl + H \rightleftharpoons H_2 + Cl$	2.30×10^{13}		3500
31.	$HCl + O \rightleftharpoons OH + Cl$	5.24×10^{12}		6400
32.	$HCl + OH \rightleftharpoons Cl + H_2O$	2.45×10^{12}		1100
33.	$Cl_2 + H \rightleftharpoons HCl + Cl$	8.59×10^{13}		1170
34.	$Cl_2 + O \rightleftharpoons Cl + ClO$	2.51×10^{12}		2720
35.	$CH_3Cl \rightleftharpoons CH_3 + Cl$	1.31×10^{37}	−6.92	90650
36.	$CH_3Cl \rightleftharpoons CH_2^* + HCl$	1.10×10^{28}	−5.15	109670

	Reactions	$k = AT^n \exp(-E/RT)^a$		
		A	n	E
37.	$CH_3Cl + H \rightleftharpoons CH_3 + HCl$	6.64×10^{13}		7620
38.	$CH_3Cl + Cl \rightleftharpoons CH_2Cl + HCl$	3.16×10^{13}		3300
39.	$CH_3Cl + O \rightleftharpoons CH_2Cl + HO$	1.70×10^{13}		7300
40.	$CH_3Cl + OH \rightleftharpoons CH_2Cl + H_2O$	2.45×10^{12}		2700
41.	$CH_3Cl + HO_2 \rightleftharpoons CH_2Cl + H_2O_2$	1.00×10^{13}		21660
42.	$CH_3Cl + O_2 \rightleftharpoons CH_2Cl + HO_2$	2.02×10^{13}		54000
43.	$CH_3Cl + ClO \rightleftharpoons CH_2Cl + HOCl$	3.03×10^{11}		10700
44.	$CH_3Cl + CH_3 \rightleftharpoons CH_4 + CH_2Cl$	3.30×10^{11}		9400
45.	$CH_3Cl + CH_2^* \rightleftharpoons C_2H_4 + HCl$	1.60×10^{18}	–1.47	2710
46.	$CH_3Cl + CH_2^* \rightleftharpoons C_2H_5 + Cl$	3.09×10^{7}	1.70	520
47.	$CH_2Cl_2 \rightleftharpoons CHCl + HCl$	1.82×10^{37}	–7.43	85730
48.	$CH_2Cl_2 \rightleftharpoons CH_2Cl + Cl$	1.60×10^{40}	–7.84	83600
49.	$CH_2Cl_2 + H \rightleftharpoons CH_2Cl + HCl$	7.00×10^{13}		7100
50.	$CH_2Cl_2 + Cl \rightleftharpoons CHCl_2 + HCl$	2.79×10^{13}		2940
51.	$CH_2Cl_2 + O \rightleftharpoons CHCl_2 + OH$	6.00×10^{12}		5760
52.	$CH_2Cl_2 + OH \rightleftharpoons CHCl_2 + H_2O$	2.83×10^{12}		2090
53.	$CH_2Cl_2 + O_2 \rightleftharpoons CHCl_2 + HO_2$	1.35×10^{13}		51800
54.	$CH_2Cl_2 + HO_2 \rightleftharpoons CHCl_2 + H_2O_2$	6.67×10^{12}		18270
55.	$CH_2Cl_2 + CH_3 \rightleftharpoons CH_4 + CHCl_2$	6.76×10^{10}		7200
56.	$CH_2Cl_2 + CH_3 \rightleftharpoons CH_3Cl + CH_2Cl$	1.40×10^{11}		4900
57.	$CH_2Cl + H \rightleftharpoons CH_3Cl$	3.04×10^{12}	–4.47	3490
58.	$CH_2Cl + H \rightleftharpoons CH_2^* + HCl$	9.48×10^{4}	1.91	2600
59.	$CH_2ClH \rightleftharpoons CH_3 + Cl$	5.12×10^{12}	–0.22	310
60.	$CH_2Cl + O \rightleftharpoons CH_2ClO$	1.29×10^{15}	–1.98	1100
61.	$CH_2Cl + O \rightleftharpoons CH_2O + Cl$	5.59×10^{13}	–0.13	710
62.	$CH_2Cl + OH \rightleftharpoons CH_2O + HCl$	1.24×10^{22}	–2.72	3860
63.	$CH_2Cl + OH \rightleftharpoons CH_2OH + Cl$	2.00×10^{12}	0.29	3270
64.	$CH_2Cl + HO_2 \rightleftharpoons CH_2ClO + OH$	1.00×10^{13}		
65.	$CH_2Cl + ClO \rightleftharpoons CH_2ClO + Cl$	4.15×10^{12}	0.07	1110
66.	$CH_2Cl + ClO \rightleftharpoons CHClO + HCl$	4.13×10^{19}	–2.22	2360
67.	$CH_2Cl + H_2 \rightleftharpoons CH_3Cl + H$	3.90×10^{12}		14059
68.	$CH_2Cl + O_2 \rightleftharpoons CH_2O + ClO$	1.91×10^{14}	–1.27	3810
69.	$CH_2Cl + O_2 \rightleftharpoons CHClO + OH$	4.00×10^{13}		34000
70.	$CH_2Cl + CH_3 \rightleftharpoons C_2H_4 + HCl$	3.50×10^{28}	–4.49	9180
71.	$CH_2Cl + CH_3 \rightleftharpoons C_2H_5 + Cl$	9.27×10^{19}	–2.07	10130
72.	$CH_2Cl + CH_2O \rightleftharpoons CH_3Cl + HCO$	2.00×10^{11}		6000
73.	$CHCl_2 + H \rightleftharpoons CH_2Cl_2$	4.81×10^{26}	–4.82	3810
74.	$CHCl_2 + H \rightleftharpoons CH_2Cl + Cl$	1.25×10^{14}	0.03	570

	Reactions	$k = AT^n \exp(-E/RT)^a$		
		A	n	E
75.	$CHCl_2 + H_2 \rightleftharpoons CH_2Cl_2 + H$	4.63×10^{12}		15295
76.	$CHCl + O \rightleftharpoons CHClO$	1.00×10^{13}		
77.	$CHCl + O_2 \rightleftharpoons CHClO + O$	1.50×10^{13}		2860
78.	$CHCl + O_2 \rightleftharpoons CO + HOCl$	1.20×10^{11}		
79.	$CH_2ClO \rightleftharpoons CHClO + H$	1.83×10^{27}	–5.13	21170
80.	$CH_2ClO \rightleftharpoons CH_2O + Cl$	4.53×10^{31}	–6.41	22560
81.	$CHClO \rightleftharpoons HCO + Cl$	8.86×10^{29}	–5.15	92920
82.	$CHClO + H \rightleftharpoons CO + HCl$	1.10×10^{30}	–5.19	92960
83.	$CHClO + H \rightleftharpoons HCO + HCl$	8.33×10^{13}		7400
84.	$CHClO + H \rightleftharpoons CH_2O + Cl$	6.99×10^{14}	–0.58	6360
85.	$CHClO + Cl \rightleftharpoons CClO + HCl$	1.25×10^{13}		500
86.	$CHClO + O \rightleftharpoons CClO + OH$	8.80×10^{12}		3500
87.	$CHClO + OH \rightleftharpoons CClO + H_2O$	7.50×10^{12}		1200
88.	$CHClO + O_2 \rightleftharpoons CClO + HO_2$	4.50×10^{12}		41800
89.	$CHClO + ClO \rightleftharpoons CClO + HOCl$	1.10×10^{13}		500
90.	$CHClO + CH_3 \rightleftharpoons CClO + CH_4$	2.50×10^{13}		6000
91.	$CHClO + CH_3 \rightleftharpoons HCO + CH_3Cl$	1.50×10^{13}		8800
92.	$COCl_2 + M \rightleftharpoons CClO + Cl + M$	1.20×10^{16}		75500
93.	$COCl_3 + H \rightleftharpoons CClO + HCl$	5.00×10^{13}		6300
94.	$COCl_2 + Cl \rightleftharpoons CClO + Cl_2$	3.20×10^{14}		23500
95.	$COCl_2 + O \rightleftharpoons CClO + ClO$	2.00×10^{13}		17000
96.	$COCl_2 + HO \rightleftharpoons CClO + HOCl$	1.00×10^{13}		23300
97.	$COCl_2 + CH_3 \rightleftharpoons CClO + CH_3Cl$	1.90×10^{13}		12900
98.	$CClO \rightleftharpoons CO + Cl$	1.30×10^{14}		8000
99.	$CClO + HO \rightleftharpoons CO + HOCl$	3.30×10^{12}		
100.	$CClO + O_2 \rightleftharpoons CO_2 + ClO$	1.00×10^{13}		
101.	$CClO + Cl \rightleftharpoons CO + Cl_2$	4.00×10^{14}		800
102.	$CH_2Cl + CH_3 \rightleftharpoons C_2H_5Cl$	3.27×10^{40}	–8.49	10590
103.	$C_2H_5Cl + H \rightleftharpoons C_2H_5 + HCl$	1.00×10^{14}		7900
104.	$C_2H_5Cl + Cl \rightleftharpoons HCl + CH_3CHCl$	3.55×10^{13}		1500
105.	$C_2H_5Cl + Cl \rightleftharpoons HCl + CH_2ClCH_2$	1.12×10^{13}		1500
106.	$C_2H_5Cl + OH \rightleftharpoons H_2O + CH_3CHCl$	2.00×10^{13}		4000
107.	$C_2H_5Cl + OH \rightleftharpoons H_2O + CH_2ClCH_2$	3.00×10^{13}		4000
108.	$CH_2Cl + CH_2Cl \rightleftharpoons C_2H_4Cl_2$	7.84×10^{45}	–10.21	13150
109.	$C_2H_4Cl_2 \rightleftharpoons C_2H_3Cl + HCl$	6.76×10^{19}	–1.93	58710
110.	$C_2H_4Cl_2 + H \rightleftharpoons CH_2ClCH_2 + HCl$	1.00×10^{14}		7900
111.	$C_2H_4Cl_2 + Cl \rightleftharpoons CH_2ClCHCl + HCl$	5.00×10^{13}		1500
112.	$C_2H_4Cl_2 + OH \rightleftharpoons H_2O + CH_2ClCHCl$	5.00×10^{13}		4000

	Reactions	$k = AT^n \exp(-E/RT)^a$		
		A	n	E
113.	$CH_2Cl + CH_2Cl \rightleftharpoons CH_2ClCH_2 + Cl$	9.34×10^{29}	–4.95	14070
114.	$C_2H_4 + Cl \rightleftharpoons CHClCH_2$	2.00×10^{13}		3500
115.	$CH_2ClCH_2 + H \rightleftharpoons C_2H_4 + HCl$	1.00×10^{14}		
116.	$CH_3 + CHCl_2 \rightleftharpoons CH_3CHCl + Cl$	2.74×10^{25}	–3.45	12810
117.	$CH_3CHCl + Cl \rightleftharpoons C_2H_3Cl + Cl$	2.00×10^{13}		
118.	$CH_2ClCHCl \rightleftharpoons C_2H_3Cl + Cl$	1.72×10^{14}		27300
119.	$CH_2ClCHCl + H \rightleftharpoons C_2H_3Cl + HCl$	1.00×10^{14}		
120.	$CH_2Cl + CH_2Cl \rightleftharpoons C_2H_3Cl + HCl$	3.75×10^{35}	–6.73	13160
121.	$CHCl_2 + CH_3 \rightleftharpoons C_2H_3Cl + HCl$	1.35×10^{30}	4.96	11550
122.	$C_2H_3Cl \rightleftharpoons C_2H_2 + HCl$	1.62×10^{28}	–4.29	75780
123.	$C_2H_3Cl \rightleftharpoons C_2H_3 + Cl$	1.71×10^{38}	–7.13	100870
124.	$C_2H_3Cl + H \rightleftharpoons CH_2ClCH_2$	5.01×10^{23}	–4.21	8470
125.	$C_2H_3Cl + H \rightleftharpoons C_2H_4 + Cl$	1.55×10^{13}	–0.02	5840
126.	$C_2H_3Cl + H \rightleftharpoons C_2H_3 + HCl$	1.20×10^{12}		15000
127.	$C_2H_3Cl + O \rightleftharpoons CH_3 + CClO$	1.92×10^{7}	1.80	220
128.	$Cl_2 + C_2H_3 \rightleftharpoons C_2H_3Cl + Cl$	5.25×10^{12}		–480
129.	$CH_2CCl_2 + H \rightleftharpoons C_2H_3Cl + Cl$	7.21×10^{12}		7510
130.	$CH_2CCl_2 + H \rightleftharpoons C_2HCl + HCl$	1.45×10^{14}		69220
131.	$C_2HCl + H \rightleftharpoons HCl + C_2H$	1.00×10^{13}		17030
132.	$C_2HCl + H \rightleftharpoons C_2H_2 + Cl$	2.00×10^{13}		2100

[a]The units are g mol, s, cm, and cal

Effect of CH_3Br: The suppression of CH_3Br on methane combustion in premixed hydrogen-oxygen flames had also been studied[40]. The results indicated that at 1000 and 1300 K, the rate of reaction $H + CH_3Br = CH_3 + HBr$ was about 120 times faster than that of $CH_4 + H = CH_3 + H_2$. Both reaction rates were significantly higher than the reaction rate of $H + O_2 = OH + O$. It was proposed that the reactions $CH_3 + O = HCHO + H$ and $HBr + H = H_2 + Br$ were important in removing O and H from the flame, contributing to the breaking of the chain reaction for combustion.

The temperature and composition profiles of low pressure, premixed, lean methane-oxygen flames inhibited by CH_3Br were investigated by Wilson[41]. The following reactions:

$$CH_3Br = CH_3 + Br$$

$$H + Br + M = HBr + M^*$$

were involved in the mechanisms. It was concluded that the reactions $CH_2Br + OH = HCHO + HBr$ and $CH_3Br + OH = CH_2Br + H_2O$ were the important inhibiting reactions by removing OH.

The effects of the addition of CH_3Br on the combustion of methane with air were studied by using an emission infrared spectrometer in an opposed-jet diffusion

flame burner[42]. The results obtained support the mechanisms proposed by Fenimore and Jones[40] and by Wilson[41]. Further, the narrowing of the main reaction zone and the subsequent development of a higher average flame temperature has been confirmed. However, the authors also pointed out that it was not possible to say with complete certainty that the reactions discussed completely describe the inhibition of combustion of methane by CH_3Br.

Effect of CF_3Br: CF_3Br is an efficient fire suppressant for oxidation of hydrocarbon fuels. Experimental and numerical studies have shown that CF_3Br is considerably more effective than nitrogen in extinguishing flames[43]. Effects can be summarized on premixed and non-premixed flame.

The inhibiting effect of CF_3Br on methane oxidation in premixed flames was investigated[28]. The results showed that the addition of CF_3Br remarkably decreased the conversion of methane and oxygen and the selectivity in ethane formation. The major steps accounting for the inhibiting effect of CF_3Br determined by sensitivity analysis are shown in Table-11.

TABLE-11
RATE-DETERMINING REACTIONS OF INHIBITING EFFECT OF CF_3Br ON METHANE OXIDATION IN PERMIXED FLAMES

Initiation	Terminations	Propagations
$H + O_2 \longrightarrow OH + O$	$2CH_3 \longrightarrow C_2H_6$	$CH_4 + OH \longrightarrow CH_3 + H_2O$
$H_2O_2 + M \longrightarrow OH + OH + M$	$2HO_2 \longrightarrow H_2O_2 + O_2$	$CH_3Br + H \longrightarrow HBr + CH_3$
$CH_3Br \longrightarrow Br + CH_3$	$Br + HO_2 \longrightarrow HBr + O_2$	$HBr + CH_3 \longrightarrow CH_4 + Br$
$CF_3Br \longrightarrow Br + CF_3$	$Br + CH_3 \longrightarrow CH_3Br$	$Br + CH_4 \longrightarrow HBr + CH_3$
		$HBr + H \longrightarrow H_2 + Br$
		$H_2 + Br \longrightarrow HBr + H$

The radicals are mainly produced by the following two processes:

Branching step: $H + O_2 \longrightarrow OH + O$

Degenerate branching step: $H_2O_2 + M \longrightarrow OH + OH + M$

The main termination steps are the pathways which involve CH_3 and HO_2 radicals. The inhibiting effect of CF_3Br on methane oxidation seems to be mainly due to a cycle, among Br, HBr, and CH_3Br, which acts as a termination step between CH_3 and H radicals.

The inhibiting mechanism of CF_3Br on the structure of non-premixed methane-air flames that include various elementary reactions are shown in Table-12[43]. The forward and backward rates of the reversible elementary reactions $H + Br_2 \longrightarrow HBr + Br$ and $OH + HBr \longrightarrow H_2O + Br$ are very fast and a balance is maintained between the concentrations of HBr and Br. The reversible reaction $Br + Br + M \Leftrightarrow Br_2 + M$ is found to maintain a balance between the concentrations of Br and Br_2. In the asymptotic model, these reversible reactions inhibit the flame in an indirect manner by maintaining a balance between the concentrations of HBr, Br and Br_2, whereas the elementary step $H + Br_2 \longrightarrow HBr + Br$ plays a dominant role in flame inhibition. It increases the rates by which radicals recombine in the oxidation layer. The influence of the chain-breaking reaction between CF_3Br and radicals on inhibition is found to be small.

TABLE-12
INHIBITING MECHANISM OF CF_3Br ON THE STRUCTURE OF NON-PREMIXED METHANE-AIR FLAMES

No.	Reaction	$k_n = B_n T^{\alpha_n} \exp(-E_n/RT)^a$		
		B_n	α_n	E_n
1f	$O_2 + H \longrightarrow OH + O$	2.000×10^{14}	0.00	70.30
1b	$O + OH \longrightarrow H + O_2$	1.568×10^{13}	0.00	3.52
2f	$H_2 + O \longrightarrow OH + H$	5.060×10^{04}	2.67	26.30
2b	$H + OH \longrightarrow O + H_2$	2.222×10^{04}	2.67	18.29
3f	$H_2 + OH \longrightarrow H_2O + H$	1.000×10^{08}	1.60	13.80
3b	$H + H_2O \longrightarrow OH + H_2$	4.312×10^{08}	1.60	76.46
4f	$OH + OH \longrightarrow H_2O + O$	1.500×10^{09}	1.14	0.42
4b	$O + H_2O \longrightarrow OH + OH$	1.473×10^{10}	1.14	71.09
5	$H + O_2 + M \longrightarrow HO_2 + M$	2.300×10^{18}	–0.80	0.00
6f	$CO + OH \longrightarrow CO_2 + H$	4.400×10^{06}	1.50	–3.10
6b	$H + CO_2 \longrightarrow OH + CO$	4.956×10^{08}	1.50	89.76
7	$CH_4 + H \longrightarrow CH_3 + H_2$	2.200×10^{04}	3.00	36.60
8	$H + Br_2 \longrightarrow HBr + Br$	6.457×10^{12}	0.50	4.64
9f	$H + HBr \longrightarrow H_2 + Br$	7.586×10^{11}	0.50	4.64
9b	$H_2 + Br \longrightarrow H + HBr$	3.467×10^{10}	1.00	69.60
10f	$HBr + OH \longrightarrow Br + H_2O$	1.000×10^{14}	0.00	0.00
10b	$Br + H_2O \longrightarrow HBr + OH$	1.288×10^{14}	0.00	133.00
11f	$Br + Br + M \longrightarrow Br_2 + M$	1.000×10^{16}	0.00	0.00
12	$H + CF_3Br \longrightarrow CF_3 + HBr$	2.188×10^{14}	0.00	39.60
13	$CF_3Br \longrightarrow CF_3 + Br$	1.995×10^{13}	0.00	270.00

[a]Units are mol, cm^3, s, kJ, K

The reaction mechanism in CH_4-O_2-Ar flame containing 1.1% CF_3Br at low pressure was deduced by analyzing the net reaction rate profiles of the bromine and fluorine-containing species observed[44]. The reactions found to be significant in the formation and decay of CH_3Br in the flame are shown in Table-13.

TABLE-13
SIGNIFICANT REACTIONS IN THE FORMATION AND DECAY OF CH_3Br IN THE FLAME

Formation:
$CH_3 + CF_3Br \longrightarrow CH_3Br + CF_3$
$CH_3 + Br_2 \longrightarrow CH_3Br + Br$
Decay:
$CH_3Br + H(OH) \longrightarrow HBr(HOBr) + CH_3$
$CH_3Br + Br \longrightarrow HBr + CH_2Br$
$CH_3Br \longrightarrow CH_3 + Br$

The presence of molecular bromine, though anticipated cannot be accounted for quantitatively. The reactions considered to be primarily responsible for the major stable species containing fluorine are shown in Table-14. They are mostly radical-radical reactions involving CF_2 and the fluorocarbon chemistry occurring in this flame is due primarily to the CF_2 and not the CF_3 radical.

TABLE-14
REACTIONS RESPONSIBLE FOR THE MAJOR STABLE SPECIES CONTAINING FLOURINE IN CH_3Br INHIBITED FLAMES

CH_2CF_2:	*HF*:
$CH_3 + CF_2 \longrightarrow (CF_2CH_3)^* \longrightarrow CH_2CF_2 + H$	$CF_3 + H \longrightarrow HF + CF_2$
F_2CO:	$CF_2 + H \longrightarrow HF + CF$
$CF_2 + OH \longrightarrow F_2CO + H$	$CF_2 + OH \longrightarrow HF + CO + F$
$CF_2 + O \longrightarrow F_2CO$	$CF_2 + O \longrightarrow CO + F\cdots F$
$CH_2CF_2 + O \longrightarrow F_2CO + CH_2$	$F\cdots F + 2RH \longrightarrow 2HF + 2R$

Effect of CF_3I: Halogenated compounds such as chlorofluorocarbons (CFCs) and halons (mainly halon 1301 (CF_3Br) and halon 1211 (CH_3BrCl)) are widely used for fire suppression (mainly to protect valuable electronics), in oil and gas production, and on civilian aircrafts. They are also used by the military to extinguish fires and suppress explosions. However, it has been confirmed that the halogenated compounds have very high ozone depletion potential. The bromine atoms can be released from halons by photolysis and have the largest potential to deplete ozone once they reach the stratosphere. In recent years, great efforts have been made to find suitable replacements for halons[45, 46]. Despite good progress, the ideal replacements have not yet been found. Some studies[47] have shown that iodinated compounds such as CF_3I are efficient fire extinguishers as halons and have essentially a zero ozone depletion potential (ODP)[48], since its residence time in the atmosphere is very short and a negligible fraction of this compound would therefore reach the stratosphere to cause ozone loss.

The inhibiting effect of CF_3I on methane combustion in a premixed flame was studied[29]. The results showed that CF_3I is a chemical inhibiting agent at least as efficient as CF_3Br under the experimental conditions. Its inhibiting effect slightly increased when the amount of additive decreased. The main observed effects of the addition of CF_3I were a substantial decrease of the conversion of methane and oxygen, a reduction of the selectivity in ethane formation and a significant increase of the selectivity in ethylene formation. The proposed mechanism is shown in Table-15, which contains 26 reversible reactions. The reacting species considered include I, HI, CH_3I, CF_3I and I_2. The inhibiting effect of CF_3I on methane oxidation seems to be mainly due to the two following steps:

$$I + CH_4 \longrightarrow HI + CH_3$$

$$I + HO_2 \longrightarrow O_2 + HI$$

These two steps form a cycle which acts as a termination reaction between HO_2 and CH_3 radicals to give CH_4 and O_2. The mechanism is able to reproduce the experimental data.

TABLE-15
REACTION MECHANISM OF INHIBITING EFFECT OF CF_3I ON METHANE COMBUSTION[a]

Reactions	A	n	E
Reactions of I:			
$I + H + M \rightleftharpoons HI + M$	1.0×10^{19}	–1	0
$I + H_2 \rightleftharpoons HI + H$	1.7×10^{14}	0	33640
$I + CH_3 \rightleftharpoons CH_3I$	5.6×10^{13}	0	261
$I + CH_4 \rightleftharpoons HI + CH_3$	5.0×10^{14}	0	34130
$I + C_2H_3 \rightleftharpoons C_2H_3I$	5.0×10^{11}	0	0
$I + C_2H_5 \rightleftharpoons C_2H_5I$	2.9×10^{12}	0	0
$I + OH \rightleftharpoons HI + O$	1.9×10^{13}	0	32718
$I + CH_2O \rightleftharpoons HI + HCO$	8.3×10^{13}	0	17450
$I + HO_2 \rightleftharpoons HI + O_2$	9.0×10^{12}	0	2168
$I + H_2O_2 \rightleftharpoons HI + HO_2$	6.0×10^{12}	0	17600
$I + CF_3 \rightleftharpoons CF_3I$	1.2×10^{13}	0	490
$I + CHF_3 \rightleftharpoons CF_3 + HI$	4.0×10^{13}	0	36330
$I + I + M \rightleftharpoons I_2 + M$	5.8×10^{13}	0	0
Reaction of HI:			
$HI + C_2H_5 \rightleftharpoons C_2H_6 + I$	2.7×10^{12}	0	–764
$HI + C_2H_5 \rightleftharpoons C_2H_5I + H$	1.3×10^{12}	0	20000
$HI + C_2H_3 \rightleftharpoons C_2H_4 + I$	5.0×10^{12}	0	500
$HI + C_2H_3 \rightleftharpoons C_2H_3I + H$	7.2×10^{12}	0	10320
$HI + OH \rightleftharpoons H_2O + I$	6.9×10^{12}	0	0
$HI + F \rightleftharpoons HF + I$	4.4×10^{14}	0	1400
$HI + CF_3 \rightleftharpoons H + CF_3I$	1.6×10^{11}	0	15500
$HI + HI \rightleftharpoons H_2 + I_2$	3.4×10^{13}	0	43300
$HI + I \rightleftharpoons I_2 + H$	3.9×10^{13}	0	36800
Reactions of CH_3I:			
$CH_3I + H \rightleftharpoons HI + CH_3$	2.0×10^{14}	0	2000
$CH_3I + CF_3 \rightleftharpoons CH_3 + CF_3I$	2.5×10^{10}	0	6000
$CHI + I \rightleftharpoons I_2 + CH_3$	1.5×10^{14}	0	23000
Reactions of CF_3I:			
$CF_3I + I \rightleftharpoons I_2 + CF_3$	2.0×10^{13}	0	16985

[a]Rate constants are given at 1 bar as $k = AT^n \exp(-E/RT)$ and expressed in cm^3, mol, s, cal, K units.

Fundamental kinetics of methane oxidation in supercritical water

Supercritical water oxidation (SCWO) refers to the technology that the organic compounds are oxidized under the conditions exceeding the critical temperature and pressure of water ($T_c = 374°C$, $P_c = 221$ bar). Supercritical water oxidation is a rapidly developing technology for the destruction of a wide variety of organic hazardous wastes[49] and is also currently being investigated as a method for treating spacecraft wastewater for recycle[50].

In supercritical water oxidation, the typical reactor conditions are temperature above 400°C and pressure of 250 bar. The oxidation of organics is initiated spontaneously and the released heat of combustion within the fluid will increase the temperature to 550–650°C. Organics are oxidized rapidly with conversions in excess of 99.99% at reactor residence time of 1 min. Under proper operating conditions of temperature and pressure, oxidation of organics to carbon dioxide and nitrogen is complete without the formation of noxious byproducts such as NO_x compounds[51].

The development of SCWO technology depends on the understanding of the reaction kinetics of compounds at typical process conditions, which can elucidate the reaction pathways that control oxidation in supercritical water[52]. Predictive chemistry models are useful for resolving the following problems: (i) predicting the reaction rate dependency on temperature, pressure and species concentrations, (ii) calculating the heat release rates and temperature histories during the reaction, (iii) predicting the reaction completeness and byproduct profiles, (iv) estimating the catalytic effects and (v) scaling the laboratory and bench-scale experimental results to commercial-scale reactors[6].

In the study of supercritical water oxidation, methane was given special interest as it is a simple organic whose oxidation kinetics in the gas phase have been well studied. In addition, methane is frequently an intermediate in the oxidation of higher organics and represents the rate-limiting step in the overall oxidation to carbon dioxide and water.

The oxidation kinetics of methane in supercritical water in an isothermal, plug flow reactor over the temperature range 560–650°C at 245.8 bar were studied[53]. The activation energy over the temperature range was 42.8 ± 4.3 kcal/mol. The proposed elementary reaction model for oxidation of methane in supercritical water is shown in Table-16. The variation of the rate constants for a few important reactions within their uncertainty limits resulted in reasonable agreement with the experimental data.

Methane oxidation in supercritical water at 250 atm and at temperature between 525–587°C was studied by Savage *et al.*[54]. The experimental results were used to test the predictions of a detailed chemical kinetics model which comprised 150 elementary reaction steps. The results showed that the methane conversion rates predicted by the model were about 30–50% faster than the experimental data. However, the model can accurately predict the yields of CO and CO_2 as a function of the methane conversion.

TABLE-16
REACTION MECHANISM OF METHANE OXIDATION IN SUPERCRITICAL WATER

1.	$H + O_2 \rightleftharpoons OH + O$	34.	$CHO + O \rightleftharpoons CO + OH$
2.	$O + H_2 \rightleftharpoons OH + H$	35.	$CHO + O \rightleftharpoons CO_2 + H$
3.	$OH + H_2 \rightleftharpoons H_2O + H$	36.	$CHO + HO \rightleftharpoons CO + H_2O$
4.	$H_2O + O \rightleftharpoons OH + OH$	37.	$CHO + O_2 \rightleftharpoons CO + HO_2$
5.	$H_2 + M \rightleftharpoons H + H + M$	38.	$CHO + M \rightleftharpoons CO + H + M$
6.	$H_2O + M \rightleftharpoons OH + H + M$	39.	$H_2O_2 + H \rightleftharpoons H_2O + OH$
7.	$HO_2 + M \rightleftharpoons H + O_2 + M$	40.	$H_2O_2 + O \rightleftharpoons OH + HO_2$
8.	$H + HO_2 \rightleftharpoons OH + OH$	41.	$HCOH + O_2 \rightleftharpoons HO_2 + CHO$
9.	$H + HO_2 \rightleftharpoons H_2 + O_2$	42.	$HCHO + HO_2 \rightleftharpoons H_2O_2 + CHO$
10.	$O + HO_2 \rightleftharpoons OH + O_2$	43.	$CH_4 + CHO \rightleftharpoons CH_3 + HCHO$
11.	$OH + HO_2 \rightleftharpoons H_2O + O_2$	44.	$HCHO \rightleftharpoons H + CHO$
12.	$CO + OH \rightleftharpoons CO_2 + H$	45.	$CH_3OH \rightleftharpoons CH_3 + OH$
13.	$CO + O_2 \rightleftharpoons CO_2 + O$	46.	$CH_3OH + O_2 \rightleftharpoons CH_2OH + HO$
14.	$H_2O_2 + OH \rightleftharpoons H_2O + HO_2$	47.	$CH_3OH + OH \rightleftharpoons CH_2OH + H_2O$
15.	$H_2O_2 + O_2 \rightleftharpoons HO_2 + HO_2$	48.	$CH_3OH + O \rightleftharpoons CH_2OH + OH$
16.	$H_2O_2 \rightleftharpoons OH + OH$	49.	$CH_3OH + H \rightleftharpoons CH_2OH + H_2$
17.	$H_2O_2 + H \rightleftharpoons HO_2 + H_2$	50.	$CH_3OH + H \rightleftharpoons CH_3 + H_2O$
18.	$O + H + M \rightleftharpoons OH + M$	51.	$CH_3OH + CH_3 \rightleftharpoons CH_2OH + CH_4$
19.	$O + O + M \rightleftharpoons O_2 + M$	52.	$CH_3OH + HO_2 \rightleftharpoons CH_2OH + H_2O_2$
20.	$CO + HO_2 \rightleftharpoons CO_2 + OH$	53.	$CH_2OH \rightleftharpoons HCHO + H$
21.	$CO_2 + M \rightleftharpoons CO + O + M$	54.	$CH_2OH + O_2 \rightleftharpoons HCHO + HO_2$
22.	$CH_4 \rightleftharpoons CH_3 + H$	55.	$CH_3 + O_2 \rightleftharpoons CH_3O + O$
23.	$CH_4 + O_2 \rightleftharpoons CH_3 + HO_2$	56.	$CH_3 + HO_2 \rightleftharpoons CH_2O + OH$
24.	$CH_4 + H \rightleftharpoons CH_3 + H_2$	57.	$CH_3O \rightleftharpoons HCHO + H$
25.	$CH_4 + O \rightleftharpoons CH_3 + OH$	58.	$CH_3O + O_2 \rightleftharpoons HCHO + HO_2$
26.	$CH_4 + OH \rightleftharpoons CH_3 + H_2O$	59.	$CH_3O + H \rightleftharpoons HCHO + H_2$
27.	$CH_4 + HO_2 \rightleftharpoons CH_3 + H_2O_2$	60.	$CH_3O + O \rightleftharpoons HCHO + OH$
28.	$CH_3 + O \rightleftharpoons HCHO + H$	61.	$CH_3O + OH \rightleftharpoons HCHO + H_2O$
29.	$CH_3 + OH \rightleftharpoons HCHO + H_2$	62.	$CH_3O + HO_2 \rightleftharpoons HCHO + H_2O_2$
30.	$HCHO + H \rightleftharpoons CHO + H_2$	63.	$CH_3O + CH_4 \rightleftharpoons CH_3OH + CH_3$
31.	$HCHO + O \rightleftharpoons CHO + OH$	64.	$CH_3O + HCHO \rightleftharpoons CH_3OH + CHO$
32.	$HCHO + OH \rightleftharpoons CHO + H_2O$	65.	$CH_3O + CO \rightleftharpoons CH_3 + CO_2$
33.	$CHO + H \rightleftharpoons CO + H_2$	66.	$CH_3O + CHO \rightleftharpoons CH_3OH + CO$

The sensitivity analysis revealed that the calculated methane concentration is most sensitive to the reactions:

$$OH + H_2O_2 \rightleftharpoons HO_2 + H_2O$$

$$OH + HO_2 \rightleftharpoons H_2O + O_2$$

$$H_2O_2 \rightleftharpoons OH + OH$$

$$HO_2 + HO_2 \rightleftharpoons O_2 + H_2O_2$$

These reactions control the concentration of OH radical, which is the main oxidant under SCWO conditions.

A study of the oxidation of methane in supercritical water by oxygen over a pressure range from 35–270 bar and a temperature range from 390–440°C was reported by Steeper *et al.*[6]. Reaction orders with respect to methane and oxygen were close to two and zero, respectively at 270 bar and at methane concentrations near 0.1 mol/L. At constant reactants concentration and temperature, methane consumption rate first increased with water concentration but reached a maximum near 5 mol/L. Further increase in water concentration led to a sharp decrease in the rate of methane consumption. A model based on a high-pressure elementary reaction mechanism reproduced this downturn in rates and provided insight into the reasons for this behaviour.

Conclusion

Some recent studies on chemical mechanisms of methane combustion have been reviewed. Detailed combustion mechanism, the identification of important reactions and some reduction mechanisms under different conditions have been introduced. The methodology employed and the results achieved are helpful for studying the combustion of other organic comounds of higher molecular weight. The calculation of heat of combustion indicates that the value of 13.1 MJ/kg is applicable for evaluating the heat release of methane burning in air.

The studies on suppression of methane combustion were mainly focused on the halogenated organic compounds. Because of their high ozone depletion potential and toxicity (CF_3I), halogen-free suppressing agents should be developed. This cannot be achieved without a deep understanding of the inhibition mechanisms.

Supercritical water oxidation (SCWO) is an advanced technology for the destruction of hazardous chemical wastes. A good understanding of the mechanism of methane oxidation in supercritical water is valuable for the study of organics of higher molecular weight.

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