# **CHAPTER 2**

# THEORY

#### **2.1 Biomass Properties**

Biomass is carbonaceous fuel composed of organic and inorganic compounds. The main part is organic materials which comprises of C, H, O and N, including mineral such as S, Fe, Ca, Al, Si, Zn, Na, K, Mg, Cl, heavy metal, etc. The basic analyses to determine the basic part and atomic composition are proximate and ultimate analyses. The structure of biomass is also determined, and it is mainly composed of cellulose, hemicellulose, lignin and extractive matter, shown in Table 2.1 composition. Holocellulose is general composition of biomass that consists of hemicellulose and cellulose.

Fuel sample	Holocellulose	Hemicelluloses	Cellulose	Lignin	Extractive
					matter
Beech wood	76.5	31.2	45.3	21.9	1.6
Spruce wood	70.5	20.7	49.8	27.0	2.5
Wheat straw	68.2	39.4	28.8	18.6	—
Corncob	81.5	31.0	50.5	15.0	3.5
Tea waste	50.1	19.9	30.2	40.0	9.9
Olive husk	47.6	23.6	24.0	48.4	9.4
Hazelnut shell	57.2	30.4	26.8	42.9	3.3
Walnut shell	48.3	22.7	25.6	52.3	2.8
Almond shell	79.6	28.9	50.7	20.4	2.5
Sunflower shell	83	34.6	48.4	17.0	2.7

Table 2.1 Structural analyses of selected biomass samples (wt.%daf)

Source: (Demirbas, 1997)

Biomass also can be classified by proximate and elemental analyses into volatile, fixed carbon and ash, including carbon(C), hydrogen (H), oxygen (O) and nitrogen (N), as shown in Tables 2.2 and 2.3. Volatile matter is a fundamental composition of biomass. In the gasification process, when biomass is heated at high temperature, the remaining components are char and ash. Fixed carbon is mainly composed of Carbon (C) which has high calorific value.

Fuel sample	Ash	Volatile matter	Fixed carbon
Hazelnut shell	1.5	76.3	21.2
Sawdust	2.8	82.2	15.0
Corn stover	5.1	84.0	10.9
Poplar	1.3	-	16.4
Sugarcane bagasse	11.3	− /	15.0
Peach pit	1.0	4 -	19.9
Rice husk	22.6	61.0	16.7
Alfafa stalk	6.5	76.1	17.4
Switchgrass	8.9	76.7	14.4
Beech wood bark	5.7	65.0	29.3
Oak wood	0.5	77.6	21.9
Wheat straw	13.7	66.3	21.4
Olive husk	4.1	77.5	18.4
Beech wood	0.5	82.5	17.0
Spruce wood	1.7	80.2	18.1
Corncob	1.1	87.4	11.5
Tea waste	1.5	85.5	13.0
Walnut shell	2.8	59.3	37.9
Almond shell	3.3	74.0	22.7
Sunflower shell	4.0	76.2	19.8
Colza seed	6.5	78.1	15.4
Pine one	1.0	73.3	21.7
Cotton refuse	6.6	81.0	12.4
Olive refuse	9.2	66.1	24.7

Table 2.2 Proximate analyses of typical fuel samples (wt.% of dry fuel)

Source: (Demirbas, 1997)

	Fuel sample	С	Н	Ν	0	H/C	O/C.	Higher
	0				(diff.)	(mol/mol)	(mol/mol)	heating value
				5			62	(MJ/kg
wood	Softwood	52.1	6.1	0.2	41	1.40	0.59	20
	Hardwood	48.6	6.2	0.4	41.1	1.53	0.63	18.8
	Red oak wood	50.0	6.0	0.3	42.4	1.44	0.64	
	Beech wood	49.5	6.2	0.4	41.2	1.50	0.62	19.2
	Spruce wood	51.9	6.1	0.3	40.9	1.41	0.59	20.1
	Sawdust	46.9	5.2	0.1	37.8	1.33	0.60	-
	Poplar	48.4	5.9	0.4	39.6	1.46	0.61	-
Stalk	Cotton gin	42.8	5.4	1.4	35.0	1.51	0.61	3
and straw	Sugarcane bagasse	44.8	5.4	0.4	39.6	1.45	0.66	200
	Alfafa stalk	45.4	5.8	2.1	36.5	1.53	0.60	_
	Switchgrass	46.7	5.9	0.8	37.4	1.52	0.60	-
	Wheat straw	41.8	5.5	0.7	35.5	1.58	0.64	17
	Peach pit	53.0	5.9	0.3	39.1	1.34	0.55	S
	Corncob	49.0	5.4	0.5	44.5	1.32	0.68	17
	Corn stover	42.5	5.0	0.8	42.6	1.41	0.75	17.8
	Tea waste	48.0	5.5	0.5	44.0	1.38	0.69	17.1
Husk	Olive husk	49.9	6.2	1.6	42.0	1.49	0.63	-
and	Rice husk	47.8	5.1	0.1	38.9	1.28	0.61	-
shell	Hazelnut shell	52.8	5.6	1.4	42.6	1.27	0.61	19.3
	Walnut shell	53.5	6.6	1.5	45.4	1.48	0.64	-
	Almond shell	47.8	6.0	1.1	41.5	1.51	0.65	-
	Sunflower shell	47.4	5.8	1.4	41.3	1.47	0.65	-
	Coal type 1	81.5	4.0	1.2	3.3	0.59	0.03	-

Table 2.3 Ultimate analyses of typical fuel samples (wt.% of dry fuel with ash)

The main composition of biomass is carbon (C), hydrogen (H) and oxygen (O). Molar ratios of H/C, O/C and (H+O)/C are shown in Figure 2.1. Carbon contents of biomass are in a range of 30-60 (% dry basis). H/C ratio is generally higher than O/C ratio by two times. Coalification diagram, on Figure 2.2, shows the atom ratios between H/C with O/C. Biomass varies widely and can be separated from other solid fuels such as coal. Biomass has higher content of oxygen and hydrogen than coal. The heating value of biomass is lower than coal because coal has lower O/C and H/C ratios and higher content of Carbon (C) than hydrogen (H) and oxygen (O). Biomass has higher content of oxygen than coal, making it more environmental friendly.



∆ O/C

• (H+O)/C

□ H/C

Figure 2.1 Molar ratios of hydrogen and oxygen to carbon in biomass (Jenkins et al., 1998)



Figure 2.2 Diagram showing compositional differences among biomass and coals (Jenkins et al., 1998)

#### 2.2 Thermogravimetry Analysis

# 2.2.1 Definitions

Thermogravimetry (TG) is an experimental technique used in a complete evaluation and interpretation of results when it is known as thermogravimetric analysis (TGA). This technique was defined by the International Confederation for Thermal Analysis and Calorimetry (ICTAC). The sample is heated to monitor the mass change as a function of temperature and time. The temperature is controlled as isothermal or non-isothermal. Mass loss is seen if a process occurs. Mass is plotted against temperature (T) or time (t). The mass loss appears as a step when increasing temperature. In an inert atmosphere, first step is a process of decrease of moisture at 100-120°C, and second is volatile component process at 180-600 °C, and the last is carbonization process. There are reactions occurring with no mass loss in a process. It can be detected by coupling thermogravimetric analyzer with differential scanning calorimeter (DSC), fourier transform infrared spectrometer (FT-IR) and mass spectrometer (MS).

It should be noted that mass loss occurs around one temperature, where line is steepest. Some reaction starts well before the main reaction temperature. There is still some residual mass loss well after the main reaction (Haines, 2002).

#### 2.2.2 Reaction Kinetics

Kinetics of non-isothermal behavior was analyzed to determine apparent activation energy and pre-exponential factor for the thermal degradation. Thermal decomposition behavior of biomass under flowing nitrogen, air and oxygen was obtained. The results of thermogravimetric experiments were expressed as conversion  $\alpha$ , defined as:

$$\alpha = \frac{W_i - W_t}{W_i - W_f} \tag{2.1}$$

where  $W_i$ ,  $W_t$  and  $W_f$  are the initial mass of the sample, the mass of oxidized sample, and the final residual mass, respectively. The kinetic parameters for the global thermal degradation process of Mimosa can be calculated using similar procedure adopted by (Haines, 2002; Wongsiriamnuay and Tippayawong, 2010). The general non-isothermal, decomposition reaction rate is:

 $\frac{d \propto}{dt} = k(1-\alpha)^n$ 

$$k = Ae^{-\left(\frac{E}{RT}\right)} \tag{2.3}$$

T is the temperature, A is the pre-exponential or frequency factor, t is the time, E is the activation energy, R is the universal gas constant in molar , n is the order of reaction. The logarithmic form for Eq. (2.2) and (2.3) is:

$$\ln\left(\frac{d\,\infty}{dt}\right) = \ln A + n\ln(1-\infty) - \frac{E}{RT}$$
(2.4)

Activation energy can be determined from the relationship between  $\ln(d \propto/dt)$ and 1/T. If the experiment is conducted at several constant temperature

When the apparent order of reaction is assumed to be 0th, 1st or 2nd, the preexponential or frequency factor can be obtained from the following equation:

$$\ln(A(1-\alpha)^n) = \ln A + n\ln(1-\alpha)$$
(2.5)

# **2.3 Gasification Process**

The gasification of biomass is a thermochemical process. The products contain various types of gas and small quantities of char, tar and ash. Gaseous product calorific value is dependent on the gasifying medium: air, steam, steam–oxygen, air–steam, oxygen-enriched air, etc. Gasification is carried out at high temperatures in order to optimize the gas production.

The resulting gas, known as producer gas, is a mixture of various fuel gases. A product gas from thermal decomposition composed of CO,  $CO_2$ ,  $H_2O$ ,  $H_2$ ,  $CH_4$ , other gaseous hydrocarbons (CHs), tars, char, inorganic constituents, and ash. Gas composition of product from the biomass gasification depends heavily on the gasification process, the gasifying agent, and the feedstock composition. Gasification of biomass is generally observed to be: Assuming a gasification process using

biomass as a feedstock, the first step of the process is a thermochemical decomposition of the cellulose, hemicelluloses and lignin compounds with production of char and volatiles.

Gasification is a thermochemical conversion process that converts solid biomass into fuel gases. It can be classified in several categories, according to different reference items. Referring to the oxidant specie used for biomass oxidation, it can be regarded as air gasification, the common way of gasifying solid fuels, meaning that it uses oxygen from the air as oxidant; pure oxygen gasification and steam gasification, when using pure oxygen or steam as oxidants. Other alternatives are a mixture of air/oxygen and steam or (less used) carbon dioxide and hydrogen. It can also, according to the energy source, be classified as autothermal, meaning that it gets energy from its self-oxidation phase to complete the process; or allothermal, meaning that energy must be supplied to "heat" the distillation phase, through pre-heating of the gasifying agent. Air biomass gasification comprises four principal stages determined by chemical changes together with energy flows in form of heat. There are four stages that can be summarized by the following reactions (Higman and Van der Burgt, 2003; Mun et al., 2010):

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$$CH_xO_y$$
 (biomass) + ( $O_2$  +3.76 $N_2$ )(Air)+  $H_2O$  (steam)  $\longrightarrow$   $CH_4$  +  $CO$  + (2.6)

 $CO_2 + H_2 + C$  (char)+H<sub>2</sub>O (unreacted steam) + tar + other CHs +ash

### **Stage 1 Drying**

Wet biomass + Heat = dry biomass +  $H_2O$ 

# Stage 2 Pyrolysis (Distillation)

Biomass + Heat = Pyrolysis gas + Charcoal

# Stage 3 Combustion (Oxidation)

Partial oxidation reaction	$2C + O_2$	→ 2CO	-246 kJ/mol	(2.7)
Complete oxidation reaction	$C + O_2$	$\rightarrow$ CO <sub>2</sub>	-408.8kJ/mol	(2.8)
oxiduation reaction	$H_2 + 1/2O_2$	$\rightarrow$ H <sub>2</sub> O	-242kJ/mol	(2.9)

### **Stage 4 Reduction**

Boudouard	$C + CO_2$		2CO	+160.5kJ/mol	(2.10)
Water-gas reaction	$C + H_2O$		$\rm CO + H_2$	+118kJ/mol	(2.11)
	$C + 2H_2O$		$\mathrm{CO}_2 + \mathrm{H}_2$	+76kJ/mol	(2.13)
Water gas shift reaction	$CO + H_2O$		$CO_2 + H_2$	-42.2kJ/mol	(2.12)
Steam methane	$CH_4 + H_2O$	$\rightarrow$	$CO + 3H_2$	+206kJ/mol	(2.14)
reforming reaction	$CH_4 + 2H_2O$	$\rightarrow$	$CO_2 + 4H_2$	+165kJ/mol	(2.15)
Methane reaction	$C + 2H_2$	$\rightarrow$	CH₄	-88 kJ/mol	(2.16)

Oxidation reactions are exothermic, which means that they release heat. Carbon (C) and hydrogen (H) that get oxidized in this phase are from the organic molecules of the solid fuel (biomass). They are transformed into carbon dioxide and water vapor, respectively. Ash is also produced during combustion, as a result of non-combustible inorganic (mineral) compounds. The products from this phase enter the

last phase where, these are subjected to reduction processes and still combustible gases such as carbon monoxide and hydrogen are produced. Energy from this process can be obtained from oxidation. In distillation, the heavier biomass molecules are converted into lighter organic molecules and carbon monoxide. In this phase, other products found from the chemical reactions, tar and char are also produced. Tar is mainly gasified in reduction phase while char, depending upon the technology used, can be significantly "burned" in reduction phase, reducing the concentration of particulates in the product. From these equations, air gasification is a partial combustion, which partially oxidizes biomass into a still combustible mixture of gases. "By-products" such as tar, char and ash, are of less importance as part of "combustible" product, and normally "washed out" from the so-called producer gas. Producer gas should be free of tar and particulates if it is to be burnt in an internal combustion engine. Therefore, the combustible content of *producer gas* is mainly carbon monoxide, with varying fractions of hydrogen and hydrocarbon gases (depending on the primary feedstock) and molecular nitrogen  $(N_2)$ . The combination of fuel gas produced directly by gasification reaction with the nitrogen from the air contributes to make its calorific value (CV) relatively low  $(4 - 6 \text{ MJ/m}^3)$ . This energy content makes producer gas (from air gasification) suitable just for combustion in adjacent internal combustion engines, boilers or kilns and, due to the dilution promoted by nitrogen, not recommendable for being transported for medium/long distances (as it becomes economically negative). For combustion far away, pure oxygen or steam should replace air as oxidant to gasify biomass. Then, the product is medium CV gas with relatively high energy density. Thus, gasification is referred as being the way of adding value to the solid biomass energy.

#### 2.4 Types of Gasification Reactor

For gasification processes, reactors are designed with different characteristics, based on transport of fluids or solids through the reactor. There are four types: quasinon-moving or self-moving feedstock, mechanical-moved feedstock, fluidicallymoved feedstock and special reactors. It also can be categorized based on types of bed and flow. There are two widely used types of gasification reactor which are fixed bed and fluidized bed, shown in Figures 2.3 and 2.4.

# 2.4.1 Fixed Bed

This gasifier can be classified based on flow as updraft (countercurrent) and downdraft (concurrent). The updraft gasifier, the biomass was feed from the top and moves downwards while gasifying agents (air, steam, etc.) are injected at the bottom of the reactor or at the grate so the producer gas moves upwards. The downdraft gasifier, both the feed and producer gas move downward and the producer gas exits at the bottom of the reactor (Kumar et al., 2009).

The advantages of fixed beds are the high carbon conversion efficiency, the wide range of ash content in the feedstock and the possibility to melt the ash. The disadvantages are a wide temperature distribution, low specific capacity, long periods for heat-up and a limited scale-up potential. A limited scale up potential. For plants with high power requirement the limited scale-up includes higher investment costs.

The downdraft gasifier or cocurrent flow produces a clean gas and low tar contents, while updraft gasifier or countercurrent flow has a high tar content with high gas calorific value and capacity than a downdraft gasifier (Warnecke, 2000).



Figure 2.3 Fixed bed reactors (Warnecke, 2000)

# 2.4.2 Fluidized Bed

The biomass is feed at the top of a bed. The feedstock is fluidized by gasifier medium, the product gas moves upward (Kumar et al., 2009). The advantages of fluidized beds are enhancing heat transfer between the gas and solid phases. It has been increasing in reaction rates and conversion efficiencies. They tolerate wide variations in fuel quality and a broad particle-size distribution. Disadvantages of fluidized beds are high dust content in the gas phase and the conflict between high reaction temperatures with good conversion efficiency and low melting points of ash components (Warnecke, 2000).

# Bubbling bed Circulating bed



Figure 2.4 Fluidized bed reactors (Warnecke, 2000)

# 2.5 Gasification Process Modeling

### 2.5.1 Introduction

Experimental work is resource-intensive with regards to time and money. A model prediction of producer gas composition using elemental analysis of biomass would be helpful. There are several models such as thermodynamic equilibrium, kinetics-free, steady-state, semi-transient and transient that can be used to predict producer gas composition. The thermodynamic equilibrium is the simplest of all models and can apply to various biomass types and reactor types with reasonable accuracy. The producer gas composition from thermodynamic equilibrium modeling provides a closer prediction when the reaction temperature is sufficiently high.

A system is in thermodynamic equilibrium when it is in thermal, mechanical and chemical equilibrium. Thermodynamic equilibrium is thermal balance in system. Mechanical equilibrium occurs when the system is not performing or receiving any work. Chemical equilibrium is the state of minimum Gibbs free energy and maximum system entropy. Equilibrium conditions are difficult to achieve in practical operating conditions. Results obtained from modeling can be used as the maximum limit on producer gas composition.

The number and variety of chemical equilibrium problems were solved by two approaches for equilibrium modeling: stoichiometric and non-stoichiometric (Van Zeggeren and Storey, 1970).

The first is the stoichiometric approach or non-linear equations approach. Reaction mechanism incorporates chemical reactions and involved species. The equation, containing C, H and O, that have the lowest value of the free energy of formation was used, by calculating the equilibrium constants. The equations are transformed numerically to a set of non-linear equations that can be solved by nonlinear solvers.

The second is the non-stoichiometric formulation approach or the optimization methods which search for the minimum or maximum of a function. It does not rely on the identification of any stoichiometric equations. None of particular reaction mechanism is involved to solve the model. The method is based on minimizing the total Gibbs free energy of a system, or total Gibbs free energy is equal zero. It uses scalar parameters which reduce to an optimization problem where specific Gibbs energy must be expressed as a function of species moles. Moles of species which minimize specific Gibbs function must be obtained.

### 2.5.2 Model Formulation

The empirical model relations were used to calculate the fraction of the producer gas. It can be used for any type of gasifier and it is more accurate for a downdraft due to its low content of tar. There are several factors affecting producer gas composition from biomass such as biomass feedstocks, biomass pre-treatment, gasifing agent, operating parameters. In this study, the model was based on the following assumptions.

• All carbon content in biomass is converted into gas and there is sufficient residence time to achieve thermodynamic equilibrium.

The producer gas products formed during the gasification process are  $H_2$ , CO, CO<sub>2</sub>, CH<sub>4</sub> and water. Other hydrocarbons gases are not present.

Biomass has low content of ash in feedstocks. Ash is not reacted even in high temperature and stays inert in all gasification reaction. Similar assumptions are used for other minerals.

All gases are ideal.

The gasification system is assumed to be adiabatic. There is no heat and work transferred. The reaction occurred under auto-thermal processes.

There are low contents of tar in products. No tar is assumed in a process.

No oxygen is left in a product. There is no free oxygen content to react with other product in secondary reaction step.

The gasification with air and steam is formed following this equation.

$$CH_{x}O_{y}N_{z} \text{ (biomass)} + x_{a} (O_{2}+3.76N_{2})(Air) + x_{w}H_{2}O \text{ (steam)} \implies x_{1}CO + x_{2}$$

$$CO_{2} + x_{3} CH_{4} + x_{4} H_{2} + x_{5}H_{2}O + (z/2 + x_{a} 3.76N_{2})$$
(2.17)

The moisture content of biomass is expressed as

$$x_w = \frac{MW_{biomass}mc}{18(1-mc)} \tag{2.18}$$

The major reaction in gasification processes which in reduction stage are as followed

Boudouard reaction	$C + CO_2$	$\rightarrow$	2CO	(2.19)
Water-gas reaction	$C + H_2O$	$\rightarrow$	$CO + H_2$	(2.20)
Water gas shift reaction	$\rm CO + H_2O$	$\rightarrow$	$\mathrm{CO}_2 + \mathrm{H}_2$	(2.21)
Hydrogasification reaction	C + 2H <sub>2</sub>	$\rightarrow$	$CH_4$	(2.22)

Equations (2.21) and (2.22) are the two major reactions that occur in gasification process. The equilibrium constants for Equations (2.21) and (2.22) as the function of their molar composition can be written as

$$K_{1} = \frac{P_{CO_{2}}P_{H_{2}}}{P_{CO}P_{H_{2}O}} = \frac{n_{CO_{2}}n_{H_{2}}}{n_{CO}n_{H_{2}O}} = \frac{x_{3}x_{2}}{x_{1}x_{4}}$$
(2.23)

$$K_{2} = \frac{P_{CH_{4}}}{\left(P_{H_{2}}\right)^{2}} = \frac{n_{CH_{4}}n_{tot}}{n_{H_{2}}^{2}} = \frac{x_{5}}{x_{2}^{2}}n_{tot}$$
(2.24)

Gibbs free energy is used in determining the value of K<sub>1</sub> and K<sub>2</sub>, as presented in Equations (2.23) and (2.24). For the ideal gas, the Gibbs free energy is a strong function of the reaction temperature and a weak function of pressure. Where  $\Delta \bar{g}_{f,T,i}^{O}$ 

is empirically calculated according to the Equation (2.30). The elemental balance for carbon, hydrogen and oxygen are described in Equations (2.25) to (2.27).

Carbon balance 
$$1 = x_1 + x_2 + x_3$$
 (2.25)

- Hydrogen balance  $x + 2x_w = 4x_3 + 2x_4 + 2x_5$  (2.26)
- Oxygen balance  $y + 2x_a 0 + x_w = x_1 + 2x_2 + x_5$  (2.27)

The energy balance for biomass gasification including all of chemical enthalpy and sensible enthalpy can be written as following

$$\begin{split} H_{f(biomass)}^{o} + x_{w} \left( H_{f(H_{2}O(l))}^{o} + H_{vap} \right) + x_{a} \left( H_{f(O_{2})}^{o} + 3.76H_{f(N_{2})}^{o} \right) &= x_{1} \left( H_{f(CO)}^{o} + \int_{298}^{T_{g}} C_{P(CO)} dT \right) + x_{2} \left( H_{f(CO_{2})}^{o} + \int_{298}^{T_{g}} C_{P(CO_{2})} dT \right) + x_{3} \left( H_{f(CH_{4})}^{o} + \int_{298}^{T_{g}} C_{P(CH_{4})} dT \right) \\ &+ x_{4} \left( H_{f(H_{2})}^{o} + \int_{298}^{T_{g}} C_{P(H_{2})} dT \right) + x_{5} \left( H_{f(H_{2}O)}^{o} + \int_{298}^{T_{g}} C_{P(H_{2}O)} dT \right) + \\ & \left( \frac{z}{2} + x_{a} 3.76 \right) \int_{298}^{T_{g}} C_{P(N_{2})} dT \end{split}$$

Specific heat capacity can be determined by using an empirical relation for a wide range temperature (shown in Table 2.4)

$$C_p(T) = c_1 + c_2 T + c_3 T^2 + c_4 T^3 (kJ/kg)$$
(2.29)

_	Species	<i>c</i> <sub>1</sub>	<i>c</i> <sub>2</sub>	<i>c</i> <sub>3</sub>	<i>c</i> <sub>4</sub>
ปสก	N <sub>2</sub>	31.2	$-1.36 \times 10^{-2}$	$2.68 \times 10^{-5}$	$-1.17 \times 10^{-8}$
	CO <sub>2</sub>	19.8	$7.34 \times 10^{-2}$	$-5.60 \times 10^{-5}$	1.72 × 10 <sup>-8</sup>
	$H_2$	29.1	$-1.92 \times 10^{-3}$	$4.00 \times 10^{-6}$	$-8.7 \times 10^{-10}$
		; II L	- <b>3</b>	<u> </u>	

Table 2.4 Coefficients of specific heat capacity for various gases

СО	30.9	$-1.29 \times 10^{-2}$	2.79 × 10 <sup>-5</sup>	$-1.23 \times 10^{-8}$
$CH_4$	19.3	$5.21 \times 10^{-2}$	1.20 × 10 <sup>-5</sup>	$-1.13 \times 10^{-8}$
$H_2O(g)$	32.2	$1.92 \times 10^{-3}$	1.06 × 10 <sup>-5</sup>	$-3.60 \times 10^{-9}$

Standard Gibbs function of formation can be calculated from

$$\Delta \bar{g}^{o}_{f,T,i} = \bar{h}^{o}_{f} - \acute{a}T \ln(T) - \acute{b}T^{2} - \left(\frac{\acute{c}}{2}\right)T^{3} - \left(\frac{\acute{d}}{3}\right)T^{4} + \left(\frac{\acute{e}}{2T}\right) + f^{2} + g\hat{T}$$
(2.30)

Coefficients of specific heat capacity for various gases (shown in Table 2.5) are used for calculating Gibbs formation at standard reference state of 298 K and 1 atm and other temperatures.

Species	$\overline{H}^o_{f,298}$	á	<i>b</i>	ć
CH <sub>4</sub>	-74.8	$-4.62 \times 10^{-2}$	1.13 × 10 <sup>-5</sup>	1.32 × 10 <sup>-8</sup>
СО	-110.5	$5.62 \times 10^{-3}$	$-1.19 \times 10^{-5}$	6.38 × 10 <sup>-9</sup>
CO <sub>2</sub>	-393.5	$-1.95 \times 10^{-2}$	3.12 × 10 <sup>-5</sup>	$-2.45 \times 10^{-8}$
H <sub>2</sub> O(g)	-241.8	$-8.95 \times 10^{-3}$	$-3.67 \times 10^{-6}$	5.21 × 10 <sup>-9</sup>
Species	d j	é	Af E	ģ
CH <sub>4</sub>	$-6.65 \times 10^{-12}$	$-4.89 \times 10^{-2}$	14.1	-0.223
СО	$-1.85 \times 10^{-12}$	$-4.89 \times 10^{-2}$	0.868	-0.0613
CO <sub>2</sub>	$6.95 \times 10^{-12}$	$-4.89 \times 10^{-2}$	5.27 S	e-0.121

Table 2.5 Coefficients of specific heat capacity for various gases

# $H_2O(g) -1.48 \times 10^{-12}$ 0 2.87 -0.0172

# 2.6 Fixed and Fluid Beds

Fluidization can be classified on the flow regime, shown in Figure 2.5. Fluidization occurs when fluid or gas flow through solids particles, and fluid turns solids particles in a static bed into a dynamic bed when the minimum fluidization velocity is reached. A gravitational force plays an important role. There is a minimum fluid flow required to overcome the gravitational force. From force balance,

drag force and buoyant force = gravitational force

$$\frac{\Delta P}{L} = (\rho_p - \rho_g)g(1 - \varepsilon_{mf})$$
<sup>(2.31)</sup>

The fluid flows upward can be a gas or a liquid or both. A particulate or smooth fluidization is a homogeneous bed in a liquid fluidized. The bed expands depending on the upward liquid flow rate, and due to this expansion the bed can become much higher than its initial or incipient height. In contrast, a gas fluidized bed is heterogeneous called bubbling or slugging fluidization. Its expansion is limited, unlike what happens in a liquid fluidized bed. At high velocities of gas, slugging fluidized bed occurs with a narrow diameter column and a deep bed.

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The minimum bubbling velocity is the velocity at which the bubbles are just born at the distributor. The bubbling bed at velocities greater than the minimum bubbling velocity tends to slug, especially in a deep and/or narrow column, and the slugging is due to the coalescence of bubbles. When the bubbles grow as large as the diameter of the column, a slug is initiated. Now solids move above the gas slug like a piston, and they rain through the rising slugs. Here the gas–solid contact is poor. The slugging regime, through a transition point, attains a turbulent condition of the bed, and this process is often termed fast fluidization. When velocity is equal or more than particle terminal velocity at very high velocities, solid particles are carryover or elutriation of the bed. Pneumatic transport of solid particles by the gas stream occurs at and above the particle terminal velocity. Liquid and gas fluidized beds for various gas flow rates are illustrated in Figure 2.6 (Kunii and Levenspiel, 1991; Sathiyamoorthy, 1998)



Figure 2.5 Schematic representation of fluidized beds in different regimes



Figure 2.6 Liquid and gas fluidized beds at various operating velocities.

(Sathiyamoorthy, 1998)

#### 2.6.1 Pressure Loss in Bed

A bed pressure drop versus superficial velocity for a typical gas-solid system is of interest. The superficial velocity is the net volume of fluid crossing a horizontal (empty) plane per unit area per unit time. This superficial velocity is less than the interstitial fluid velocity inside the bed. Superficial velocity is considered because it is convenience for measurement. The bed is a settled bed or an expanded bed. In a settled bed, the bed voidage ( $\varepsilon$ ), is relatively low, and the pressure drop obtained initially by passing the gas upward is of a relatively high magnitude, as depicted by line A–B in Figure 2.7. At point B, a fixed bed is turned to a fluidized bed and it is a complete fluidized bed at point C. Between C and D, the bed pressure drop remains constant in an ideal when the superficial velocity (U) is increased. The bed pressure drop beyond point D



Figure 2.7 The bed pressure drop with superficial velocity (Sathiyamoorthy, 1998)

is not constant, and it increases in with a terminal velocity similar to an empty column. The particles are carried away from the bed when the superficial velocity equals the particle terminal velocity. In this situation, the bed voidage ( $\varepsilon$ ) is unity, or the volume fraction of solid particles  $(1 - \varepsilon)$  is zero. Line EDF corresponds to the pressure drop in the empty column. When the upward flow of gas is gradually decreased, the bed pressure drop assumes its original path on a pressure drop versus velocity plot as long as the bed continues to be in a state of fluidization. Line DCG, indicates that the pressure drop obtained for a fixed bed during its settling is lower than that obtainable for increasing upward flow of gas. Point C on line GCD is the transition point between a fixed and a fluidized bed, and the velocity corresponding to

this is the minimum fluidization velocity. It may be observed that during increasing flow through the bed, there is no distinct point marking the transition, except that zone which corresponds to B–C with a peak. The relatively high value of the pressure drop  $(\Delta P)$  along line AB in a fixed bed when the flow is in the laminar regime compared to line GC of an expanded settled bed is due to low bed permeability. The fluid dynamic aspects at points A and B, in laminar flow conditions, most correlations for the pressure drop  $(\Delta P)$  through a packed bed of monodispersed spheres, is given by the Ergun equation:

$$\frac{\Delta P}{L} = \frac{150(1-\epsilon)^2}{\epsilon^3} \frac{\mu U}{\left(\emptyset d_p\right)^2} + \frac{1.75(1-\epsilon)\rho_g U^2}{\epsilon^3} \frac{1.75(1-\epsilon)\rho_g U^2}{\emptyset d_p}$$
(2.32)

where U is the gas superficial velocity, L is the bed height,  $d_p$  is particle diameter,  $\emptyset$  is the particle sphericity (if particle assumed sphere then  $\emptyset = 1$ ),  $\mu$  is the gas viscosity,  $\rho_g$  is the gas density, and  $\varepsilon$  is the voidage of the bed. The first term on the right hand side of Equation (2.32) represents the pressure loss through viscous effects and is the dominant term in the laminar flow region; the second term is the loss due to inertial forces and will be dominant at high Reynolds numbers (Sathiyamoorthy, 1998).

#### 2.6.2 Minimum Fluidization

At  $U_{mf}$  the weight of the bed is fully supported by the flow of gas, and the pressure drop through the bed is then equal to the bed weight per unit area in Equation (2.31). Minimum fluidization velocity for low Reynolds number, Re<20 as follow

 $\frac{\Delta P}{L} = (\rho_p - \rho_g)g(1 - \varepsilon_{mf}) = \frac{150(1 - \varepsilon_{mf})^2}{\varepsilon_{mf}^3} \frac{\mu U_{mf}}{(\phi d_p)^2}$ 

$$U_{mf} = \frac{(\rho_p - \rho_g)g(1 - \varepsilon_{mf})}{\left[\frac{150(1 - \varepsilon_{mf})^2}{\varepsilon_{mf}^3} \frac{\mu}{(\emptyset d_p)^2}\right]} \qquad Re_{p,mf} < 20 \qquad (2.33)$$

For high Reynolds number Re>1000

Effects of temperature and pressure on the minimum fluidization velocity  $(U_{mf})$  have been investigated by many researchers. It is dependent on particle size as shown in Figures 2.8 and 2.9. Temperature and pressure do not affect  $U_{mf}$  for particles smaller than 100 microns. For bigger particles,  $U_{mf}$  decrease when pressure is increased but increase with increasing temperature.

For small particles ( $\operatorname{Re}_{p,mf} < 20$ ), gas viscosity does not vary significantly with pressure, the only parameter which changes with pressure is the gas density. Most materials  $\rho_p$  are much larger than  $\rho_g$  even at elevated pressures, the term  $\rho_p - \rho_g$ essentially does not change with pressure. For small particles,  $U_{mf}$  will not change with pressure. The simplified equation for large ( $\operatorname{Re}_{p,mf} > 1000$ ), reduces to the only term which is influenced by pressure is  $\rho_g$  because  $\rho_p - \rho_g$  does not change with pressure. For large particles,  $U_{mf}$  should decrease with pressure for large particles.

The variation of  $U_{mf}$  with temperature is also strongly affected by particle size. For large particles, temperature causes  $\rho_g$  to decrease,  $U_{mf}$  should increase with temperature for large particles. For small particles,  $U_{mf}$  should decrease with temperature for small particles, where viscous effects predominate. Calculated  $U_{mf}$  versus temperature curves are shown in Figure 2.8 for several different particle sizes. As indicated above,  $U_{mf}$  increases with increasing temperature for large particles (where turbulent effects dominate), and decreases with increasing temperature for small particles (when viscous effects dominate) (Yates, 2003).



Figure 2.8 Effect of temperature on minimum fluidization velocity (Yates, 2003).

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Figure 2.9 The effect of pressure on minimum fluidization velocity (Yates, 2003)

#### 2.6.3 Gas Distributor and Plenum

The plenum, or wind box, is the chamber immediately below the grid. If the bedpressure-drop-to-grid-pressure-drop ratio is high enough, the plenum design will probably not be that important. However, for the case where this ratio is marginal, the plenum design may determine whether the bed will operate satisfactorily. The typical plenum designs showing various configurations for introducing gas into the plenum are illustrated in Figure. 2.10. Common sense dictates that certain plenum designs may be preferred over others. If the gas enters the plenum from the bottom, it is preferable that the plenum has a large enough distance between the outlet of the supply pipe and the grid to prevent the gas from preferentially passing through the middle of the grid. When gas enters a plenum from the side, it is preferable to route the gas to the middle of the plenum (Figure 2.10 c) rather than have the supply pipe end at the wall of the plenum. In addition, horizontal-to-vertical down gas entry (Figure 2.10 c) is preferable over the horizontal-to-vertical up gas entry (Figure 2.10 b) (Yang, 1999; Karri and Joachim, 2003).



Figure 2.10 Plenum configurations (Yang, 1999).

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