# ANEXOS

# ANEXO I. ESTRUCTURA DEL PROGRAMA PARA LOS MODELOS ESTEQUIOMÉTRICO Y PSEUDO-EXPERIMENTAL

## "REQUIRED DATA"

### "BIOMASS COMPOSITION (WET BASIS)"

Carbon=

Hydrogen=

Oxygen=

Nitrogen=

Sulfur=

Ash=

h2o=

Temperature= "Temperature must be in Celsius degrees"

### "GASIFICATION AGENT"

Steam=0 "Write 1 if this gasification agent is chosen or 0 if it is not. Also, two gasification agents can be used by adding 1 in two of them"

Air=1

Only_Oxygen=0

### "GASIFICATION RATIO"

Steam_biomass_ratio=

Air_biomass_ratio=

ER_oxygen=

### "FRACTION OF UNCONVERTED CARBON"

f= "Write the percentage of unconverted carbon that remains as char"

## "CALCULATIONS"

molC=Carbon*10/12

molH=Hydrogen*10/1

molO=Oxygen*10/16

molnitrogen=Nitrogen*10/14

molsulfur=Sulfur*10/32

molash=Ash*10/68,61

molh2o=h2o*10/18

## "GASIFICATION AGENTS"

### "STEAM"

T=Temperature

w=Steam_biomass_ratio

steamcalc=((1000-h2o*10)*w-h2o*10)/18 "The amount of steam required is determined by the parameter w, which is equal to the kilograms of water introduced (water contained in the biomass together with the steam introduced as a gasification agent) divided by the kilograms of dry biomass. Setting the value of w we can obtain the amount of steam that has to be introduced"

boolean_steam=Steam

steammols=boolean_steam* steamcalc “Depending on which gasification agent is chosen, boolean parameter will be 1 in case that it is selected and 0 in case that it is not. Therefore, the amount of mols of a gasification agent will be zero in case that this agent is not selected"

### "AIR"

"Calculation of stochiometric amount of oxygen"

"Firstly, we have to calulate the mols of stochiometricmols for a complete combustion"

molCstoch=molC

molHstoch=molH/4

molSstoch=molsulfur

moloxygenstoch=(molCstoch+molHstoch+molSstoch)*2

"Amount of oxygen introduced"

"Later, we obtain the total amount of air introduced. Normally, for gasification process, ratio biomass/oxygen varies between 0,2 and 0,4"

rair=Air_biomass_ratio

moloxygencalc=moloxygenstoch*rair

boolean_air=Air

moloxygen=boolean_air*moloxygencalc

"Amount of nitrogen introduced"

N2air=moloxygen/2*79/21 "Amount of nitrogen mols that comes with air"

"OXYGEN"

"Amount of oxygen introduced"

roxygen=ER_oxygen

molOcalc=moloxygenstoch*roxygen

boolean_oxygen=Only_Oxygen

molOagent=boolean_oxygen*molOcalc

"TOTAL AMOUNT OF NITROGEN"

totalnitrogen=molnitrogen+N2air*2 "Total amount of nitrogen is the sum of the biomass nitrogen and the nitrogen that comes with air"

xn2=totalnitrogen/2/totalmols

"AMOUNT OF CHAR"

char=f*molC "The amounf of char mols is equal to the mols of incoming carbon multiply by the unconverted fraction of carbon"

"LOW HEATING VALUE"

LHV_CO=67,6 "Lower heating values of the products. They are expressed in kcal/mol units"

LHV_H2=57,8

LHV_CH4=191,76

# "FINAL RESULTS"

## "SYSTEM OF EQUATIONS"

“Atomic balance of hydrogen:"

molC-char-xco*totalmols-xco2*totalmols-xch4*totalmols=0

molH+2*molh2o+steammols*2-xh2*totalmols*2-xh2o*totalmols*2-xch4*totalmols*4=0

"Atomic balance of oxygen"

molO+molh2o+steammols+molOagent+moloxygen-xco*totalmols-xco2*totalmols*2-xh2o*totalmols=0

"Sum of molar fractions"

xco+xco2+xh2o+xch4+xh2+xn2+molsulfur/totalmols=1

“Water-gas shift reaction: Only for stoichiometric model”

xco2*xh2/xco/xh2o=exp(-(37,4-41200/(273+T)+720/((273+T)/8,314)

"Relation between CO and CO2 exit concentration is set by the parameter B. This parameter can be obtained by a correlation that depends on the char surface temperature"

B=2400*exp(-6234/T)

“Relation between CO and CO2: Only for pseudo-experimental model"

xco=xco2*B

“Methanation reaction”

xch4/xh2^2=exp(-(86,2-74900/(273+T)+8020/(273+T))/8,314)

## "LOWER HEATING VALUE OF THE PRODUCER GAS"

"Molecular weight of the producer gas"

Molecular_weight_gas=xco*28+xh2*2+xch4*16+xco2*44+xh2o*18+xn2*28

"Lower heating value of the product gas in kcal/mol"

LHVgas_kcal_mol=LHV_CO*xco+LHV_H2*xh2+LHV_CH4*xch4

"Lower heating value of the product gas in kcal/kg"

LHVgas_kcal_kg=LHVgas_kcal_mol/Molecular_weight_gas

"Lower heating value of the product gas in kcal/m3N"

LHVgas_kcal_m3N=LHVgas_kcal_mol/22,4*1000

"Lower heating value of the product gas in MJ/m3N"

LHVgas_MJ_m3N=LHVgas_kcal_m3N*4,18/1000

## "RELATION H2/CO"

Relation_h2_co=xh2/xco "This relation will give us the relation of H2/CO which is very important in case of bio-SNG production"

# ANEXO II. TABLAS PARA EL CÁLCULO DE LAS CONSTANTES DE EQUILIBRIO

La obtención de los valores de las constantes de equilibrio de las reacciones de metanación y water-gas shift (Ecuaciones 3 y 5) se lleva a cabo mediante la energía libre de Gibbs:

$$K_i = e^{\frac{-\Delta \mathrm{GT}°}{RT}}, i = 1,2$$ Ecuación 1

$$\frac{\Delta G_m^0(T)}{T} = F_0(T) + \frac{\Delta H_m^0(T^*)}{T} - \left[\frac{\Delta H_m^0(T^*) - \Delta H_m^0(0\ K)}{T}\right]$$ Ecuación 2

En las tablas 11 y 12 se encuentran los datos de energía libre de Gibbs de formación, entalpía de formación y entalpía de combustión estándar de los distintos compuestos presentes durante las reacciones de gasificación. A partir de estos datos se puede obtener una ecuación para la constante de reacción dependiente de la temperatura.

**Tabla 1. Energías libre de Gibbs, entalpías de formación, entalpías de combustión y entropías estándar (14)**

| Compuesto | $\Delta G_f^0, Kj/mol$ | $\Delta H_f^0, Kj/mol$ | $\Delta H_c^0, Kj/mol$ | $\Delta S^0, Kj/mol$ |
|---|---|---|---|---|
| $CO_2$ | -394.64 | -393.78 | 0 | 213.82 |
| CO | -137.24 | -110.6 | -283 | -197.68 |
| $CH_4$ | -50.85 | -74.86 | -802.6 | 186.44 |
| $H_2O$ | -228.76 | -241.98 | 0 | 188.85 |
| $H_2$ | 0 | 0 | 0 | 130.61 |
| $N_2$ | 0 | 0 | 0 | 191.62 |
| C | 0 | 0 | -393.78 | 5.74 |

**Tabla 2. Funciones de energía libre**

| Compuesto | -$F_0$, J/(mol·K) | $\Delta H_m{}^0(T^*) - \Delta H_m{}^0(0K)$ |
|---|---|---|
| C | 11.6 | 1.05 |
| $H_2$ | 137.0 | 8.5 |
| CO | 204.1 | 8.67 |
| $CO_2$ | 226.4 | 9.36 |
| $CH_4$ | 199.4 | 10.03 |
| $H_2O$ | 196.7 | 9.91 |

Para una mejor comprensión del método utilizado, se va a realizar el cálculo de una de las constantes a modo de ejemplo:

$$C + CO_2 \leftrightarrow 2CO, \quad \Delta H = +172.6\,\frac{KJ}{mol}$$ Ecuación 3

$$\Delta G_m^0 = 2\cdot\mu(CO) - \mu(C) - \mu(CO_2) = 2\cdot\mu(CO) - \mu(CO_2),$$ Ecuación 4

$$\Delta G_m^0 = 2\cdot(-137.24) - (-394.64) = 120.08\,\frac{KJ}{mol},$$ Ecuación 5

$$\Delta H_m^0(298\ k) = 172.6\ KJ/mol,$$ Ecuación 6

$$F_0(T) = 2\cdot F_0(CO) - F_0(C) - F_0(CO_2),$$ Ecuación 7

$$F_0(T) = -170.2\, J/(mol\cdot K),$$ Ecuación 8

$$\Delta H_m^0(T^*) - \Delta H_m^0(0\ K) = 2\cdot[\Delta H_m^0(T^*) - \Delta H_m^0(0\ K)](CO) - [\Delta H_m^0(T^*) - \Delta H_m^0(0\ K)](C) - [\Delta H_m^0(T^*) - \Delta H_m^0(0\ K)](CO_2),$$ Ecuación 9

$$\Delta H_m^0(T^*) - \Delta H_m^0(0\ K) = 6.93\,\frac{KJ}{mol}.$$ Ecuación 10

$$\frac{\Delta G_m^0(T)}{T} = -170.2 + \frac{172.6\cdot 10^3}{T} - \left[\frac{6.93\cdot 10^3}{T}\right] = -170.2 + \frac{165.67\cdot 10^3}{T}\ J/(mol\cdot K)$$ Ecuación 11

$$\ln K = -\frac{\Delta G_m^0(T)}{T}.$$ Ecuación 12

$$\ln K = -\frac{-170.2+\frac{165.67\cdot 10^{3}}{T}}{8.314}.$$ Ecuación 13

Si la temperatura seleccionada es 800ºC:

$$\ln K = -\frac{-15.80}{8.314} = 1.90 \rightarrow K = 6.69.$$ Ecuación 14

# ANEXO III. MODELO EXPERIMENTAL

## a) Modelo de gasificación con vapor de agua en reactor de lecho fluidizado.

En la tabla 10 figuran los valores de las variables objeto para los que el modelo tiene validez.

Los datos de hidrógeno y oxígeno están referidos a la suma del contenido en la biomasa junto con la humedad.

**Tabla 3. Rango de valores de las variables objeto para el modelo experimental de gasificación con vapor de agua en reactor de lecho fluidizado**

| Variable | Valor mínimo | Valor máximo |
|---|---|---|
| Temperatura (°C) | 600 | 902 |
| Ratio $H_2O$/biomasa (kg/kg) | 0.2 | 2.11 |
| Hidrógeno (kg/kg) | 4.89 | 7.58 |
| Carbono (kg/kg) | 43.3 | 52.8 |
| Oxígeno (kg/kg) | 44.6 | 59.15 |

A continuación se detallan las ecuaciones para el cálculo de las composiciones de salida del gas de síntesis (base seca) en función de los variables de entrada.

$$H_2 = -4064.06 + 44.19 \cdot C + 380.78 \cdot H + 30.99 \cdot O + 1.49 \cdot T + 93.37 \cdot SB - 4.41 \cdot C \cdot H + 0.1226 \cdot C \cdot O - 0.016258 \cdot C \cdot T - 1.455 \cdot C \cdot SB - 3.656 \cdot H \cdot O + 4.16 \cdot H \cdot SB - 0.0113 \cdot O \cdot T - 0.888 \cdot O \cdot SB \tag{Ecuación 15}$$

$$CO = 3798.3 - 43.41 \cdot C - 367.57 \cdot H - 19.48 \cdot O - 1.541 \cdot T - 79.70 \cdot SB + 4.94 \cdot C \cdot H - 0.224 \cdot C \cdot O + 0.0182 \cdot C \cdot T + 1.083 \cdot C \cdot SB + 2.508 \cdot H \cdot O - 8.132 \cdot H \cdot SB + 0.01025 \cdot O \cdot T + 1.527 \cdot O \cdot SB \tag{Ecuación 16}$$

$$CO_2 = -1178.02 + 13.57 \cdot C + 26.41 \cdot H + 5.26 \cdot O + 1.38 \cdot T + 2.52 \cdot SB + 0.0151 \cdot C \cdot O - 0.0155 \cdot C \cdot T - 0.722 \cdot C \cdot SB - 0.032 \cdot H \cdot T - 0.006983 \cdot O \cdot T + 0.0481 \cdot T \cdot SB \tag{Ecuación 17}$$

$$CH_4 = 909.68 - 9.48 \cdot C - 16.51 \cdot H - 5.98 \cdot O - 1.077 \cdot T + 19.15 \cdot SB + 0.0113 \cdot C \cdot T + 0.0166 \cdot H \cdot T + 4.282 \cdot H \cdot SB - 0.0482 \cdot T \cdot SB$$ Ecuación 18

Siendo: T la temperatura de gasificación (ºC), SB el ratio $H_2O$/biomasa (kg/kg) y H, C y O la cantidad de carbono, hidrógeno y oxígeno introducidos por cada 100 kg de biomasa húmeda (sin tener en cuenta las cenizas).

En la Tabla 11 se representan los puntos que se han empleado para generar el modelo

Tabla 4. Datos experimentales utilizados para el modelo experimental de gasificación en lecho fluidizado

| Composición biomasa (kg en base húmeda) | | | Condiciones operación | | Composición gas de síntesis (% volumen en base seca) | | | |
|---|---|---|---|---|---|---|---|---|
| C | H | O | T (°C) | SB(kg/kg) | $H_2$ | CO | $CO_2$ | $CH_4$ |
| 49,07 | 4,89 | 55,35 | 690,00 | 1,32 | 50,50 | 14,30 | 26,60 | 8,60 |
| 49,07 | 4,89 | 55,35 | 730,00 | 1,32 | 52,20 | 16,40 | 23,50 | 7,90 |
| 49,07 | 4,89 | 55,35 | 750,00 | 1,00 | 49,50 | 23,70 | 21,20 | 5,60 |
| 49,07 | 4,89 | 55,35 | 750,00 | 1,32 | 52,46 | 17,80 | 22,32 | 7,42 |
| 49,07 | 4,89 | 55,35 | 750,00 | 1,70 | 52,90 | 16,40 | 22,90 | 7,80 |
| 49,07 | 4,89 | 55,35 | 770,00 | 1,32 | 54,40 | 18,50 | 19,40 | 7,70 |
| 50,80 | 6,11 | 49,35 | 700,36 | 0,30 | 28,94 | 40,56 | 18,20 | 12,30 |
| 51,60 | 6,23 | 53,40 | 730,06 | 0,80 | 27,17 | 45,18 | 14,01 | 13,64 |
| 51,60 | 6,23 | 53,40 | 799,89 | 0,80 | 32,38 | 41,64 | 14,87 | 11,10 |
| 51,60 | 6,23 | 53,40 | 840,06 | 0,80 | 31,59 | 40,05 | 15,70 | 12,65 |

| Composición biomasa (kg en base húmea) | | | Condiciones de operación | | Composición gas de síntesis (base seca) | | | |
|---|---|---|---|---|---|---|---|---|
| C | H | O | T(°C) | SB(kg/kg) | $H_2$ | CO | $CO_2$ | $CH_4$ |
| 51,60 | 6,23 | 53,40 | 890,86 | 0,80 | 34,17 | 39,57 | 14,31 | 11,94 |
| 51,60 | 6,23 | 53,40 | 800,00 | 0,48 | 22,69 | 49,04 | 13,07 | 15,20 |
| 51,60 | 6,23 | 53,40 | 800,00 | 0,61 | 34,65 | 40,90 | 13,44 | 11,01 |
| 51,60 | 6,23 | 53,40 | 800,00 | 0,79 | 33,14 | 41,20 | 14,24 | 11,42 |
| 51,60 | 6,23 | 53,40 | 800,00 | 0,80 | 30,00 | 40,48 | 15,27 | 14,24 |
| 51,10 | 6,35 | 53,40 | 730,06 | 0,80 | 27,10 | 45,08 | 13,98 | 13,84 |
| 51,10 | 6,35 | 53,40 | 799,89 | 0,80 | 32,37 | 41,63 | 14,86 | 11,14 |
| 51,10 | 6,35 | 53,40 | 840,06 | 0,80 | 31,54 | 39,98 | 15,67 | 12,80 |
| 51,10 | 6,35 | 53,40 | 890,86 | 0,80 | 34,13 | 39,53 | 14,29 | 12,05 |
| 52,80 | 7,58 | 47,80 | 782,63 | 0,80 | 35,02 | 31,66 | 20,93 | 12,39 |
| 52,80 | 7,58 | 47,80 | 800,65 | 0,80 | 31,73 | 34,23 | 21,82 | 12,22 |
| 52,80 | 7,58 | 47,80 | 852,05 | 0,80 | 33,38 | 35,56 | 19,08 | 11,97 |
| 49,4 | 4,9 | 55,73 | 650,00 | 1,32 | 47,25 | 11,25 | 31,90 | 9,60 |
| 49,4 | 4,9 | 55,73 | 690,00 | 1,32 | 50,50 | 12,83 | 28,51 | 8,16 |
| 49,4 | 4,9 | 55,73 | 730,00 | 1,32 | 52,20 | 15,90 | 25,65 | 6,25 |
| 49,4 | 4,9 | 55,73 | 770,00 | 1,32 | 53,08 | 17,85 | 23,90 | 5,17 |
| 49,4 | 4,9 | 55,73 | 750,00 | 1,00 | 48,88 | 22,70 | 22,20 | 6,22 |
| 49,4 | 4,9 | 55,73 | 750,00 | 1,32 | 51,17 | 19,65 | 23,15 | 6,03 |
| 49,4 | 4,9 | 55,73 | 750,00 | 1,70 | 51,38 | 18,19 | 24,57 | 5,86 |
| 51,44 | 6,03 | 47,23 | 800,00 | 1,86 | 26,78 | 33,21 | 22,97 | 17,05 |
| 51,44 | 6,03 | 47,23 | 900,00 | 1,56 | 37,27 | 29,32 | 22,89 | 10,52 |

| Composición biomasa (kg en base húmeda) | | | Condiciones de operación | | Composición gas de síntesis (% volumen en base seca) | | | |
|---|---|---|---|---|---|---|---|---|
| C | H | O | T(°C) | SB(kg/kg) | $H_2$ | CO | $CO_2$ | $CH_4$ |
| 51,44 | 6,03 | 47,23 | 599,15 | 1,56 | 24,62 | 41,21 | 19,91 | 14,26 |
| 51,44 | 6,03 | 47,23 | 701,37 | 1,56 | 27,71 | 35,16 | 22,85 | 14,27 |
| 51,44 | 6,03 | 47,23 | 797,79 | 1,56 | 35,39 | 29,81 | 23,17 | 11,63 |
| 51,44 | 6,03 | 47,23 | 902,36 | 1,56 | 37,63 | 29,09 | 23,03 | 10,24 |
| 51,44 | 6,03 | 47,23 | 800,00 | 1,56 | 35,68 | 29,07 | 23,52 | 11,72 |
| 51,44 | 6,03 | 47,23 | 800,00 | 1,85 | 27,12 | 33,73 | 22,98 | 16,17 |
| 51,44 | 6,03 | 47,23 | 800,00 | 2,11 | 22,86 | 37,48 | 20,96 | 18,70 |
| 43,30 | 6,71 | 59,15 | 800,00 | 0,20 | 29,35 | 48,10 | 8,57 | 13,98 |
| 43,30 | 6,71 | 59,15 | 800,00 | 0,41 | 40,09 | 40,09 | 8,50 | 11,32 |
| 43,30 | 6,71 | 59,15 | 800,00 | 0,60 | 41,33 | 39,14 | 8,20 | 11,34 |
| 43,30 | 6,71 | 59,15 | 800,00 | 0,80 | 41,26 | 37,87 | 11,84 | 9,03 |
| 43,30 | 6,71 | 59,15 | 800,00 | 1,00 | 41,18 | 33,39 | 16,76 | 8,67 |
| 43,30 | 6,71 | 59,15 | 750,58 | 0,60 | 34,92 | 44,93 | 6,98 | 13,16 |
| 43,30 | 6,71 | 59,15 | 800,11 | 0,60 | 41,88 | 39,60 | 7,69 | 10,84 |
| 50,26 | 7,28 | 47,16 | 800,00 | 0,20 | 29,74 | 43,02 | 18,72 | 8,52 |
| 50,26 | 7,28 | 47,16 | 800,00 | 0,59 | 37,37 | 37,37 | 17,85 | 7,40 |
| 50,26 | 7,28 | 47,16 | 800,00 | 0,80 | 37,36 | 34,82 | 19,84 | 7,98 |
| 50,26 | 7,28 | 47,16 | 800,00 | 1,00 | 38,27 | 33,52 | 20,56 | 7,65 |
| 50,26 | 7,28 | 47,16 | 749,69 | 0,60 | 30,05 | 46,79 | 14,18 | 8,98 |
| 50,26 | 7,28 | 47,16 | 800,23 | 0,60 | 37,38 | 37,95 | 18,00 | 6,68 |

## b) Modelo de gasificación con vapor de agua en reactor de lecho fijo.

**Tabla 5. Rango de valores de las variables objeto para el modelo experimental de gasificación con vapor de agua en reactor de lecho fijo**

| Variable | Valor mínimo | Valor máximo |
|---|---|---|
| Temperatura (°C) | 600 | 928 |
| Ratio $H_2O$/biomasa (kg/kg) | 0.12 | 2.79 |
| Hidrógeno | 4.12 | 8.42 |
| Carbono | 43.62 | 72.15 |
| Oxígeno | 23.71 | 59.74 |

$$H_2 = -4064.06 + 44.19 \cdot C + 380.78 \cdot H + 30.99 \cdot O + 1.49 \cdot T + 93.37 \cdot SB - 4.41 \cdot C \cdot H + 0.1226 \cdot C \cdot O - 0.016258 \cdot C \cdot T - 1.455 \cdot C \cdot SB - 3.656 \cdot H \cdot O + 4.16 \cdot H \cdot SB - 0.0113 \cdot O \cdot T - 0.888 \cdot O \cdot SB$$

Ecuación 19

$$CO = +3798.32 - 43.42 \cdot C - 367.57 \cdot H - 19.47 \cdot O - 1.54 \cdot T - 79.70 \cdot SB + 4.94 \cdot C \cdot H - 0.224 \cdot C \cdot O + 0.018 \cdot C \cdot T + 1.083 \cdot C \cdot SB + 2.508 \cdot H \cdot O - 8.132 \cdot H \cdot SB + 0.0103 \cdot O \cdot T + 1.528 \cdot O \cdot SB$$

Ecuación 20

$$CO_2 = -1178.024 + 13.57 \cdot C + 26.41 \cdot H + 5.26 \cdot O + 1.38 \cdot T + 2.52 \cdot SB + 0.015 \cdot C \cdot O - 0.015 \cdot C \cdot T - 0.722 \cdot C \cdot SB - 0.032 \cdot H \cdot T - 0.00698 \cdot O \cdot T + 0.048 \cdot T \cdot SB$$

Ecuación 21

$$CH_4 = +909.69 - 9.47 \cdot C - 16.51 \cdot H - 5.98 \cdot O - 1.077 \cdot T + 19.15 \cdot SB + 0.011 \cdot C \cdot T + 0.016 \cdot H \cdot T + 4.28 \cdot H \cdot SB + 0.0076 \cdot O \cdot T - 0.283 \cdot O \cdot SB - 0.047 \cdot T \cdot SB$$

Ecuación 22

En la Tabla 12 se encuentran los puntos experimentales que se han empleado para el modelo de lecho fijo.

**Tabla 6. Datos experimentales utilizados para el modelo experimental de gasificación en lecho fluidizado**

| Composición biomasa (kg en base húmeda) | | | Condiciones operación | | Composición gas de síntesis (% volumen en base seca) | | | |
|---|---|---|---|---|---|---|---|---|
| C | H | O | T(°C) | SB(kg/kg) | $H_2$ | CO | $CO_2$ | $CH_4$ |
| 49,07 | 4,89 | 55,35 | 690,00 | 1,32 | 50,50 | 14,30 | 26,60 | 8,60 |
| 49,07 | 4,89 | 55,35 | 730,00 | 1,32 | 52,20 | 16,40 | 23,50 | 7,90 |
| 49,07 | 4,89 | 55,35 | 750,00 | 1,00 | 49,50 | 23,70 | 21,20 | 5,60 |
| 49,07 | 4,89 | 55,35 | 750,00 | 1,32 | 52,46 | 17,80 | 22,32 | 7,42 |
| 49,07 | 4,89 | 55,35 | 750,00 | 1,70 | 52,90 | 16,40 | 22,90 | 7,80 |
| 49,07 | 4,89 | 55,35 | 770,00 | 1,32 | 54,40 | 18,50 | 19,40 | 7,70 |
| 50,80 | 6,11 | 49,35 | 700,36 | 0,30 | 28,94 | 40,56 | 18,20 | 12,30 |
| 51,60 | 6,23 | 53,40 | 730,06 | 0,80 | 27,17 | 45,18 | 14,01 | 13,64 |
| 51,60 | 6,23 | 53,40 | 799,89 | 0,80 | 32,38 | 41,64 | 14,87 | 11,10 |
| 51,60 | 6,23 | 53,40 | 840,06 | 0,80 | 31,59 | 40,05 | 15,70 | 12,65 |
| 51,60 | 6,23 | 53,40 | 890,86 | 0,80 | 34,17 | 39,57 | 14,31 | 11,94 |
| 51,60 | 6,23 | 53,40 | 800,00 | 0,48 | 22,69 | 49,04 | 13,07 | 15,20 |
| 51,60 | 6,23 | 53,40 | 800,00 | 0,61 | 34,65 | 40,90 | 13,44 | 11,01 |
| 51,60 | 6,23 | 53,40 | 800,00 | 0,79 | 33,14 | 41,20 | 14,24 | 11,42 |
| 51,60 | 6,23 | 53,40 | 800,00 | 0,80 | 30,00 | 40,48 | 15,27 | 14,24 |
| 51,10 | 6,35 | 53,40 | 730,06 | 0,80 | 27,10 | 45,08 | 13,98 | 13,84 |
| 51,60 | 6,23 | 53,40 | 800,00 | 0,48 | 22,69 | 49,04 | 13,07 | 15,20 |

| Composición biomasa (kg en base húmeda) | | | Condiciones de operación | | Composición gas de síntesis (% Volumen en base seca) | | | |
|---|---|---|---|---|---|---|---|---|
| C | H | O | T(°C) | SB(kg/kg) | $H_2$ | CO | $CO_2$ | $CH_4$ |
| 51,10 | 6,35 | 53,40 | 840,06 | 0,80 | 31,54 | 39,98 | 15,67 | 12,80 |
| 51,10 | 6,35 | 53,40 | 890,86 | 0,80 | 34,13 | 39,53 | 14,29 | 12,05 |
| 52,80 | 7,58 | 47,80 | 782,63 | 0,80 | 35,02 | 31,66 | 20,93 | 12,39 |
| 52,80 | 7,58 | 47,80 | 800,65 | 0,80 | 31,73 | 34,23 | 21,82 | 12,22 |
| 52,80 | 7,58 | 47,80 | 852,05 | 0,80 | 33,38 | 35,56 | 19,08 | 11,97 |
| 38,43 | 4,07 | 45,30 | 650,00 | 1,32 | 47,25 | 11,25 | 31,90 | 9,60 |
| 38,43 | 4,07 | 45,30 | 690,00 | 1,32 | 50,50 | 12,83 | 28,51 | 8,16 |
| 38,43 | 4,07 | 45,30 | 730,00 | 1,32 | 52,20 | 15,90 | 25,65 | 6,25 |
| 38,43 | 4,07 | 45,30 | 770,00 | 1,32 | 53,08 | 17,85 | 23,90 | 5,17 |
| 38,43 | 4,07 | 45,30 | 750,00 | 1,00 | 48,88 | 22,70 | 22,20 | 6,22 |
| 38,43 | 4,07 | 45,30 | 750,00 | 1,32 | 51,17 | 19,65 | 23,15 | 6,03 |
| 38,43 | 4,07 | 45,30 | 750,00 | 1,70 | 51,38 | 18,19 | 24,57 | 5,86 |
| 51,44 | 6,03 | 47,23 | 800,00 | 1,86 | 26,78 | 33,21 | 22,97 | 17,05 |
| 51,44 | 6,03 | 47,23 | 900,00 | 1,56 | 37,27 | 29,32 | 22,89 | 10,52 |
| 51,44 | 6,03 | 47,23 | 599,15 | 1,56 | 24,62 | 41,21 | 19,91 | 14,26 |
| 51,44 | 6,03 | 47,23 | 701,37 | 1,56 | 27,71 | 35,16 | 22,85 | 14,27 |
| 51,44 | 6,03 | 47,23 | 797,79 | 1,56 | 35,39 | 29,81 | 23,17 | 11,63 |
| 51,44 | 6,03 | 47,23 | 902,36 | 1,56 | 37,63 | 29,09 | 23,03 | 10,24 |
| 51,44 | 6,03 | 47,23 | 800,00 | 1,56 | 35,68 | 29,07 | 23,52 | 11,72 |
| 51,44 | 6,03 | 47,23 | 800,00 | 1,85 | 27,12 | 33,73 | 22,98 | 16,17 |
| 51,44 | 6,03 | 47,23 | 800,00 | 2,11 | 22,86 | 37,48 | 20,96 | 18,70 |

| Composición biomasa (kg en base húmeda) | | | Condiciones de operación | | Composición gas de síntesis (% volumen en base seca) | | | |
|---|---|---|---|---|---|---|---|---|
| C | H | O | T(°C) | SB(kg/kg) | $H_2$ | CO | $CO_2$ | $CH_4$ |
| 43,30 | 6,71 | 59,15 | 800,00 | 0,20 | 29,35 | 48,10 | 8,57 | 13,98 |
| 43,30 | 6,71 | 59,15 | 800,00 | 0,41 | 40,09 | 40,09 | 8,50 | 11,32 |
| 43,30 | 6,71 | 59,15 | 800,00 | 0,60 | 41,33 | 39,14 | 8,20 | 11,34 |
| 43,30 | 6,71 | 59,15 | 800,00 | 0,80 | 41,26 | 37,87 | 11,84 | 9,03 |
| 43,30 | 6,71 | 59,15 | 800,00 | 1,00 | 41,18 | 33,39 | 16,76 | 8,67 |
| 43,30 | 6,71 | 59,15 | 750,58 | 0,60 | 34,92 | 44,93 | 6,98 | 13,16 |
| 43,30 | 6,71 | 59,15 | 800,11 | 0,60 | 41,88 | 39,60 | 7,69 | 10,84 |
| 50,26 | 7,28 | 47,16 | 800,00 | 0,20 | 29,74 | 43,02 | 18,72 | 8,52 |
| 50,26 | 7,28 | 47,16 | 800,00 | 0,59 | 37,37 | 37,37 | 17,85 | 7,40 |
| 50,26 | 7,28 | 47,16 | 800,00 | 0,80 | 37,36 | 34,82 | 19,84 | 7,98 |
| 50,26 | 7,28 | 47,16 | 800,00 | 1,00 | 38,27 | 33,52 | 20,56 | 7,65 |
| 50,26 | 7,28 | 47,16 | 749,69 | 0,60 | 30,05 | 46,79 | 14,18 | 8,98 |
| 50,26 | 7,28 | 47,16 | 800,23 | 0,60 | 37,38 | 37,95 | 18,00 | 6,68 |

# ANEXO IV. RESULTADOS DE LA SIMULACIÓN EN ASPEN HYSYS®

## *a) Planta de producción de bio-metano*

Tal y como se ha comentado, para el diseño de esta planta se ha tomado la topología de la tecnología MILENA, que combina gasificación en lecho fluidizado, con un sistema de limpieza de gas OLGA y la tecnología de metanación TREMP™.

El diseño del presente proyecto presenta algunas modificaciones, como la ausencia del sistema de limpieza, o la instalación de un solo reactor.

Para la simulación se ha escogido como "fluid package" el modelo de PRSV. Éste es una modificación del Peng-Robinson (utilizado para cálculos de equilibrio líquido-vapor) para modelar sistemas no ideales.

La biomasa utilizada corresponde a restos madereros que el propio ECN emplea para sus investigaciones. (31). El valor de la cantidad de biomasa alimentada (2700 kg/h) se ha tomado también de las investigaciones de dicho centro sobre la planta de gasificación.

En las tablas 18 y 19 se representan las composiciones, caudales másico y molar, presión y temperatura de las principales corrientes de la planta.

**Tabla 7. Datos de composición de las corrientes para la simulación en Hysys de la planta de producción de bio-metano**

| Corriente | Composición de la corriente (% Volumen) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | CH4 | O2 | H2 | H2O | CO | CO2 | C | Sulfuro | MEA |
| Agua fresca | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 |
| Vapor alimentado | 0 | 0 | 0 | 1 | 1 | 1 | 1 | 1 | 0 |
| Biomasa | 0 | 0.15 | 0.32 | 0.10 | 0 | 0 | 0.43 | 0 | 0 |
| Char | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| Biomasa alimentada | 0 | 0.15 | 0.33 | 0.11 | 0 | 0 | 0.42 | 0 | 0 |
| Gas de síntesis | 0 | 0 | 0.39 | 0.34 | 0.16 | 0.11 | 0 | 0 | 0 |
| Sulfuros | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| Corriente rica en metano | 0.18 | 0 | 0.02 | 0.61 | 0 | 0.18 | 0 | 0 | 0 |
| Agua líquida | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 |
| Metano+Dióxido de carbono | 0.44 | 0 | 0.06 | 0.06 | 0 | 0.44 | 0 | 0 | 0 |
| MEA nueva | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| MEA alimentada | 0 | 0 | 0 | 0.06 | 0 | 0 | 0 | 0 | 0.94 |
| Bio-metano | 0.87 | 0 | 0.13 | 0 | 0 | 0 | 0 | 0 | 0 |
| Amina rica | 0 | 0 | 0 | 0.05 | 0 | 0.01 | 0 | 0 | 0.94 |
| CO2 | 0.1 | 0 | 0 | 0.1 | 0 | 0.68 | 0 | 0 | 0.12 |
| MEA limpia | 0 | 0 | 0 | 0.05 | 0 | 0 | 0 | 0 | 0.95 |

**Tabla 8. Caudales másico y molar, presión y temperatura de las corrientes para la simulación en Hysys de la planta de producción de bio-metano**

| Corriente | Caudal másico (kg/h) | Caudal molar (kmol/h) | Presión (Kpa) | Temperatura (ºC) |
|---|---|---|---|---|
| Agua fresca | 89.24 | 4.95 | 101 | 25 |
| Agua alimentada | 2898 | 160.8 | 101 | 39.7 |
| Vapor alimentado | 2898 | 160.8 | 101 | 400 |
| Biomasa | 2700 | 227.4 | 101 | 25 |
| Biomasa alimentada | 2644 | 222.8 | 101 | 25 |
| Gas de síntesis | 5344 | 340.7 | 101 | 900 |
| Gas de síntesis (3) | 5344 | 340.7 | 2800 | 350 |
| Corriente rica en metano | 5344 | 246 | 2800 | 350 |
| Corriente con agua condensada | 5344 | 246 | 120 | 30 |
| Agua líquida | 2665 | 147.9 | 120 | 40 |
| Metano+dióxido de carbono | 2679 | 98 | 120 | 40 |
| MEA nueva | 316.8 | 5.19 | 110 | 40 |
| MEA alimentada | 433900 | 7264 | 110 | 40 |
| Bio-metano | 691 | 44.93 | 100 | 40 |
| Amina rica | 435900 | 7318 | 120 | 40.7 |
| Amina rica (2) | 435900 | 7318 | 200 | 104 |
| CO2 | 2389 | 58.31 | 200 | 128.2 |
| MEA limpia | 433500 | 7259 | 200 | 186.4 |
| MEA reciclada (2) | 433500 | 7259 | 110 | 40 |

### *b) Planta de generación de energía (CHP)*

En este caso el diseño se inspira en la planta de gasificación con aire presente en Lahti de la empresa Lahti Energia Oy. La cantidad de biomasa alimentada se extrae del dato proporcionado por la empresa corresponiente a la cantidad de fuel procesado, y que es de 250000 toneladas al año (28000kg/h). Dado que no se tenían datos de composición, y que el material utilizado es el mismo que para la anterior simulación (restos madereros), se ha tomado dicha composición.

La corriente de oxígeno es una corriente vacía ya que se ha instalado para realizar simulaciones con aire enriquecido, el cual no es el caso.

En las tablas 20 y 21 se encuentran las características de las principales corrientes.

**Tabla 9. Datos de composición de las corrientes para la simulación en Hysys de la planta de generación de energía (CHP)**

| Corriente | Composición de la corriente (% Volumen) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | CH4 | O2 | H2 | H2O | CO | CO2 | N2 | C | Sulfuros |
| Entrada aire | 0 | 0.21 | 0 | 0 | 0 | 0 | 0.79 | 0 | 0 |
| Biomasa | 0 | 0.14 | 0.35 | 0.1 | 0 | 0 | 0 | 0 | 0 |
| Char | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| Biomasa alimentación | 0 | 0.14 | 0.36 | 0.1 | 0 | 0 | 0.40 | 0 | 0 |
| Gas de síntesis | 0 | 0 | 0.18 | 0.12 | 0.17 | 0.1 | 0.44 | 0 | 0 |
| Sulfuros | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 |
| Aire de combustión | 0 | 0.21 | 0 | 0 | 0 | 0 | 0.79 | 0 | 0 |
| Gas de combustión | 0 | 0.04 | 0 | 0.15 | 0 | 0.13 | 0.68 | 0 | 0 |

**Tabla 10. Caudales másico y molar, presión y temperatura de las corrientes para la simulación en Hysys de la planta generación de energía (CHP)**

| Corriente | Caudal másico (kg/h) | Caudal molar (kmol/h) | Presión (Kpa) | Temperatura (ºC) |
|---|---|---|---|---|
| Entrada aire | 57520 | 1994 | 101 | 25 |
| Aire alimentado | 57520 | 1994 | 101 | 600 |
| Biomasa | 28500 | 2408 | 101 | 25 |
| Gas de síntesis | 85420 | 3602 | 101 | 900 |
| Aire de combustión | 120200 | 4168 | 101 | 600 |
| Aire de alimentación | 5344 | 340.7 | 101 | 900 |
| Gas de combustión | 205700 | 7161 | 1869 | 101 |

# ANEXO V. PROYECTO FIN DE CARRERA ORIGINAL (PRESENTADO Y EVALUADO EN LAPPEENRANTA UNIVERSTY OF TECHNOLOGY)

Lappeenranta University of Technology
Faculty of Technology

*Daniel Borniquel Moreno*

# Development of mathematical models for biomass gasification

Examiner: Professor, Ph.D. Esa K. Vakkilainen

# ABSTRACT

Lappeenranta University of Technology

Faculty of Technology

Degree Programme in Energy Technology

Daniel Borniquel Moreno.

**Development of mathematical models for biomass gasification**

Master's Thesis

2013

Examiners: Professor, Ph.D. Esa Vakkilainen

Ph.D. researcher Alena Aleshina

Keywords: gasification, biomass, mathematical models

Nowadays, the decrease of oil reserves has promoted development of renewable energies. Among them, biomass has grown especially and it has become one of the most promising in the future. This energy source presents some advantages that differentiate him from the other ones: low carbon emissions, flexibility in the use of different types of biomass (forestry, agricultural, urban waste…). However, its main advantages are that it is the only real alternative for oil, because it can be used either for energy and heat production or for fuel and chemicals production, such as natural gas or methanol.

There are several processes concerning biomass: pyrolysis, combustion and gasification. During the last decades, gasification is grabbing more interest, because it leads to higher energy efficiency and gaseous products can be used in several processes.

Simultaneously with biomass gasification growth, several mathematical models that allow optimizing the process have been developed. These models can be kinetics, which study evolution of reaction process inside the particles and thermodynamics, which focus on composition calculation of exit gas.

The goal of the thesis is the development of two thermodynamic models. The first one is a purely theoretical model, based on reaction constant. The second one pretends to include some experimental correlation, in order to reflect more accurate experimental results. Operation parameters (gasification agent, temperature and moisture) are analyzed and optimized for a bio-SNG production process and an energy production process.

# ACKNOWLEDGEMENTS

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I would like to thank to my parents, José Manuel and Rocío, for giving me the opportunity of living this experience.

Finally, I would not want to forget my friends from Lappeenranta. Thanks for making this year the best of our lives, and having helped me during good and bad moments.

# *TABLE OF CONTENTS*

# 1. INTRODUCTION

In the beginning of the XIX century, coal became the main source of energy, due to the Industrial revolution.  During the middle ages of XIX century, oil began replace coal, especially when gasoline was obtained.  In the XX century, oil production grew, as the same way as its price. In 1973, it took place the known as “oil crisis”, which caused a strong rise on oil price. Governments began to think about new sources of energy.

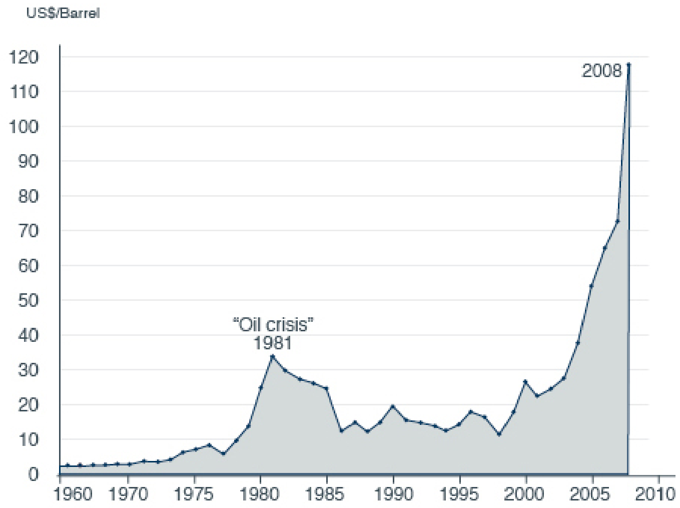


Figure 1.1 Evolution of oil price along history.

During the last decades, developments of renewable sources of energy, such as solar, geothermal or wind energy   are reducing the dependence on oil, and the problems that it entails.

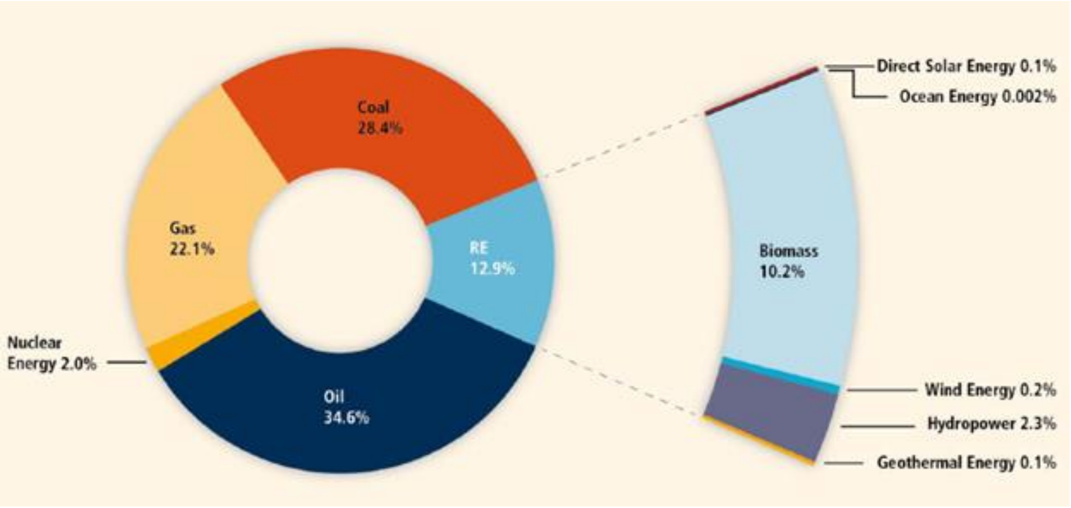


Figure 1.2 Global Primary Energy Distribution 2008.

In this context, biomass has become in one of the most promising source of energy. Actually, biomass is the only source of energy that can replace fossil fuels. Main advantages of biomass are the following ones:

Mitigate climate impacts: biomass technologies emit much lower green-house gases and $CO_2$ compared to fossil-based fuels. However, it emits more emissions of CO, $NO_x$ and HC.

Capable of being widely used: a widely range of feedstock can be used: wood, rice husk, coconut residues, corncob, straw, etc. Electric power, or heating value for the syngas will depend on the heating value of the raw material.

Reduction of energy dependent: this source of energy is available for almost every country, using different kinds of raw material. This fact makes countries more energy-independent, and it brings big amount of saved money. In addition, development of biomass will produce many job opportunities. For instance, employment the U.S. Biofuels industry has increase and average of 8.9% annually since 2004.

Enhance sustainability: biomass technology avoid fossil-based impacts associated with extraction and transport.

Low investment cost.

Rise of rural areas: breakthroughs in biomass technology will cause production growth that will help the development of agricultural areas.

Renewable source of energy: during biomass gasification, steam and $CO_2$ are release, which are also the reagent for biomass formation, as can be seen in the following mechanism:

$$nCO_2 + nH_2O + \text{solar light} + \text{chlorophyll} \rightarrow nO_2 + \text{biomass}[1] \qquad (1.\ 1)$$

Furthermore, biomass can be used to produce either electricity or other products, like liquid transportation fuels such as diesel and gasoline, alternative fuels, such as methanol and dimethyl ether (DME), ethanol and other chemicals. Biomass can be applied for developed countries as well as for rural electrification in isolated installations or in developing countries.

Biomass is defined as organic matter originated in a biological process, which can be spontaneous or induced, and that can be used as a source of energy. Biomass involves a wide range of materials. According to Chemical Engineering in University of Technology in Vienna, there are 647 species of biomass, which can be classified into 8 groups.

Wood

Straw

Wood waste

Bark

Energy crops

Shells, husks, rinds, shucks

Grass

Other (sewage sludge, pulp, seeds, paper)

Suitable technology and heating value of the producer gas depend strongly on the kind of biomass fed.

Biomass treatments can be classified in biological and thermochemical processes.

In the first one, biomass is converted into a biofuel called “biogas” through an anaerobic digestion. The composition of biogas varies depending upon the origin of the anaerobic digestion process. Landfill gas typically has methane concentrations around 50%. The other main component of biomass is $CO_2$. Biogas can burned directly for cooking, heating, lighting, process heat, absorption refrigeration, and generating electricity.

The second group includes processes of pyrolysis, combustion and gasification. The last one has grown more significantly during the last decades. It consists on the gasification of cellulosic materials. The product gas of the process is a biofuel called “bio-SNG” (bio-Synthetic Natural Gas). It can be used in a similar way to biogas. However, the main advantages of this biofuel are that it can be added to the natural gas grid, replacing this fossil fuel (only with steam gasification) and it can be used to produce chemical products. By contrast, it is a more complex process that involves several steps with a high investment cost compared to biogas production process. (32)

# 2. TECHNOLOGIES OF BIOMASS GASIFICATION

## 2.1 INTRODUCTION

First of all, gasification term has to be defined. Gasification is a thermo-chemical process which converts carbonaceous materials, such as biomass or coal, into gaseous component by a partial oxidation at elevated temperature. The outlet gas is composed by carbon monoxide (CO), hydrogen ($H_2$), methane ($CH_4$), traces of higher hydrocarbons such as ethane ($C_3H_6$) or ethylene ($C_2H_4$) and undesirable products like tar, dust, alkali vapors, water, carbon dioxide ($CO_2$), sulfur and nitrogen compounds ($SO_x$ and $NO_x$) and nitrogen ($N_2$). (14)

There are many reactors types, depending on the criteria selected:

Depending on the gasification agent, we can find: air-blown gasifiers, oxygen-blown gasifiers, steam gasifiers or a combination of oxygen-steam or air-steam. Producer gas from air-blown gasifiers has low heating value (5000to 6000 KJ/Kg or 3 to 6MJ/m3) compared to oxygen-blown ones (15000 kJ/kg or 10 to 12 MJ/m3). However, the last ones are more expensive than the first ones. Steam gasifiers are suitable when the goal of the gasification is the production of syngas.

Depending on the heat supply for the gasification, we can work with autothermal (or direct) gasifiers or allothermal (or indirect) gasifiers. Direct gasifiers provide energy required for gasification reactions by partial oxidation of the biomass. It produces a less-heating-value gas. Indirect gasifiers use an external source of heat, or a second chamber, where the combustion takes place, and heat is transferred by an inert product at high temperature.

Depending on the pressure in the gasifier, there are atmospheric and pressurized gasifiers.

Depending how gas and solid contact each other, we can work with entrained beds, fluidized beds (circulating or bubbling), spouted bed, fixed or moving bed, and dual fluidized bed gasifiers. Typical reactors are filled with solid fuel with or without inert solid, like sand.

The most common criterion for classifying reactor is the last one. There are different states of gas-solid contact. As there is shown in figures2.1 and 2.2, the different states can be classified basing on two parameters: pressure drop and U, fluid superficial velocity. Fluid superficial velocity is defined as the average velocity of the fluid (gas or liquid) in the axial or vertical direction, measured as if no particle or packing is present in the equipment. (15)

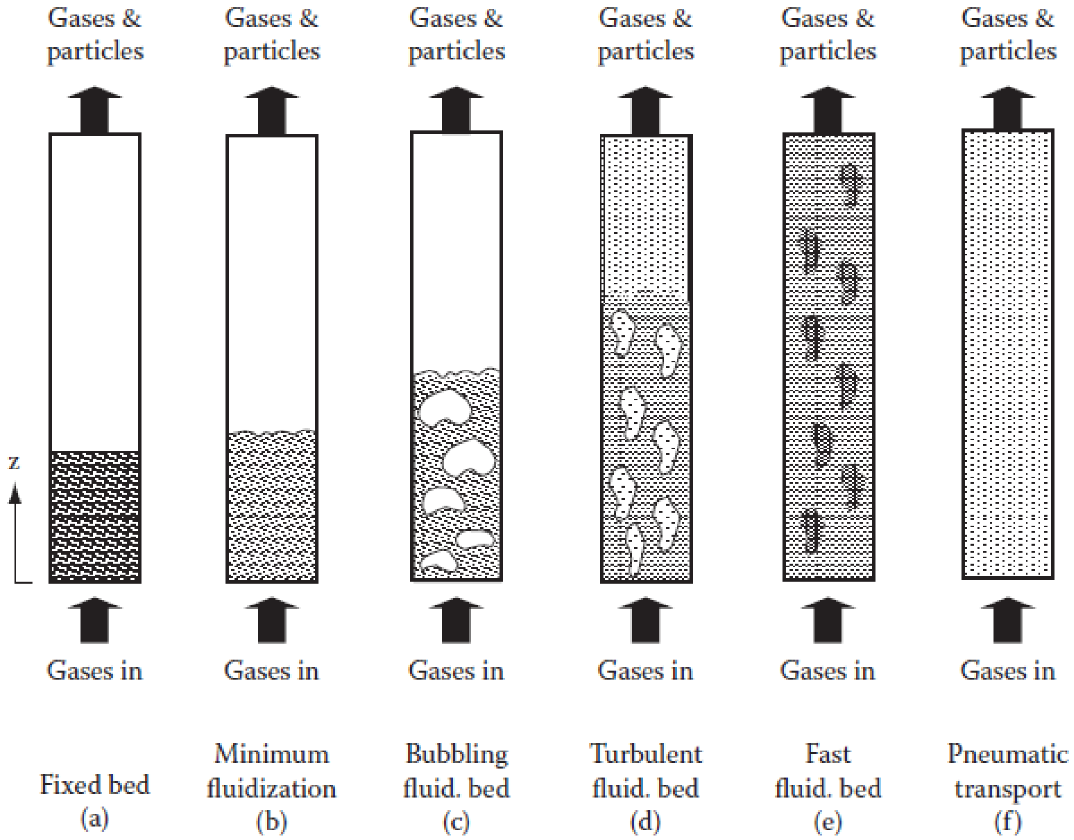


Figure 2.1Various  situations for beds of particles

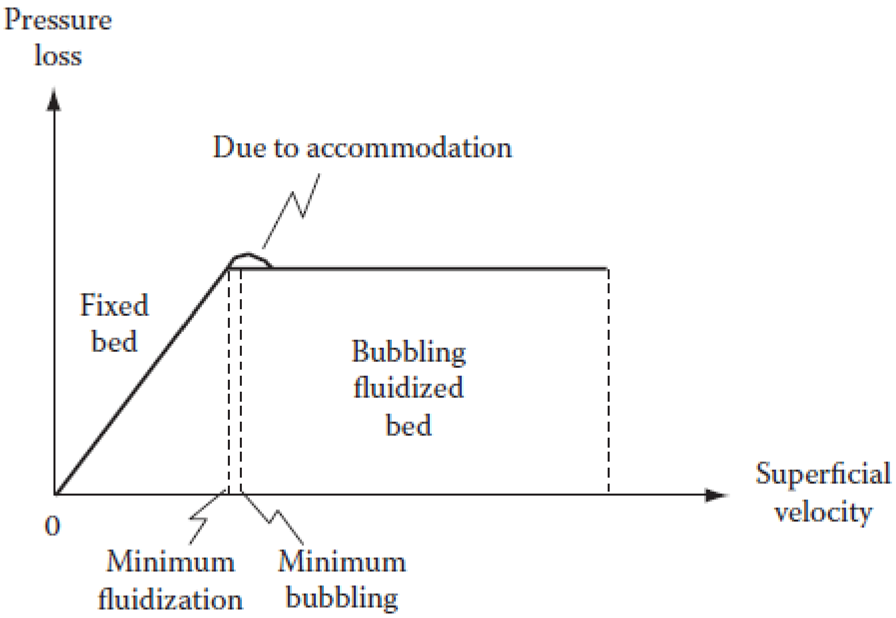


Figure 2.2 Superficial velocity against pressure drop

Initially, the momentum due to gas force is not enough to overcome the gravity force, and the particles remain fixed. This state is called fixed-bed and gives the name to updraft and downdraft gasifiers. Usually they are also called moving bed, because gas force makes the particles move but without detaching from each other.  During this region, pressure drop increases lineally with gas velocity.

If gas velocity continue increasing, bed begin to expand, and particles detach from each other and a combination of circular paths is produced. At this point, gas velocity is called minimum fluidization velocity, $U_{mf}$. Specifically, minimum fluidization is reached when U is increased slightly, because some particles present resistance to movement due to electrostatic charges, or to accommodation among particles.

From minimum fluidization, fluidized bed state has been reached. Pressure drop keeps constant with increases in gas velocity. After increase slightly gas velocity, bubbles begin to appear. A gas velocity growth will produce a bed expansion as well as a reduction in bubbles size.

Above the bed, there is a space called freeboard, whose mission is let the particles separate from exit gas.

If gas velocity increases at higher ratios, a state called turbulent fluidization can be achieved. It is characterized by sizable crossing of particles through bubbles. If U is increased, fast fluidization can be reached, where bubbles are not distinguishable and bed surface is not easily recognizable. Above fast fluidization, we can find the state pneumatic transport, where the gas velocity overcomes the velocity of the particles.

## ***2.2 TYPES OF GASIFIERS***

### 2.2.1 **FIXED BED GASIFIER**

#### Updraft gasifier

In an updraft gasifier, feedstock is fed in the top and gasification agent, in the bottom. The gasification agent is preheated and enters in the chamber through a grid, which can have different shapes. During gas ascent, it meets with fuel and ash, and different reactions take place.

In the bottom of the fed, air or steam meets hot ash and unconverted char, and combustion and partial combustion reactions occur. These reactions are exothermic, so heat is released and heats the upward gas and the descending solids. This zone is known as combustion zone. These reactions are very fast and consume most of the oxygen available. Products of this process are CO, $CO_2$ and an increase in air/steam temperature.

The mixed composed by CO, $CO_2$ and steam enter into the gasification area. Here, the following reactions take place:

$$\boldsymbol{C + CO_2 \rightarrow 2CO, \quad \Delta H = +172\frac{KJ}{mol}} \tag{2. 1}$$

$$\boldsymbol{C + H_2O \rightarrow CO + H_2, \quad \Delta H = 131KJ/mol} \tag{2. 2}$$

Due to the lack of oxygen, there are no more combustion reactions, and char reacts with $CO_2$, steam and hydrogen. This group of reactions is endothermic, and the heat required is taken from the heat released from the exothermic reactions, producing a temperature decrease.

After gasification zone, pyrolysis zone can be found. Here, the dried fuel is decomposed in ash, volatile compounds and char.

In the zone above, the gas dries the fuel, and the producer gas composed of CO, $CO_2$, $H_2$, $CH_4$ and $H_2O$ releases the chamber, as well as big amount of tar. (17)

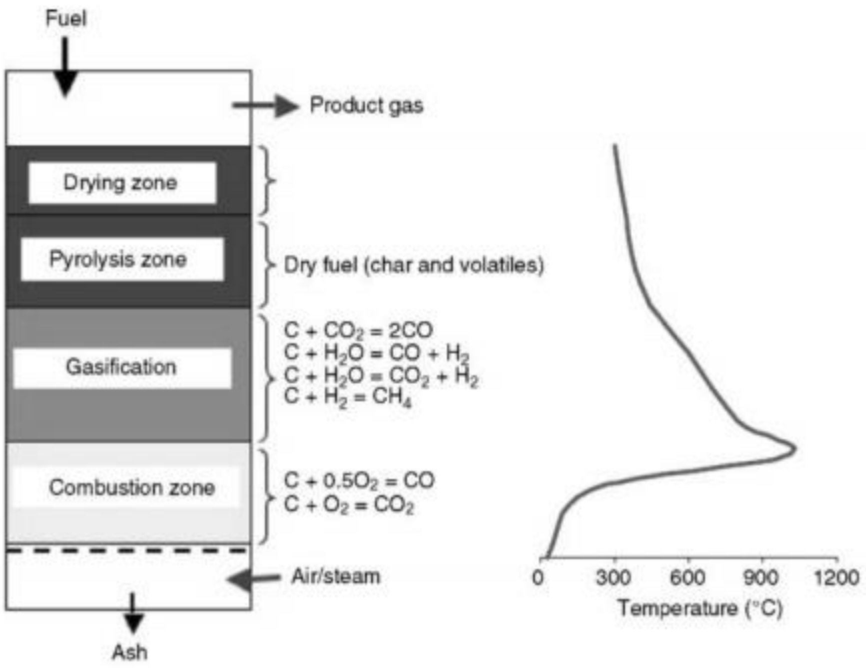


Figure 2.3 Stages of gasification in an updraft gasifier

**Downdraft gasifier**

In this type of fixed bed gasifier, both fuel and gasification agent, move in the same direction. Air or steam is fed in the middle of the chamber, and fuel is added in the top. Drying and pyrolysis zones are placed on top of the reactor, as the same way as updraft gasifiers. The differences between them are reduction and combustion zones. In downdraft gasifier, after pyrolysis process, the carbon in fuel is reacted with oxygen, taking placed the reactions commented above. On the bottom, the absence of oxygen makes possible reduction reactions. Char and ash are removed through a grid. (17)

Downdraft gasifier produces much less tar than updraft.

There are several factors affecting the suitability of fixed bed gasification:

Physical shape and size

Bulk density

Moisture content

Volatile matter content

Ash content

Ash composition

Heating value

For fixed bed reactors, moisture should be less than 30%. Higher moisture content produces high tar in the producer gas. Fuels having lower volatile matter content are better for gasification, particularly for engine applications.

Fixed bed gasifiers are suitable for small capacities, normally less than $100KW_{th}$ and a few higher than $10MW_{th}$.

Ash content in biomass is a problem that has to be accounted. Ash is composed by oxides of mineral matter, mainly CaO and $K_2O$. These oxides have low melting point, and tend to form agglomerates inside the gasifier. Therefore, is necessary removal and cleaning of the gasifier frequently.

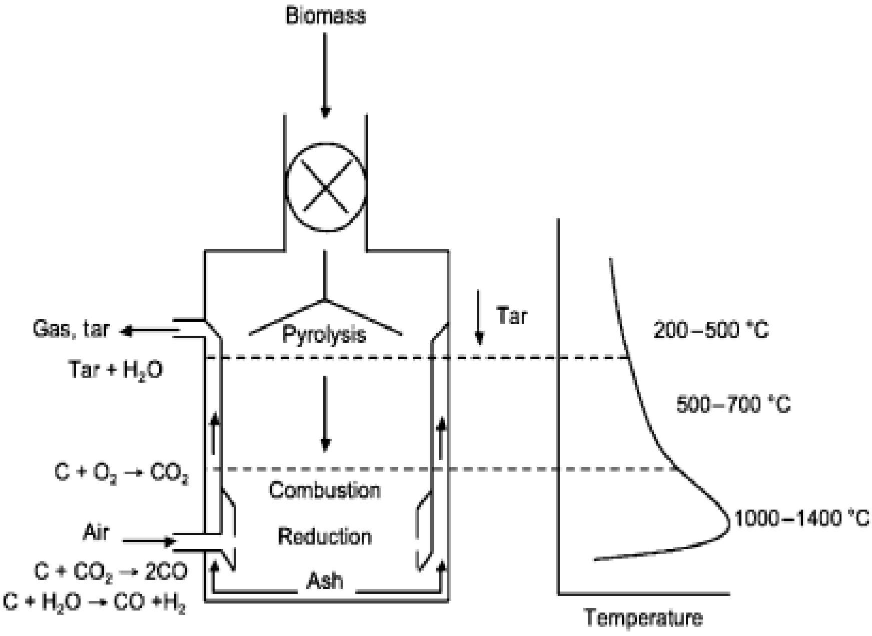


Figure 2.4 Gasification process in a downdraft gasifier.

## 2.2.2 FLUIDIZED GASIFIER

Fluidized bed reactors let more fuel flexibility, have higher conversion efficiency and produce less tar in producer gas (the last feature is referred only for updraft gasifiers, because fluidized bed gasifiers produce more tar compared to downdraft gasifiers). They are especially suitable for large scale capacities. They can be used for either coal or biomass gasification. The principal feature of these reactors is that the different zones concerning gasification (drying, pyrolysis, reduction and combustion) occur simultaneously.

Unlike fixed bed reactors, where flow can be considered as pug-flow, in fluidized beds, the flow is more homogeneous, reaching almost the perfect-mixed state.

We can distinguish two types of fluidized beds: bubbling and circulating beds.

### Bubbling bed gasifier

Fuel, as well as gasification agent, is feed on the bottom of the bed. Air and/or steam are introduced through a distributor, which usually is built with porous or perforated plates. This distributor produces bubbles, which increase their size during the ascent, and burst in the top of the bed. Most of the particles contained in the bubbles return to the bed, but some of them don´t, and need to be recover through a cyclone, which separate the solid particles and the producer gas.

Bubbling beds cannot achieve complete carbon conversion due to back-mixing of solids.

### Circulating bed gasifier

They are modified bubbling beds. They operate with higher velocities, and they solve partially the problem of back-mixing solid. Therefore, carbon conversion in circulating beds is higher compared to bubbling beds. Their main advantages are higher processing capacity, better gas-solid mixing capability, capability for consumption of a wide range of feedstock with low heating value and better sulfur removal. (14)

There are several problems in these gasifiers with corrosion and fouling, especially if the waste fuels contain amounts of chlorine and alklali metals or aluminium. These problems can be solved by reducing the temperature and increasing the pressure, although the carbon conversion also decreases. (33)

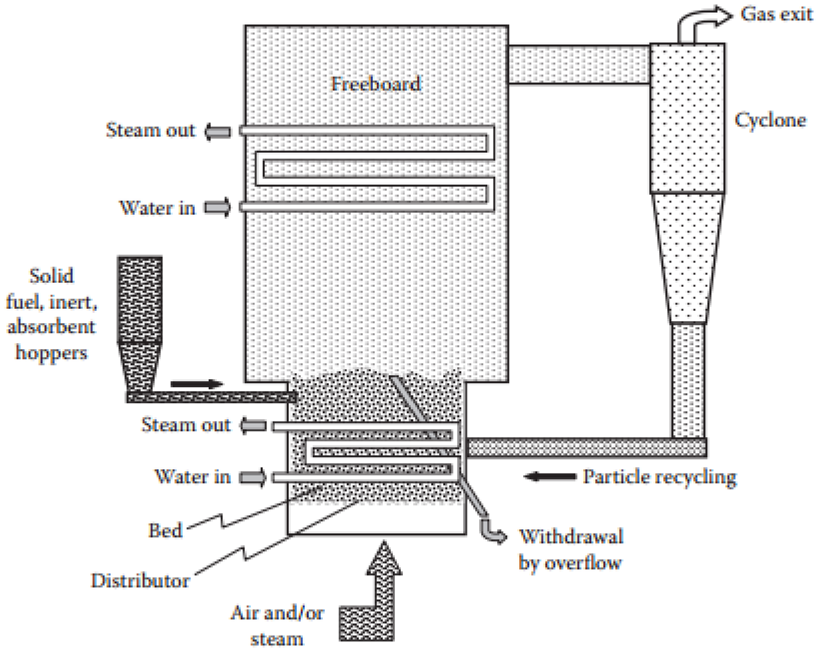


Figure 2.5 A basic scheme of fluidized-bed equipment

### 2.2.3 ENTRAINED FLOW GASIFIER

In entrained-flow gasifiers, feedstock as well as gasification agent are feed by means of a burner. High velocities allow establish a pneumatic transport regime. This kind of reactors works at higher temperatures than bubbling and circulating beds (1200-1500°C). Therefore, chemical equilibrium compositions are almost reached. This allows thermal conversion of tar and also of methane. Their main disadvantages are that biomass or coal has to be pretreated, in order to reduce the particle size. Moreover, higher temperatures produce molten ash (slag) that can block the bed or fouling the heat exchange equipment, so the bed needs to be cleaned frequently. (34)

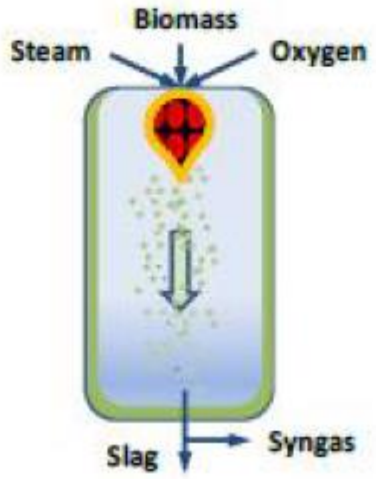
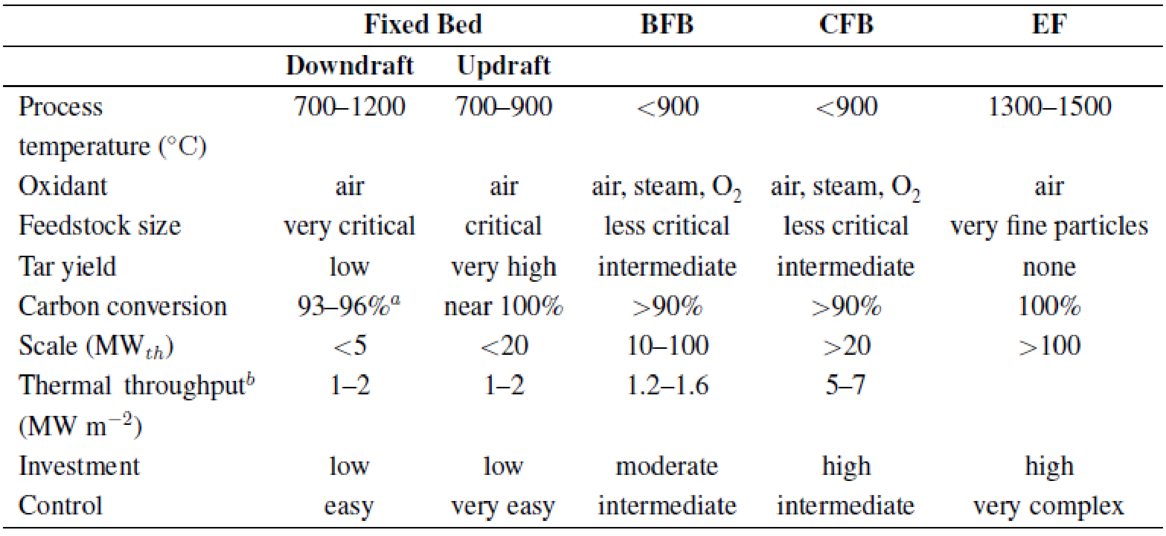


Figure 2.6 A scheme of entrained-flow gasifier

Table 2.1Main characteristics of the five established gasification reactor types



| | Fixed Bed | | BFB | CFB | EF |
|---|---|---|---|---|---|
| | Downdraft | Updraft | | | |
| Process temperature (°C) | 700–1200 | 700–900 | <900 | <900 | 1300–1500 |
| Oxidant | air | air | air, steam, $O_2$ | air, steam, $O_2$ | air |
| Feedstock size | very critical | critical | less critical | less critical | very fine particles |
| Tar yield | low | very high | intermediate | intermediate | none |
| Carbon conversion | 93–96%[a] | near 100% | >90% | >90% | 100% |
| Scale ($MW_{th}$) | <5 | <20 | 10–100 | >20 | >100 |
| Thermal throughput[b] ($MW\ m^{-2}$) | 1–2 | 1–2 | 1.2–1.6 | 5–7 | |
| Investment | low | low | moderate | high | high |
| Control | easy | very easy | intermediate | intermediate | very complex |

### 2.2.4 DUAL FLUIDIZED BED GASIFIER

This technology is based on the idea of having gasification and combustion processes separately. This separation let obtain a nearly free nitrogen gas.

Typical dual fluidized bed system is composed by two units. The main one is a bubbling fluidized bed gasifier working at bubbling/transport state. These condoneis a pneumatic riser combustor.

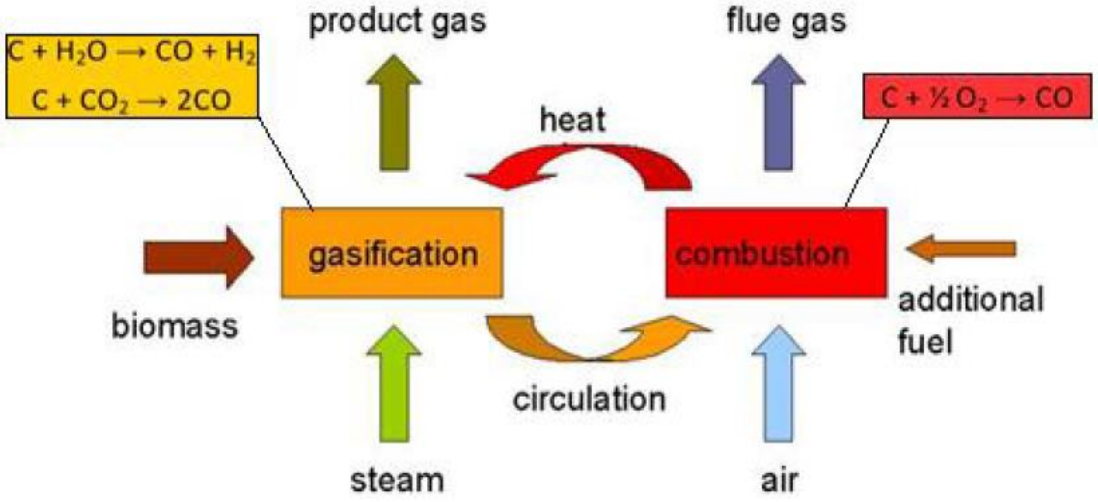


Figure 2.7 The basic idea of dual fluidized bed technology

Feedstock is introduced in the gasifier together with steam, which is used as a gasification and fluidization agent. Gasification process takes place inside. Producer gas rise along the freeboard the freeboard and finally, in a cyclone, syngas is separated from solid particles, that return to the bed.

On the other hand, non-converted char as well as inert particles are sent into the combustor chamber, where they are burnt by means of oxygen supply. Typical temperature in the combustion chamber is around 900°C. Transport regime makes all the products (gas and solids) move up, and through a cyclone, fuel gas is separated from solid particles, which are deposited on the top of the gasifier. High temperature inert particles let endothermic reactions of gasification occur.

Although gasification temperature is lower than combustion one (around 850°C), is enough to supply heat required for this process.

There is a seal loop that connects combustor and gasification chamber. Its mission is avoids the mixing between product gas (from gasification) and flue gas (from combustion).

The main advantage of dual fluidized bed gasifier, as it has already said, is that it produces high caloric product gas free of nitrogen. (14)

There are several commercial dual fluidized bed gasifier. Some of them are: the FICFB, developed by Vienna University of Technology; Silva Gas, built by Batelle (USA) and the MILENA, from ECN. These technologies are described below.

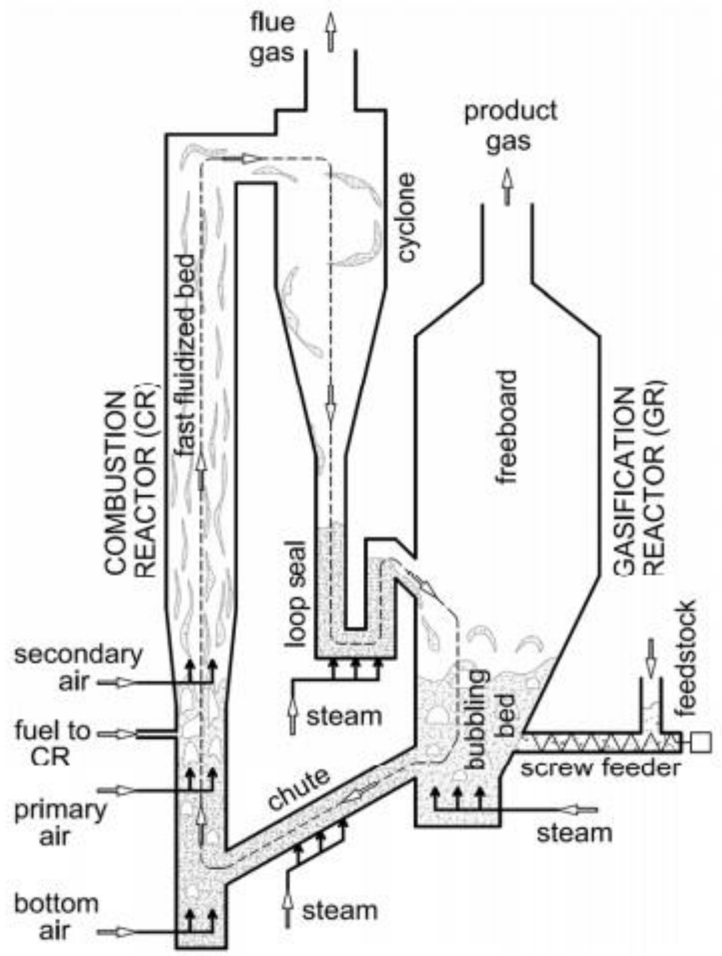


Figure 2. 8 Dual-fluidized bedgasifier

### MILENA (Energy Research Centre of Netherlands)

Milena is a compact design fluidized bed gasifier. The system is composed by two reactors for pyrolysis/gasification and combustion respectively. Its main feature is that both reactors are integrated in a single unit.

Producer gas after cleaning can be used to generate power with gas engines, gas turbines or fuel cells. It is also suitable for replace natural gas.

The gasification section is composed by a gasifier riser, settling chamber and downcomer. The biomass is heated by the hot bed material (typically 925°C sand, or olivine of 0.2-0.3 mm) and by means of steam, or air if nitrogen dilution of the producer gas is not a problem, it is convert to producer gas, and, it is move along the riser. When it reaches the settling, the velocity reduction causes separation between solid materials (bed material and char) and gas. Producer gas is sent to the cooling and gas cleaning section and solid materials move into the combustion chamber through the downcomers. Tar and dust are also transported to the combustor. Air heats the bed material to approximately 925°C. Secondary air is added in the freeboard in order to reduce CO and $C_xH_y$ emissions. The heated bed material is introduced to the gasification chamber through a hole on the bottom of the riser.

The main benefits of MILENA technology are:

Complete conversion, no carbon-containing ash

High efficiency

Essentially N2-free producer gas, LHV~ 15MJ/nm3 (dry basis)

No air separation unit (ASU) necessary

Compact design

Fuel flexible (tested with wood, demolition wood, lignite, grass, digestion residue…)

800 kWth MILENA pilot plant was installed in 2008. MILENA technology has combined with OLGA cleaning to remove dust and tars. A 10 MW plant is planned for the future. (19)

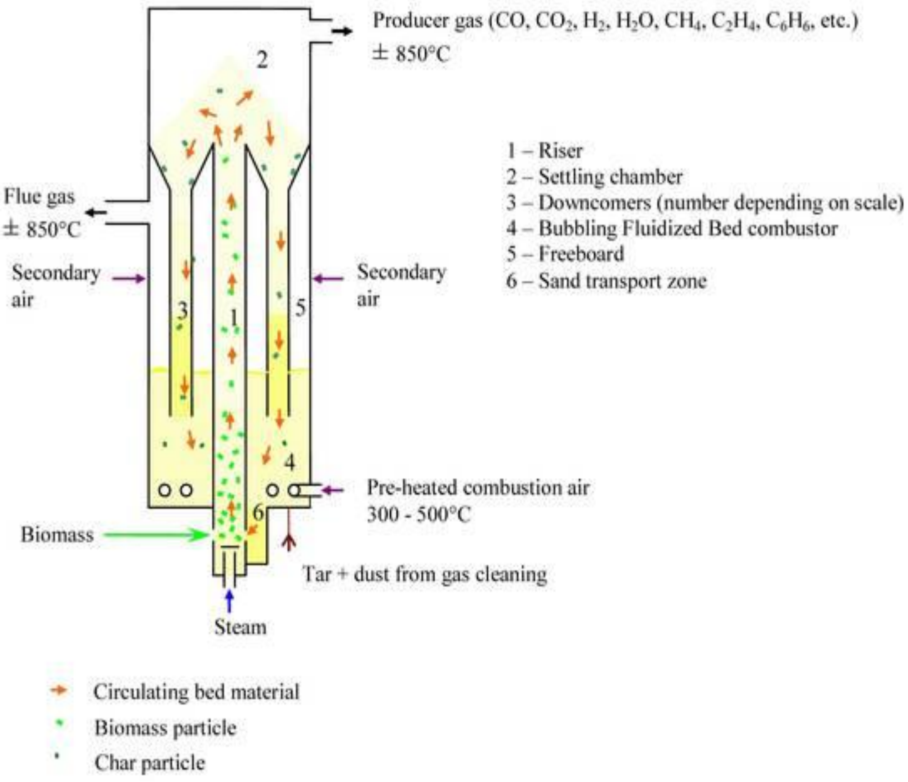


Figure 2. 9 MILENA gasifier

### Silva Gas GASIFIER

The Silva Gas technology was developed by Battelle´s Columbus Laboratories. The process uses two fluidized bed reactor. Circulating sand is used as a heat medium to heat the incoming biomass and carries the unreacted char to the combustor reactor.

This gasifier can produce syngas from a wide range of biomass feedstock and moisture content (from 10% up to 50%). This process provides a medium heating value gas (11-14 MJ/Nm3).

Producer gas in Silva Gas process can be used for:

Direct use as a fuel gas that can be interchanged with natural gas or distillate oil.

Co-fired with biomass or fossil fuels for heating or power applications

Use as a fuel for power generation cycles including turbines or fuel cells.

Use as a feed gas for synthesis applications such as production of Fisher Tropsch liquids, alcohols and hydrogen.

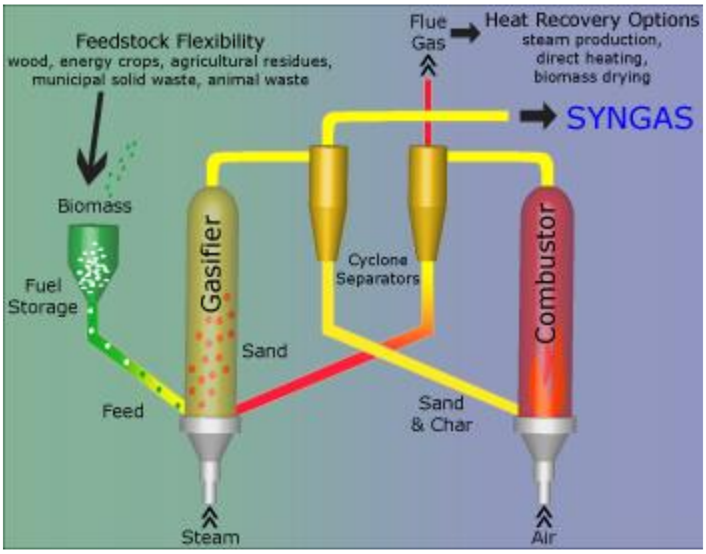


Figure 2.10SilvaGasgasifier

This technology has been tested on a commercial scale. A gasifier has been built in Burlington, state of Vermont (USA) by the company Rentech, in partnership with the DOE (Department of Energy, USA), NREL (National Renewable Energy Laboratory and Battelle Columbus Laboratory. This gasifier converts 400 dry tons per day of wood-based biomass into synthesis gas used for power production. (35)

### FICFB  (Fast Internally Circulating Fluidized Bed)

This technology was developed by Vienna University of Technology. Its main target is obtaining a high calorific value gas (up to 15MJ/Nm3) and almost free of nitrogen. Producer gas can be used for many applications, such as synthetic natural gas, for power generation, production of liquid fuels by Fischer Tropsch synthesis…

As all dual fluidized beds, it consists of a gasification reactor, fluidized by steam, and a combustor one, using air as oxidizer.

This technology has many advantages compared with air blown gasifiers, like very low tar content, independence of water content in biomass feed on gas quality, possibility of using a wide range of feedstock, possibility to use a catalyst as bed material in order to enhance gas composition or carbon conversion, etc.

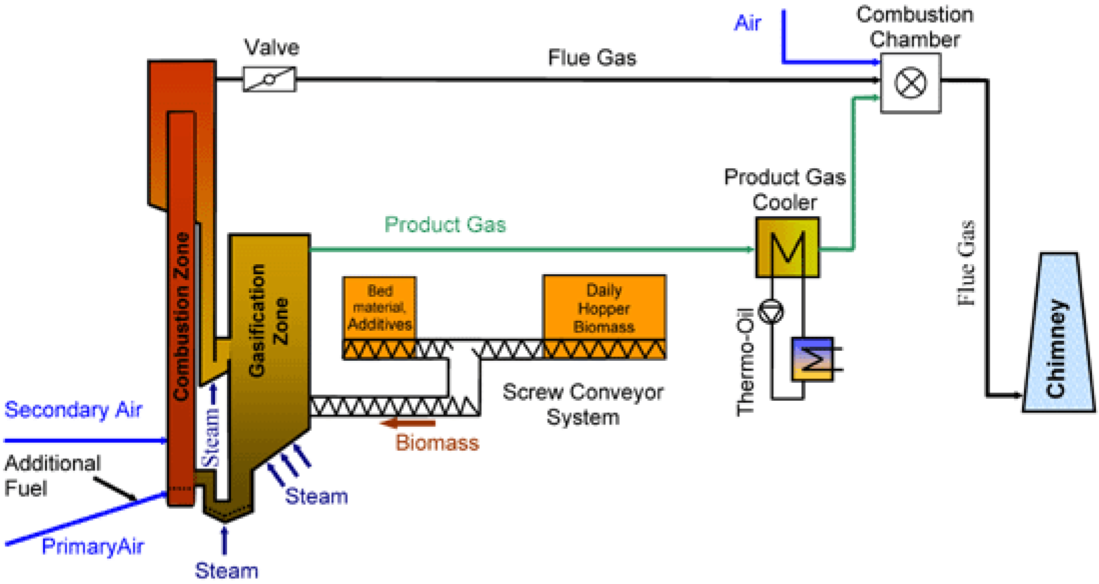


Figure 2.11 Scheme of the FICFB technology

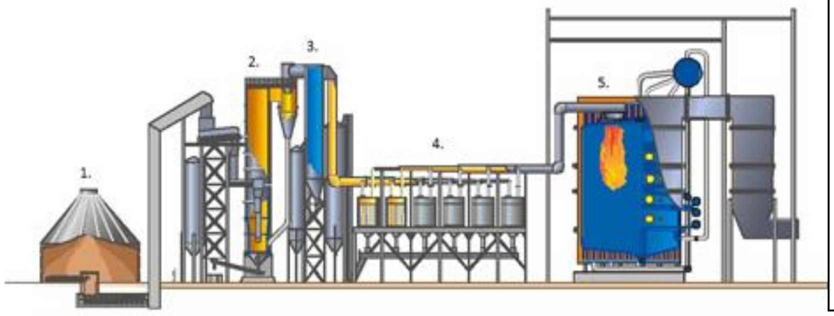
Several pilot plants have been developed. The first one began in 1997. It was a 100KWth experiment. The target was the study the optimal operation conditions for different fuels and bed materials.

The second one, a 500KWth gasification plant, was tested using catalyst bed material in order to increase hydrogen content and reduce tar content of the producer gas.

These pilot plants have been used to develop a commercial biomass CHP-plant in Güssing (Austria). It is an 8MW CHP plant that combines heat and power. (36)

# 2.3 GASIFICATION PLANTS

## 2.3.1 LAHTI ENERGIA OY



1-Feedstock warehouse

2-CFB gasifier

3-Gas cooler

4-Ceramic filters

5-Boiler

Figure 2.12 Lahti Energy plant

Lahti Energia Oy´s plant, placed in Lahti, in the south of Finland, produces 50MW of electricity and 90MW of district heat.

It process 250000 tons per year of recovered fuel. The plant can convert a wide range of waste, from food packaging, oil and juice cans, wrapping plastics to paper and cardboard packaging and paper towels.

First step includes the storage of the feedstock. After that, fuel is transport through a belt conveyor to a circulating fluidized bed gasifier (CFB) where gasification process takes place at 850-900°C. The bed material as well as the unreacted fuel is returned to the gasifier by the recycling cyclone.

Produced gas coming from the gasifier is cooled in a gas cooler (heat recovery) at 400-450°C.

The next step of the process is main one. Gas is cleaned by ceramic filters at 400-450°C. In the filtration, ash and heavy metals, and almost all of the chlorine are removed from the gas.

Ash, unburnt carbon, condensed metals and solidified chlorides form a dust cake on the surface of the filter elements. The filter elements are cleaned by frequent on-line reverse nitrogen pulses.

Cleaned gas is burnt in a boiler, producing steam, which is used for production of electricity and district heat.

The 250000 tons per year´s processing enable to replace 170000 tons of coal. (37)

### 2.2.2 GOBIGAS PROJECT (GÖTEBORG ENERGI AND E.ON)

Figure 2.13 General view of GoBiGas plant

GoBiGas is a project from Göteborg Energiand E.On companies that pretends to produce biomethane (bio-SNG) by thermal gasification of forest residues as branches, roots and tops.

Firstly, biomass is converted to a flammable gas in the gasification plant. Then, it is purified and upgraded in a methanation plant to biomass with similar properties compared with natural gas. This enables to use natural gas network.

The aim of this project is the production of 1TWh of biomethane for the city of Gothenburg and 15TWh for Sweden in 2020. It also has two performance goals: a 65-70% of the biomass into gas and a 90% of energy efficiency. (38)

The basic principles of the project are schematized in the following figure:

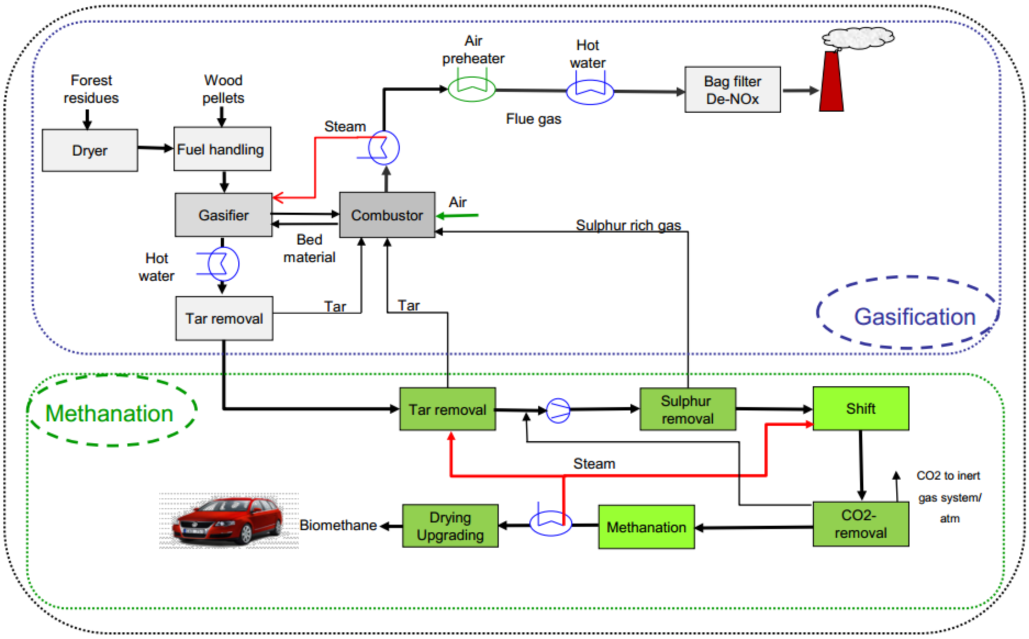


Figure 2.14 Technical principles of GoBiGas Project

### 2.2.3 JOUTSENO'S PLANT

The company Andritz has launched a project which consists of gasification of wood fuels, such as bark, forest residue, stumps or wood chips. The plant is located in Joutseno, in the southern Finland. The plant started up in summer 2012 and uses a lime kiln gasifier. The chosen reactor is a circulating fluidized bedgasifier.

The main target of the project are replacing 100% of natural gas at lime kiln with gasification gas, using side products from mill, utilizing was heat available from mill for biomass drying.

Some capacity numbers of the plant are:

Heat flow to lime kiln: 48MW

Dryer evaporation capacity: 12t/h

Fuel handling: 150 $m^3$/h

Lime kiln gasifiers have some advantages against typical gasifiers:

Fuel flexibility. Fuels with high ash content can be used

Fuel heating value depends on degree of drying

$CO_2$ benefits and short pay-back time for the investment.

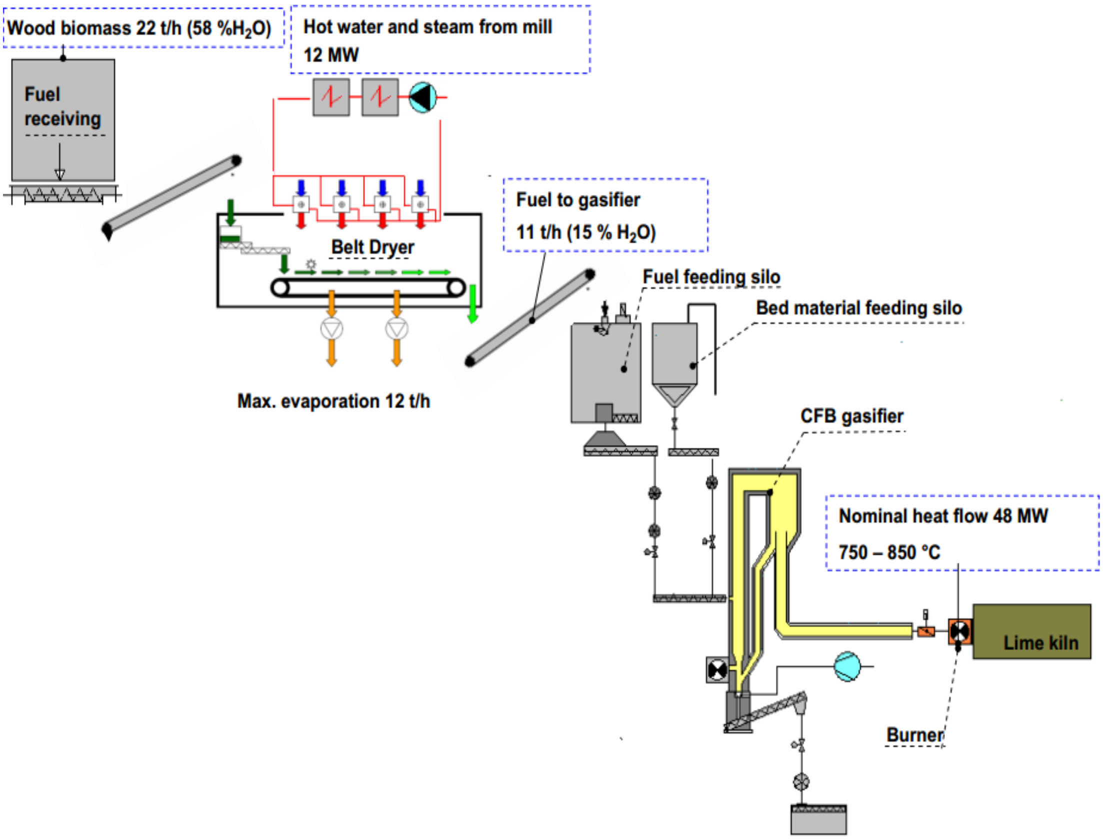


Figure 2.15 Joutseno gasification plant process

# 3. GASIFICATION PROCESS

Although the main stage of the process takes places inside the gasifier, this technology involves other steps that need to be account. The first two steps (pre-treatment and gasification)are the same for all the different processes. The last steps differ depending on the application.

For a gasification technology that converts biomass to bio-SNG, these are the main stages: biomass pre-treatment and drying, gasification, gas conditioning, methanation and gas upgrading.

## *3.1 BIOMASS PRETREATMENT AND DRYING*

Biomass feedstock varies greatly in chemical composition and physical appearance. Especially moisture and ash content move within a very wide range.

Energy processes that use biomass as feedstock are sensitive to changes in the feedstock quality. It makes necessary some pre-treatments technologies that homogenizes the fuel in terms of size, moisture content and density. Also the presence of fuel-derived sulphur in the product gas is normally problematic for gasification process and has to be removed.

Drying is the most important pre-treatment operation, and very necessary for high cold gas efficiency at the gasification stage. Drying usually reduces the moisture content from 10 to 15%. It can be either done with flue gas or with steam. Most bioenergy plants use direct rotary dryers, although the use of steam drying techniques is increasing because of easy integration to existing systems and the lack of gaseous emissions. (33)

## *3.2 GASIFICATION*

Once biomass has been pre-treated, it is fed into the gasifier. The process depends on the type of the gasifier, although general process is explained below.

Main reactions that take place inside the gasifier are the following ones: (14)

Steamgasification

$$\boldsymbol{C + H_2O \leftrightarrow CO + H_2, \quad \Delta H = +131.4\ {}^{KJ}\!/_{mol}} \tag{3.1}$$

Boudouard reaction

$$\boldsymbol{C + CO_2 \leftrightarrow 2CO, \quad \Delta H = +172.6\ {}^{KJ}\!/_{mol}} \tag{3. 2}$$

Methanation reaction

$$C + 2H_2 \leftrightarrow CH_4, \quad \Delta H = -74.9 \, {}^{KJ}/_{mol} \tag{3. 3}$$

Steam reforming reaction

$$CH_4 + H_2O \leftrightarrow CO + 3H_2, \quad \Delta H = +206.2 KJ/mol \tag{3. 4}$$

Water gas shift reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta H = -41.2 \, KJ/mol \tag{3. 5}$$

Carbon conversion

$$C + {}^{1}/_{2} \, O_2 \leftrightarrow CO \tag{3. 6}$$

$$C + O_2 \leftrightarrow CO_2 \tag{3. 7}$$

In general, gasification process is divided in three phases, which are devolatilization, reaction involving volatile products and char reaction phases.

In a first stage, called pyrolysis, due to the effect of the high temperature of the gasifier, volatile compounds are rapidly released from the biomass by thermo-chemical decomposition. During this phase, biomass is divided into volatile compounds and a solid called char. Volatile compounds are composed by a gaseous product (mainly) and a liquid. Composition of gaseous product depends on the gasification agent (air, oxygen or steam). The liquid consist on condensable gases that have not reacted with the gasification agent is generated. This liquid fraction is known as tars. Gaseous product as well as tars can be used as fuel, although a post-treatment process is required in the case of tars. Temperature of this step depends on several factors, such as biomass composition, although this process begins between 200 and 250°C.

Remained carbonaceous solid (char) also reacts with gasification agent in order to produce a gaseous product. However, unlike volatile reactions which are gas-gas, this reaction is gas-solid, which are much slower than the previous ones, and therefore, this stage limits the velocity of the gasification process. (39)

## *3.3 GAS CONDITIONING*

The product gas after gasification contains particles and different impurities (organic-tars; inorganic like sulfur compound and HCl; and chain alkanes). The product gas should be cleaned from these impurities in order to avoid damaging of process equipment and poisoning of the methanation catalyst.

Solid particles are separated from the syngas within cyclones and hot gas filters at a temperature above the tar dew point, in order to avoid fouling with condensing tars. Separated particles can be reintroduced into the combustion chamber.

Tars are removed in the tar removal system (for example, wet scrubbing) and can be recycled to the gasifier for decomposition into product gas components. If syngas scrubbing is realized via water based system whereby gas /water contact removes fine particles and tars; also it can provide a medium for the neutralization and absorption of incidental products of gasification such as HCl and ammonia. (40)

Importantly, the gas scrubbing system needs to reduce the syngas temperature below the dew point of the lightest tar fractions. The use of water-based system creates a large water demand, significant water treatment and problems with waste water.

Alkali and alkaline earth metals, especially potassium, are prevalent in many biomass feedstocks. Alkali metals vaporize at the high temperature in the gasifier. When the temperature decreases (to around 600°C) the alkali metal condenses. The alkali deposits on the metals cause the surface corrosion and can cause the erosion of turbine blades. Alkali can be removed either by adsorption or by leaching (so-called "Alkaline washing").

Gas conditioning for bio-SNG production should involve first of all the removal carbon dioxide ($CO_2$) and hydrogen sulfide ($H_2S$) from product gas. A large number of different processes have been and are used for acid gas removal, but they all are based on one of the following principles:

Absorption (physical or chemical) in a liquid solvent with subsequent desorption step;

Adsorption (again physical or chemical) onto a mass of a solid particles;

Diffusion through a permeable or semipermeable membrane;

Chemical conversion, generally on a catalyst, often as a preparatory step to one of the above three methods.

To remove sulfur from produced gas through adsorption, zinc oxide (ZnO) catalyst at 350 °C is used. An alternative to zinc oxide catalyst are wet gas scrubbing processes. One of such system is Rectisol®, developed by Linde and Lurgi, which allows capturing both sulfur and carbon dioxide; to separate these acid gases from producer gas Rectisol® process uses methanol as a solvent at subzero temperatures. But in most cases these systems are very expensive and suitable only for large-scale plants. The most inexpensive way for small-scale units is use water as a solvent.

Gas cleaning system causes energy loss from the system. The gas leaving the gasifier has a very high temperature (around 800 °C) and will carry therefore significant amount of sensible heat; this should be recovered efficiently (before gas cleaning system) for the generation of steam for use in the process and for power generation to meet plant electricity demand. Consequently, after gasifier the heat exchanger is set. We should be careful when cooling syngas before cleaning system because at definite temperature tars begin condense.

## *3.4 <u>METHANATION</u>*

After gas conditioning, gas mixture is fed in a reactor in order to produce methane. This mixture is composed by hydrogen, carbon monoxide, carbon dioxide and methane. Process is mainly based in the reaction that converts CO and $H_2$ into methane, using steam. Also $CO_2$, and other gas components, such as ethylene and BTX (bencene, toluene and xylenes) can be converted into methane.

Typically sulfur-sensitive nickel-alumina catalysts are the most spread, although iron, chromium and copper base catalysts can also be used. The reactor is pressurized in a range from 5 to 60 bar, and a moderate temperature (< 400°C).

The main reactions during the methanation process are:

- Reverse reforming reactions

$$\boldsymbol{CO + 3H_2 \leftrightarrow CH_4 + H_2O, \quad \Delta H = -218\ {}^{MJ}/_{kmol}} \tag{3. 8}$$

$$\boldsymbol{CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O, \quad \Delta H = -180\ {}^{MJ}/_{kmol}} \tag{3. 9}$$

- Water-gas shift reaction (eq. 3.5)

- Steam reforming reaction

$$\boldsymbol{C_2H_4 + 2H_2O \leftrightarrow 2CO + 4H_2, \quad \Delta H = +210\ {}^{MJ}/_{kmol}} \tag{3. 10}$$

As the above previous reactions show, $H_2$, CO, and $C_2H_4$ contained in the syngas react to produce methane and $CO_2$.

Due to the exothermicity of the process, the released heat is used to dry biomass or to generate steam for the reactor. It is important to maintain a suitable temperature, because high temperatures leads to low conversion but lower temperatures may increase the risk of carbon formation, leading to catalyst deactivation. (41)

The mixture exiting the methanation reactor is cooled down to around 30°C. This temperature allows for condensed water to be separated from the gases. If the process is operated at high pressures, this water will still contain dissolved methane; this can be extracted, and then either burnt in the gasifier combustion chamber, or be pressurized and recycled in the methanation process.

## 3.5 GAS UPGRADING

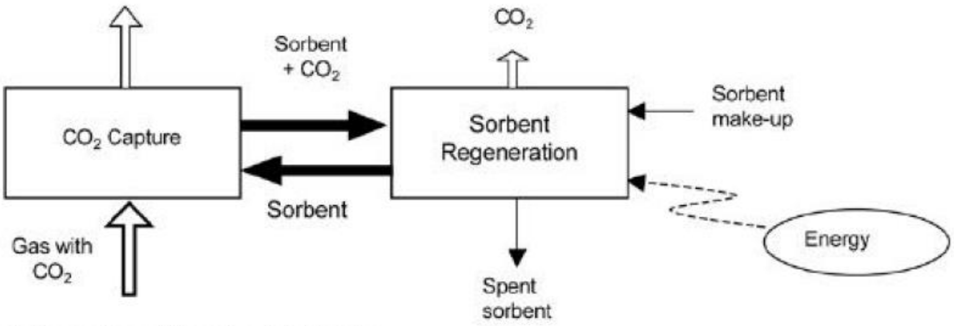
Methanation process inside the reactor takes place under high pressure. This pressure has to be adapted to the pressure in the natural gas grid. Also concentration has to be adjusted to the values of natural gas. This means that concentration of methane has to reach at least 95% (42). The gas mixture obtained after the methanation stage is mainly composed of $CO_2$ (45.9% vol.) and $CH_4$ (47.6% vol.). Especific composition of exiting bio-SNG depends on the composition requirementsof natural grid, and it differs from one country to another. In particular, composition of the natural gas in the Finland natural gas network is shown in table 3.1. (42).

Table 3.1 Composition of the natural gas in Finland gas network.

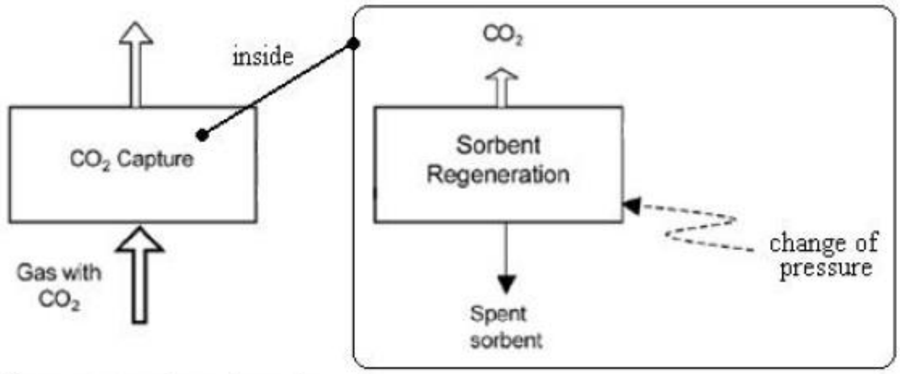
| Component | Natural gas from Siberia |
|---|---|
| Methane ($CH_4$) | 98.1% |
| Carbondioxide ($CO_2$) | 0.04% |

| | |
|---|---|
| Nitrogen ($N_2$) | 0.8% |
| Oxygen ($O_2$) | 0.01% |
| Moisture ($H_2O$) | - |
| Heavier hydro carbons | <1% |
| Calorific value | 36 $MJ/m^3$ |

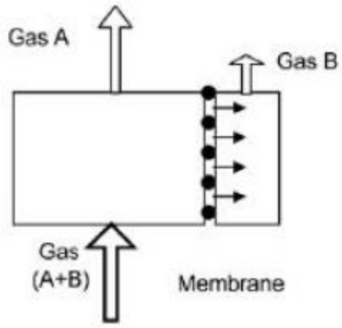
During the gas upgrading process, carbon dioxide and water are removed from the gas as much as possible without a significant loss of methane. Several technologies are commercially available for $CO_2$ separation in a methanation plant, such as physical absorption in a solvent, pressure swing adsorption, or removal using dedicated membranes. In figure 3.1.the general schemes of the main separation processes relevant for $CO_2$ capture are shown (43).



a) Separation with sorbents/solvents



b) Pressure swing adsorption



c) Separation with a membrane

Figure 3.1 General schemes of the main separation processes relevant for CO2 capture

*Separation with sorbents/solvents*

The separation is achieved by passing the $CO_2$-containing gas intimate contact with a liquid absorbent or solid sorbent that is capable of capturing the $CO_2$. The sorbent loaded with the captured $CO_2$ is transported to a different vessel, where it releases the $CO_2$ (regeneration). The sorbent resulting after the regeneration step is sent back to capture more $CO_2$ in a cyclic process. In the case that the sorbent is a solid, there is no circulation between vessels, and the sorption and regeneration are achieved by cyclic change in pressure (Pressure Swing Adsorption) or in temperature (Temperature Swing Adsorption). A make-up flow of fresh sorbent is always required to compensate for the natural decay of activity and/or sorbent losses.

*Pressure Swing Adsorption*

Pressure Swing Adsorption (PSA) is the system of choice for the purification of syngas, where high purity $H_2$ is required. This cyclic process is based on two steps: in a first stage, adsorption takes place, where the more adsorbable species are selectively removed from the feed gas. During regeneration, in this case called desorption, these species are removed from the adsorbent so that it can be ready for the next cycle. The principal disadvantage of PSA technology is that it does not separate selectively $CO_2$ from other waste gases.

*Separation with a membrane*

Membranes are specially manufactured materials that allow the selective permeation of a gas through them. The selectivity of the membrane to different gases is intimately related to the nature of the material, but the flow of gas through the membrane is usually driven by the pressure difference across the membrane. Therefore, high pressure streams are usually preferred for membrane separation. There are several types of membranes materials (polymeric, metallic, ceramic) that may find application in $CO_2$ capture systems.

# 4. BIOMASS TYPE SELECTED

Gasification process, as well as syngas composition has a great dependence on the composition of biomass. Therefore, it is necessary to set a specific type of biomass to compare the results of the model simulations.

Biomass chosen is Finnish wood. Finnish forests are composed mainly by scots pines and spruces. Figure 4.1 shows a basic scheme of both trees, which belong to the group of coniferous. (44)

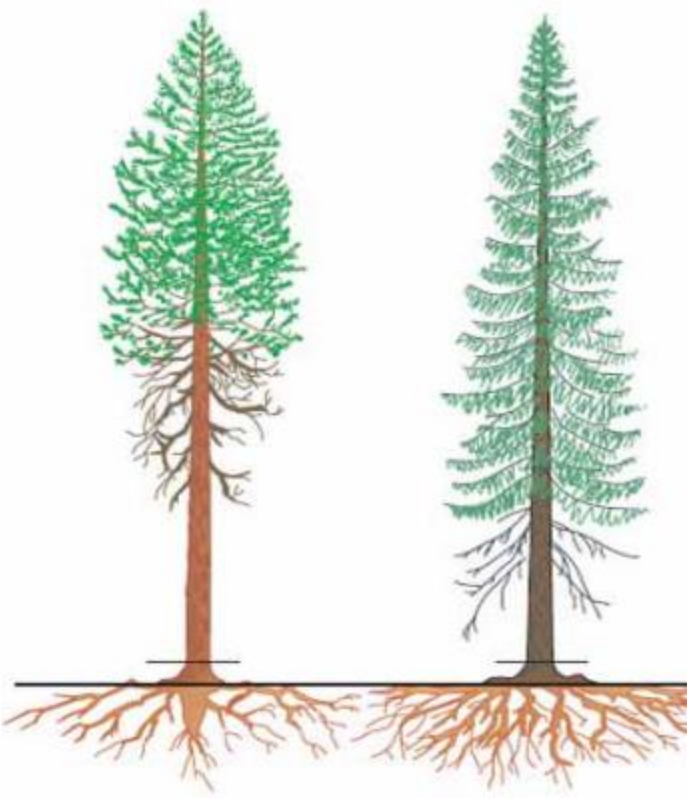


Figure 4.1 Schemes for scots pines (left) and spruces (right).

Raw material for gasification in Finland is mainly taken from logging residues and stump harvesting.

The fuel properties and chemical analyses have been taken from BIODAT (45). ID number is 152. It belongs to the category of solid biofuels and the subcategories of woody, used wood and chemical untreated wood. These properties are shown in table 4.1.

Table 4.1 Fuel properties

| WOOD BIOMASS-SAMPLE ID 152 | | |
|---|---|---|
| PROPERTY | UNIT | VALUE |
| Proximate analysis | | |
| Moisture content | Wt% a.r. | 16.70 |
| Ash content (A) at 550°C | Wt% (dry) | 2.60 |
| Fixed carbon | Wt% (dry) | 18.30 |
| Volatile matter | Wt% (dry) | 79.10 |
| Ultimate analysis | | |
| Carbon | Wt% (dry) | 49.60 |
| Hydrogen | Wt% (dry) | 5.80 |
| Oxygen | Wt% (dry) | 41.16 |
| Nitrogen | Wt% (dry) | 0.8 |
| Sulfur | Wt% (dry) | 0.04 |
| Calorific values | | |
| Lower Heating Value (LHV), dry | MJ/Kg | 18.56 |
| Higher Heating Value (HHV), dry | MJ/Kg | 19.82 |

Ultimate analysis of Wood biomass is shown in Table 4.1. To make a formula for fuel feedstock we should consider molar basis. We can determinate the chemical amount of a component, in moles, by dividing the sample's mass (mass fraction,$m_i$) by the substance's molecular weight ($M_i$).

$$\boldsymbol{n_i = \frac{m_i}{M_i}, [mol]} \tag{4. 1}$$

Where i is a component of the fuel.

To calculate mass fraction for $n_c$=1:

$$\boldsymbol{C: 3.694 \rightarrow 1} \tag{4. 2}$$

$$\boldsymbol{H: 2.525 \to x} \tag{4. 3}$$

$$\boldsymbol{x = \frac{1 \cdot 2.525}{3.634}}, \qquad \boldsymbol{x = 0.695} \tag{4. 4}$$

By this way, amount of moles for each component in the feedstock can be found. For using these values in a global gasification formula, they should be multiplied by 2 because x is associated with atom if hydrogen H, oxygen O and nitrogen N, but in feedstock the molecules of hydrogen $H_2$, oxygen $O_2$ and nitrogen $N_2$ are present.

The resulting formula for wood biomass will be the following: $CH_{1.389}O_{0.623N0.014}$.

# 5. MATHEMATICAL MODELS

## 5.1 INTRODUCTION

Understanding the behavior of the system is key to produce different products depending on the needs. Understanding the process implies obtaining information of each variable involving the system. This is the function of the methods. They can be divided into experimental method and theoretical method. A combination of both methods is the perfect solution for predicting the behavior.

The **experimental method** is based on two different groups of variables:

Controlled variables are those whose values can, within a certain range, be imposed freely. An example is the temperature of bath heated by electrical resistance.

Observed variables are those whose values can be measured, directly or indirectly. An example is the thermal conductivity of the fluid in the bath where the temperature has been controlled.

This method consist on the performance of tests, in which all the variables are maintained constant excepting controlled variables. Effects of variation of controlled variables on observed variables are analyzed.

The main advantage of this method is the reliability, because it is based on own experience. However, it is only useful when the number of variables is not high and the relation between them is not complex.

The **theoretical model** is based on fundamental equations (mass, momentum and energy conservations) and correlations obtained from well-conducted experimental procedures. It does not represents the reality in such an accurate way as experimental model, but it presents some advantages that makes it more suitable for complex processes.

The most important properties of the model are:

Lower economical requirements compared to experimental investigation

Wider range of study, including conditions that are difficult or impossible to access.

It allows a better understanding of the experimental data, and therefore, of the processes.

It can be very useful to optimize the experimental procedure.

It can be used for scaling-up phase in order to achieve an optimized design of the equipment or process unit.

It can be improved leading to a closer behavior to the reality.

Theoretical (or mathematical) models can reproduce the processes in a very accurate way depending on the complexity of the model. However, complex models require much more calculation and in some easy processes, simple models can predict reality with less effort.

Mathematical models can be classified according several criteria. The first branching corresponds to the number of space dimensions considered in the model. It divided the models in three possible levels. After that, some other criteria can be considered, such as time, steady-state or dynamic state, laminar or turbulent conditions, etc. Most industrial equipments work at or near steady-state conditions. Therefore, steady-state models are more widely used.

**Zero-dimensional models**: they set relation between input and output variables of a control volume without considering the process that take place inside that volume. Therefore, there is not description of the velocity, temperatures or concentration profiles. They are very useful when a global study of the equipment is required. They are based on the assumption of chemical and thermodynamic equilibrium.

**One-dimensional models:** dimensional models consider variation of all properties inside the gasifier in one, two or three space coordinates. They do not assume thermodynamic or chemical equilibrium. These models require introduction of chemical kinetic and transport phenomena. They are very suitable when the purpose is the design of the reactor. One-dimensional models assume that all properties inside the gasifier vary only at one space coordinate. They are useful when a more accurate study of the gasifier is required, and properties do not change in the radial direction.

**Two-dimensional models:** they are used when variations in a second dimension can no longer be neglected. These models are helpful, for instance, in a velocity study of a laminar and pug-flow reactor, where although the axial profile is the same for both, radial distribution differs.

**Three-dimensional models:** they require great mathematical and computational complexity but they lead to a more realistic representation. They are suitable when complex processes take place inside the reactor, and properties vary in the three space coordinates. (15)

The present project does not aim to a detailed study of the process taking place inside the reactor, but it pretends to analyze the composition at the gasifier outlet, and how it varies when operation parameters, such as temperature or fuel/gasification agent ratio are changed.

Therefore, the best choice for this case is a Zero-dimensional model. As it has already said, these models assume chemical and thermodynamic equilibrium, so they are applicable for gasification process, because the set of reactions are very fast and equilibrium is almost achieved.

Two thermodynamic models will be developed for this project: the first one, called "Stoichiometric model" is a purely theoretical model based only in mass balance and reaction constant. The second one ("Pseudo-experimental model") is also based on mass balance but it includes a correlation obtained from experimental results and it pretends to approach a little bit more to real results.

## 5.2 STOCHIOMETRIC MODEL

Thermodynamic models can be classified into stoichiometric and non-stoichiometric approach. A stoichiometric approach requires a clearly defined reaction mechanism incorporating all chemical reactions and species involved. In a non-stoichiometric formulation, on the other hand, no particular reaction mechanism or species are involved in the numerical solution. The only input required to specify is the feed elemental composition, which can be readily obtained from ultimate analysis data. This method is particularly suitable for problems with unclear reaction mechanism. (22)

In our case, reaction mechanism taking place inside the gasifier is known. Therefore, stoichiometric approach is selected for the development of the model.

One problem that thermodynamic models present is that they do not take account tars in the product stream.

First of all, a basis of calculation has to be set. As biomass composition is given in mass, every calculation will be referred to **100 kg/h** of wet biomass (taking account the moisture content).

The first steps to develop the mathematical model are the mass balance, or in this case, atomic balances, that can also be used. Only carbon, oxygen and hydrogen balances are considered because nitrogen content in biomass is supposed as negligible.

Atomic balances take account inputs (biomass, and gasification agents that can be steam, air and/or oxygen) and output, that corresponds to the syngas that is composed of carbon monoxide, carbon dioxide, methane, hydrogen and water.

Atomic balances

Carbon balance:

$$\begin{aligned}\%\boldsymbol{carbon}_{\boldsymbol{biomass}} \cdot \mathbf{100}\left[\frac{\boldsymbol{kg\ biomass}}{\boldsymbol{h}}\right] \cdot \frac{\mathbf{1}}{\mathbf{12}} \cdot \left[\frac{\boldsymbol{kmol}}{\boldsymbol{kg}}\right] \\ = \boldsymbol{X}_{\boldsymbol{CO}_2} \cdot \boldsymbol{m}_{\boldsymbol{totales}}[\boldsymbol{kmol}] + \boldsymbol{X}_{\boldsymbol{CO}} \cdot \boldsymbol{m}_{\boldsymbol{totales}}[\boldsymbol{kmol}] + \\ \boldsymbol{X}_{\boldsymbol{CH}_4} \cdot \boldsymbol{m}_{\boldsymbol{totales}}[\boldsymbol{kmol}] + \boldsymbol{char}[\boldsymbol{kmol}]\end{aligned} \tag{5. 1}$$

Oxygen balance:

$$\begin{aligned}\%\boldsymbol{oxygen}_{\boldsymbol{biomass}} \cdot \mathbf{100}\left[\frac{\boldsymbol{kg\ biomass}}{\boldsymbol{h}}\right] \cdot \frac{\mathbf{1}}{\mathbf{16}} \cdot \left[\frac{\boldsymbol{kmol}}{\boldsymbol{kg}}\right] + \%\boldsymbol{water}_{\boldsymbol{biomass}} \\ \cdot \mathbf{100}\left[\frac{\boldsymbol{kg\ biomass}}{\boldsymbol{h}}\right] \cdot \frac{\mathbf{1}}{\mathbf{18}} \cdot \left[\frac{\boldsymbol{kmol}}{\boldsymbol{kg}}\right] + \boldsymbol{steam}[\boldsymbol{kmol}] + \mathbf{2} \\ \cdot \boldsymbol{air}[\boldsymbol{kmol}] + \mathbf{2} \cdot \boldsymbol{oxygen}[\boldsymbol{kmol}] \\ = \mathbf{2} \cdot \boldsymbol{X}_{\boldsymbol{CO}_2} \cdot \boldsymbol{m}_{\boldsymbol{totales}}[\boldsymbol{kmol}] + \boldsymbol{X}_{\boldsymbol{CO}} \cdot \boldsymbol{m}_{\boldsymbol{totales}}[\boldsymbol{kmol}] \\ + \boldsymbol{X}_{\boldsymbol{H}_2\boldsymbol{O}} \cdot \boldsymbol{m}_{\boldsymbol{totales}}[\boldsymbol{kmol}]\end{aligned} \tag{5. 2}$$

Hydrogen balance

$$\begin{aligned}\boldsymbol{\%hydrogen_{biomass}} \cdot \mathbf{100}\left[\frac{\boldsymbol{kg\ biomass}}{\boldsymbol{h}}\right] \cdot \frac{\mathbf{1}}{\mathbf{16}} \cdot \left[\frac{\boldsymbol{kmol}}{\boldsymbol{kg}}\right] + \mathbf{2} \\ \cdot \boldsymbol{\%water_{biomass}} \cdot \mathbf{100}\left[\frac{\boldsymbol{kg\ biomass}}{\boldsymbol{h}}\right] \cdot \frac{\mathbf{1}}{\mathbf{18}} \cdot \left[\frac{\boldsymbol{kmol}}{\boldsymbol{kg}}\right] + \mathbf{2} \\ \cdot \boldsymbol{steam}[\boldsymbol{kmol}] \\ = \mathbf{2} \cdot \boldsymbol{X_{H_2}} \cdot \boldsymbol{m_{totales}}[\boldsymbol{kmol}] + \mathbf{4} \cdot \boldsymbol{X_{CH_4}} \cdot \boldsymbol{m_{totales}}[\boldsymbol{kmol}] \\ + \mathbf{2} \cdot \boldsymbol{X_{H_2O}} \cdot \boldsymbol{m_{totales}}[\boldsymbol{kmol}]\end{aligned} \tag{5. 3}$$

In these atomic balances, X represents the molar fraction of the different products.

Once mass balances have been built, the next equation is the own definition of molar fraction: the sum of all molar fractions of the products has to be equal to one:

$$\boldsymbol{X_{CO} + X_{CO_2} + X_{H_2} + X_{CH_4} + X_{H_2O} + X_{N_2}} = \mathbf{1} \tag{5. 4}$$

There are eight unknows: six molar fractions, amount of char and total amount of mols ($m_{totales}$). So far, there are four equations, so there are four more equations required.

Nitrogen molar fraction ($X_{N_2}$) can be obtained by dividing the amount of mols of nitrogen that came with air (in case of steam and oxygen gasification the amount is zero) from $m_{totales}$.

Amount of char are usually set in thermodynamic models. A fraction of unconverted carbon is fixed and mols of char are obtained by multiplying this fraction by carbon mols contained in biomass. Typical gasification conditions lead to a fraction of unconverted carbon closer to 5%.

The last two equation needed are obtained from reaction constants. The overall gasification process can be summarized through reactions (3.3) and (3.5). (16)

All gases are assumed to be ideal and all reactions form at pressure 1 atm. Therefore, the equilibrium constants, which only are function of temperature, can be expressed as follows:

Table 5.2 Equation for the equilibrium constants.

| Reaction | Equation for the equilibrium constant | Number of equation |
|---|---|---|
| $C + 2H_2 \leftrightarrow CH_4$ | $K = \frac{X_{CH4}}{{X_{H2}}^2}$ | (3.3) |
| $CO + H_2O \leftrightarrow CO_2 + H_2$ | $K = \frac{X_{CO2} \cdot X_{H2}}{X_{CO} \cdot X_{H2O}}$ | (3.5) |

The value of equilibrium constant is found out at constant temperature and pressure using standard state Gibbs function of change ($\Delta G_T°$) (46)

$$\boldsymbol{K_i} = \boldsymbol{e}^{\frac{-\boldsymbol{\Delta GT°}}{\boldsymbol{RT}}}, \boldsymbol{i} = \mathbf{1}, \mathbf{2} \tag{5. 5}$$

Where R is the universal gas constant (R=8.314 KJ/(Kmol·K)) and T is the absolute temperature in Kelvin. We can replace standard state Gibbs free energy $\Delta G_T°$ to standard molar Gibbs free energy because of we set the standard pressure equal to one atmosphere.

The standard molar Gibbs function for the reaction is found as:

$$\Delta G_m° = \Delta G_m° \text{ (products)} - \Delta G_m° \text{ (reactants)} \tag{5. 6}$$

If we consider the reaction: $aA + bB \rightarrow cC + dD$

$$\Delta G_m° = d\mu_D + c\mu C - a\mu A - b\mu_B \tag{5. 7}$$

where $\mu_i$ is the chemical potential.

If the value of Gibbs free energy is known at a temperature T* (T*=298K), its value at another temperature T can be found as follows:

$$\Delta G_f° (T) = \Delta G_f° (T^*) + RT \cdot \ln K (T) \tag{5. 8}$$

where$\Delta G_f°$ (T*) is known and for several compounds its values are introduces in Table 5.2 (column 2).

Standard Gibbs Energy of Formation $\Delta G_f°$, Enthalpy of Formation $\Delta H_f°$ and Enthalpy of Combustion $\Delta H_C°$ are shown in Table 4.2. (14)

Table 5.3 Standard Gibbs Energy of Formation ΔGf°, Enthalpy of Formation ΔHf° and Enthalpy of Combustion ΔHC° at 298 K.

| Compound | $\Delta G_f°$, KJ/mol | $\Delta H_f°$, KJ/mol | $\Delta H_C°$, KJ/mol | $\Delta S°$, KJ/(mol·K) |
|---|---|---|---|---|
| Carbondioxide | -394.64 | -393.78 | 0 | 213.82 |
| Carbonmonoxide | -137.24 | -110.60 | -283 | 197.68 |
| Methane | -50.85 | -74.86 | -802.6 | 186.44 |
| Water vapor | -228.76 | -241.98 | 0 | 188.85 |
| Hydrogen | 0 | 0 | 0 | 130.61 |
| Nitrogen | 0 | 0 | 0 | 191.62 |
| Carbon | 0 | 0 | -393.78 | 5.74 |

Also, the following equation can be written (47)

$$\frac{\Delta \boldsymbol{G}_{\boldsymbol{m}}^{\boldsymbol{0}}(\boldsymbol{T})}{\boldsymbol{T}} = \boldsymbol{F}_{\boldsymbol{0}}(\boldsymbol{T}) + \frac{\Delta \boldsymbol{H}_{\boldsymbol{m}}^{\boldsymbol{0}}(\boldsymbol{T}^{*})}{\boldsymbol{T}} - \left[\frac{\Delta \boldsymbol{H}_{\boldsymbol{m}}^{\boldsymbol{0}}(\boldsymbol{T}^{*}) - \Delta \boldsymbol{H}_{\boldsymbol{m}}^{\boldsymbol{0}}(\boldsymbol{0}\ \boldsymbol{K})}{\boldsymbol{T}}\right] \tag{5. 9}$$

Free energy function $F_0(T)$ is also known for definite temperatures and the difference $\Delta H_m^0(T^*) - \Delta H_m^0(0\ K)$ is also listed.

These values are taken from (47) and introduced in Table 5.3.

Table 5. 4 Free energyfunctions.

| Component | $-F_0(1000\ K)$ | $\Delta H_m^0(T^*)-\Delta H_m^0(0\ K)$ |
|---|---|---|
| | J/(mol·K) | KJ/mol |
| C | 11.6 | 1.05 |
| $H_2$ | 137.0 | 8.5 |
| CO | 204 | 8.67 |
| $CO_2$ | 226.4 | 9.36 |
| $CH_4$ | 199.4 | 10.03 |
| $H_2O$ | 196.7 | 9.91 |

Equilibrium constant can be calculated from tables 5.2 and 5.3 and equations 5.5 and 5.9.

In order to understand more easily how to calculate an equilibrium constant, the following example shows how to do it step by step:

$$\boldsymbol{C + CO_2 \leftrightarrow 2CO}, \quad \Delta \boldsymbol{H = +172.6\frac{KJ}{mol}} \tag{5. 10}$$

For pure compounds Gibbs free energy is zero over the temperature range.

$$\Delta \boldsymbol{G_m^0 = 2 \cdot \mu(CO) - \mu(C) - \mu(CO_2) = 2 \cdot \mu(CO) - \mu(CO_2)}, \tag{5. 11}$$

$$\Delta \boldsymbol{G_m^0 = 2 \cdot (-137.24) - (-394.64) = 120.08\frac{KJ}{mol}}, \tag{5. 12}$$

$$\Delta \boldsymbol{H_m^0(298\ k) = 172.6\ KJ/mol}, \tag{5. 13}$$

$$\boldsymbol{F_0(T) = 2 \cdot F_0(CO) - F_0(C) - F_0(CO_2)}, \tag{5. 14}$$

$$\boldsymbol{F_0(T) = -170.2\ J/(mol \cdot K)}, \tag{5. 15}$$

$$\Delta \boldsymbol{H_m^0(T^*) - \Delta H_m^0(0\ K) = 2 \cdot [\Delta H_m^0(T^*) - \Delta H_m^0(0\ K)](CO) - [\Delta H_m^0(T^*) - \Delta H_m^0(0\ K)](C) - [\Delta H_m^0(T^*) - \Delta H_m^0(0\ K)](CO_2)}, \tag{5. 16}$$

$$\Delta \boldsymbol{H_m^0(T^*) - \Delta H_m^0(0\ K) = 6.93\frac{KJ}{mol}}. \tag{5. 17}$$

$$\boldsymbol{\frac{\Delta G_m^0(T)}{T} = -170.2 + \frac{172.6 \cdot 10^3}{T} - \left[\frac{6.93 \cdot 10^3}{T}\right] = -170.2 + \frac{165.67 \cdot 10^3}{T}\ J/(mol \cdot K)} \tag{5. 18}$$

$$\boldsymbol{ln\,K = -\frac{\Delta G_m^0(T)}{T}}. \tag{5. 19}$$

$$\boldsymbol{ln\,K = -\frac{-170.2+\frac{165.67\cdot 10^3}{T}}{8.314}}. \quad (5.\,20)$$

*For instance, if selected temperature is 1073 K,*

$$ln\,K = -\frac{-15.80}{8.314} = 1.90 \rightarrow K = 6.69.$$

Table 5. 4 Results of calculation of equilibrium contants.

| Nº | Reaction | $\Delta G_f^0$, $KJ/mol$ | $\Delta H_f^0$, $KJ/mol$ | $\Delta H_m^0(T^*) - \Delta H_m^0(0\ K)$, $KJ/mol$ |
|---|---|---|---|---|
|  |  | T = 298 K |  |  |
| 1 | $C + 2H_2 \leftrightarrow CH_4$ | -50.85 | -74.9 | -8.02 |
| 2 | $CO + H_2O \leftrightarrow CO_2 + H_2$ | -28.64 | -41.2 | -0.72 |

Taking the values from the table above and replacing them in equations 5.5 and 5.9 with the desired temperature will let to obtain equilibrium constant values for each reaction.

Once there is the same number of equation as unknowns, the last step is to solve the system. The chosen program to do it is Engineering Equation Solver (EES).

Results range must be narrowed: molar fractions must be between 0 and 1 and total amount of mols ($m_{totales}$) has to be positive. Otherwise, it can be got some result that satisfy the equations but have no sense, like negative molar fractions.

## *5.3 PSEUDO-EXPERIMENTAL MODEL*

The above model, as it has already said, it is purely theoretical, so a second model has been developed in order to try to approach more to real results. That is the reason why the mode takes its name: it is still a theoretical model, but aims to reflect reality better than simple stoichiometric models. In this case, the first six equations (atomic balances, sum of molar fractions, nitrogen molar fraction equation and char equation) remain being the same as in stoichiometric model. However, this one is not based on reaction constant. It includes two different aspects:

The first one is a correlation that relates CO and $CO_2$ concentration. During combustion and gasification process, carbon can be converted into carbon monoxide and dioxide. Moreover, CO can be oxidized to $CO_2$. This means that there is a close relationship between both products, and there are lots of possible solutions that satisfy the system of equations. Therefore, a correlation that reflects real ratios CO/ $CO_2$ has to be includes in the model. This ratio has been the subject of an extensive number of research papers and it is still open to debate. The complexity of finding a suitable correlation is due to the difficulty of measure $CO/CO_2$ ratio. There are several authors that have developed correlations for this relation. In the present project, the chosen one has been taken from the book “Biomass Gasification and Pyrolysis: Practical Design and Theory” (17), written by Basu Prabir who used a widely used correlation built by J.R. Arthur (1951):

$$\frac{[\boldsymbol{CO}]}{[\boldsymbol{CO_2}]} = \boldsymbol{2400e^{-\left(\frac{6234}{T}\right)}} \tag{5.21}$$

Where T is the surface temperature of the char.

The second variation introduced is maximization of hydrogen molar fraction ($X_{H_2}$). This model is especially suitable for steam gasification, where its main target is hydrogen production. Steam gasification aims to maximize the hydrogen content in the product gas. The present model works similarly: it tries to produce the greater value of hydrogen molar fraction maintaining water or methane molars fractions as independent variables (the results obtained by using either water or methane as independent variables are the same).

Globally, the models consist of eight unknowns and seven equations. Nonetheless, maximization function works as an extra equation, matching the number of the equations to the unknowns.

## *5.4 THE USE OF THE PROGRAM*

The models are structured in three parts:

The first one (“required data”) corresponds to the information that has to be introduced from the user. It includes: biomass composition, gasification temperature, gasification agent selected, gasification agent ratio and fraction of unconverted carbon.

The second part is referred to the calculations. It is also divided in several parts: gasification agents, amount of nitrogen, amount of char and low heating value.

Gasification agents: depending on which one has been chosen, the program calculates the amount of mols of gasification agent. Calculation method is different for steam than for air and oxygen because the formula of the ratio is different. In case of steam, the ratio is define as:

$$\boldsymbol{Biomass}/_{\boldsymbol{steam-ratio}} = \frac{\boldsymbol{sum\,water\,input}\,[\boldsymbol{Kg}]}{\boldsymbol{dry\,fuel\,input}\,[\boldsymbol{Kg}]} \tag{5. 22}$$

Sum water input is the sum of steam, which is used for biomass gasification and the water content of the fuel.

On the other hand, air and oxygen ratio are defined as ER (equivalence ratio) and its formula is the following one:

$$\boldsymbol{ER} = \frac{\boldsymbol{actualair}\,(\boldsymbol{oxygen})\,(\boldsymbol{kg}\cdot\boldsymbol{s^{-1}})}{\boldsymbol{stoichiometricair}(\boldsymbol{oxygen})(\boldsymbol{kg}\cdot\boldsymbol{s^{-1}})} \tag{5. 23}$$

First, the amount of stoichiometric oxygen is calculated, and then the real one by multiplying the previous by air ER. In the case of air gasification, nitrogen has to be added to the oxygen.

Total amount of nitrogen: it is equal to the nitrogen contained in biomass and the one that comes with air.

Amount of char: calculation of unconverted carbon has already been discussed.

Lower heating value: this section contains the heating values of CO, $H_2$ and $CH_4$ (which are the only products that can be burnt.

The last part includes the final results. It is divided into three sections: “System of equations”, that is depends on the model chosen, “Lower heating value of the product gas”, which express the heating value of outlet gas in different units and “Relation $H_2/CO$”, that this ratio, which has major significance for bio-SNG production.

# *6. RESULTS*

## *6.1 COMPARISON OF THE THERMODYNAMICAL MODELS*

In this first step, both models will be compared with experimental results for steam and air gasification in order to know which one is better for each kind of gasification. After having selected a model for each kind of gasification, next step will be the study of the influence of each parameter. So, in this first section we will focus only in the comparison of trends, without trying to understand the process inside the gasifier.

Experimental data have been taken from gasification plants, as well as small scale experiments and theoretical models

### 6.1.1 STEAM GASIFICATION

#### 6.1.1.1 Current plant conditions

In the first two figures, volume concentration (%) and Lower Heating Value are represented for specific conditions of temperature, pressure and steam-biomass ratio. Experimental results have been taken from Güssing gasification plant (Austria) where REPOTEC gasifier is used.

Güssing is a small town located in eastern part of Austria, near the Hungarian Border. In 1989, a plan to supply energy demands using local resources. The target of the project is combined heat and power plant with fluidized bed steam gasification technology. The plant started operation in 2001. It has a capacity of 8MW, producing on average about 2MW of electricity and 4.5MW of heat per hour. The infeed material is wood chop which is collected from local wood farmers from the nearby forest. Olivine was selected as bed material. (48)

Mathematical models as well as Güssing plant works at atmospheric pressure. Experimental results from the plant have been obtained from a temperature range of 850-900 °C. For developed models, temperature has been set at 850°C and steam-biomass ratio at 0.3 (kg/Kg).

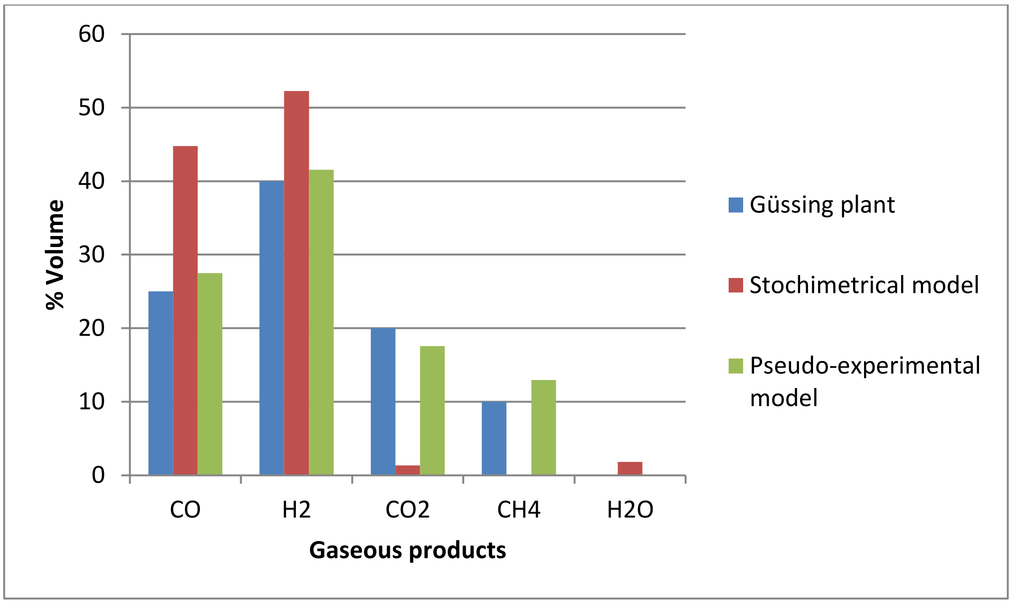


Figure 6.1 Volume concentration for different gaseous products for steam gasification

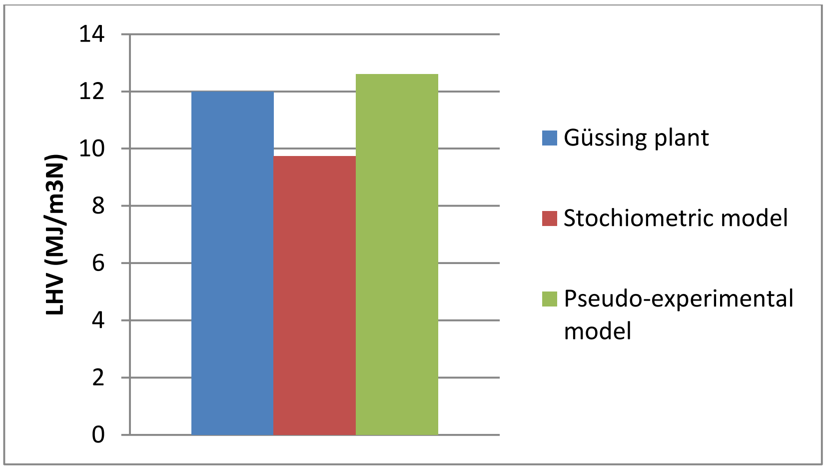


Figure 6.2 LHV (MJ/m3N) for steam gasification

It can be seen that results from pseudo-experimental model are closer to Güssing data than that of stoichiometric model. In the first figure, the main differences between both models are CO and $CO_2$ volume fractions. Most carbon in stoichiometric model goes to CO, while in pseudo-experimental, as well as in Güssing plant, there is a large amount of carbon dioxide formed. Moreover, stoichiometric simulations reach high amount of hydrogen that do not take place in real experiments. This difference in hydrogen leads to obtain lower quantities of methane. Finally, although both Güssing and pseudo-experimental model results reflect that the amount of water is negligible, in stoichiometric model, we can see that this quantity is higher.

In the second figure, we can see that LHV of the producer gas in pseudo-experimental model and Güssing experiments are almost equal, while stoichiometric model value is approximately 2MJ/$m^3$N. This difference is not as big as could be expected because only CO, $H_2$ and $CH_4$ are taken account in the LHV calculation (because are the only compounds that can be burnt). Therefore, although the positive difference in CO and $H_2$ volume percentage should provide a higher LHV, compared to the other results, the near-absence of methane reduce this value to a lower one.

#### 6.1.1.2 Variation of parameters

Once we have compared both models with specific conditions of temperature and gasification agent, we will analyze how concentrations change when we vary these parameters and if the changes are similar to experimental plots.

## Temperature

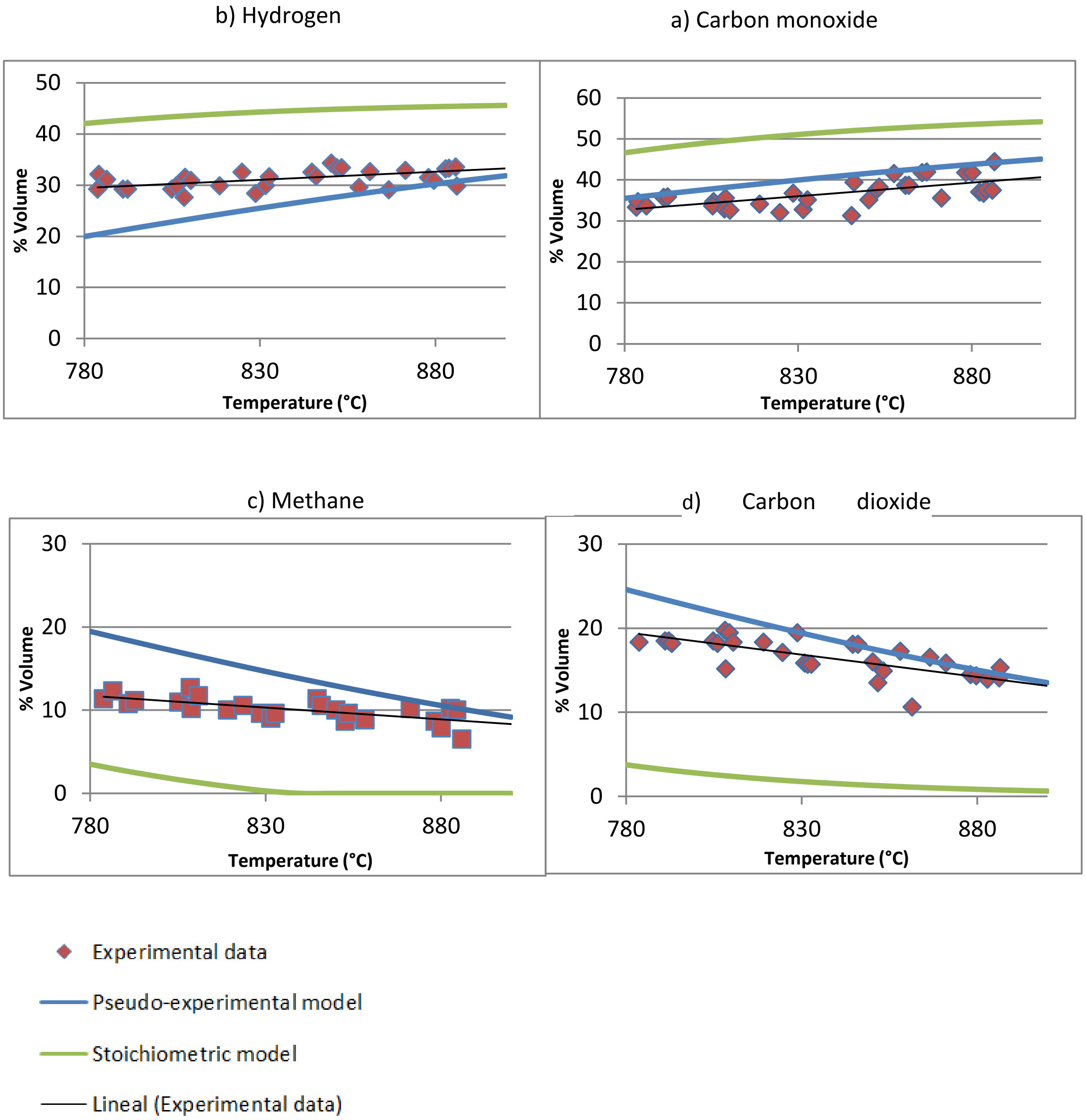


Figure 6.3 Volume percentage vs temperature of gaseous products for pseudo-experimental and stoichiometric models and experimental data. (49)for steam gasification

These figures represent molar composition (%) of gaseous products for both models as well as for experimental gasification. Steam-biomass ratio has been set at 0.3, because, it was the ratio that whit which results are more close to the experimental ones.

Experimental results have been taken from the report “Stoichiometric Water Consumption of Steam Gasification by the FICFB-Gasification Process” (4), written by H.Hofbauert and R.Rauch. In that project, authors studied during five years gasification process using FICFB reactor (Fast Internally Circulating Fluidized Bed). They focused on high grade synthetic gas production from solid fuels (around 13MJ/Nm$^3$). Experiments were carried out in a 100kW$_{th}$ pilot plant and steam was chosen as gasification agent. Wood pellets, wood chips and biomass residues were used as fuels. Bed material was quartz together with a natural catalyst.

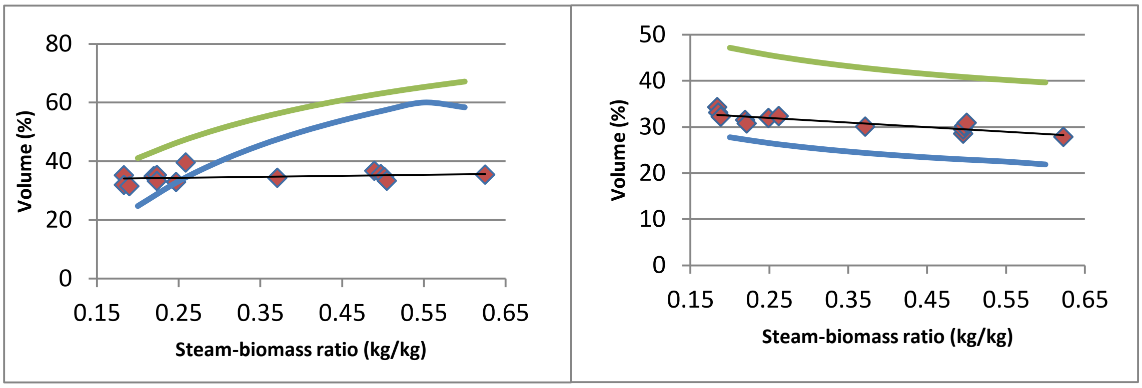
In principle, it can be said that both models have similar trends compared with the experiments. Pseudo-experimental model provides better results than stoichiometric model, especially concerning methane and carbon dioxide, where results are far from the experimental ones.

The main divergence of stoichiometric model comes from carbon dioxide values. It can be seen that the curve of the plot take values from 6 to almost zero. Stoichiometric model provides very high concentrations of CO and very low concentrations of $CO_2$. It might be thought that it is because this model supposes the equilibrium and in real experiments it is not reached. However, it should be remembered that both gasification and combustion reactions are fast and irreversible, so the equilibrium is usually reached. The real reason for this problem is mathematical: the reactions constants make the system a non-linear system, which is difficult to solve, especially if you are looking for a specific solution. It does not means that obtained solution is not correct, but it is one of the multiple solutions, and it is not the desired one. Some improvement for this model could be the reduction of the solution range.

## Steam-biomass ratio

d) Hydrogen

c) Carbon monoxide



**d)** Carbondioxide

**c)** Methane

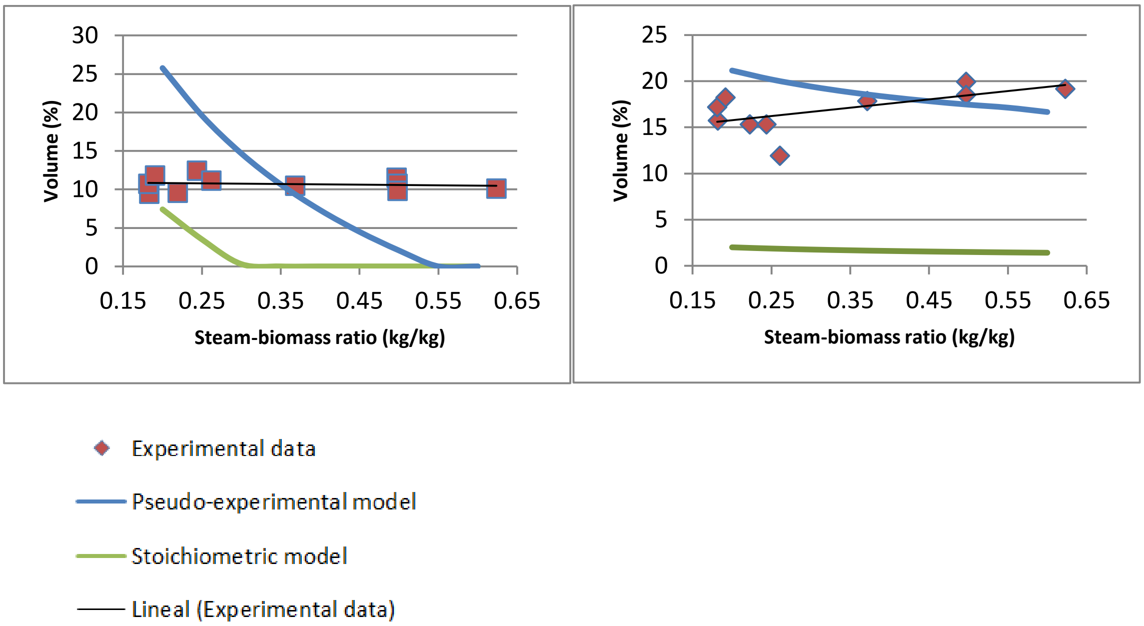


Figure 6.4 Volume percentage vs steam-biomass ratio of gaseous products for pseudo-experimental and stoichiometric models and experimental data. **(4)** for steam gasification

**Error! Not a valid bookmark self-reference.** represents the concentration for the different gaseous products versus steam-biomass ratio (kg/kg) for the mathematical models as well as for experimental data.

As a general view, steam-biomass variation reflects that model results are more distant from the experimental ones than in the case of temperature variation. Experimental results show a slight variation of concentrations with variation of steam-biomass parameter. Model results, by contrast, show a stronger influence with this parameter.

Both models suppose an increase in hydrogen concentration, due to the growth in hydrogen feed as steam. However, in real experiments, there is only a slight increase in this component. This is largely due to the assumption of the models that high hydrogen content is obtained: on the one hand, stoichiometric model supposes that almost all the hydrogen feed, contained in biomass as well as in stem, goes to hydrogen, and almost nothing goes to methane. On the other hand, pseudo-experimental model is based on a maximization of hydrogen.

In the same way as in temperature variation, stoichiometric model assumes that most carbon is converted in carbon monoxide. Therefore, the CO trend is a descending line, but the values are much higher than the real ones.

Results from Pseudo-experimental model show an opposite trend compared with experimental ones concerning carbon dioxide. The reason has already been explained: CO/ $CO_2$ relation in this model only depends on temperature, so it is not influenced on the gasification agent variation. Therefore, this relation remains constant with the variation of this parameter, although in experimental results it diminishes due to the increase in $CO_2$ concentration and the reduction in CO concentration.

Summarizing, although both models present some divergences from the experimental data, pseudo-experimental model provide better results. Therefore, hereinafter this model will be the chosen one for steam gasification.

### 6.1.2 **AIR GASIFICATION**

In this section the same stage as in steam gasification will be followed in order to choose the best model: firstly concentrations and LHV for specific concentrations will be studied, and then, we will focus on the variation of temperature and gasification agent.

#### *6.1.2.1 Current plant conditions*

In this case, experimental results have been taken from Foster Wheeler gasifier, located in Lahti (Finland). (50). This plant has already been explained in section 3 (Gasification plants).

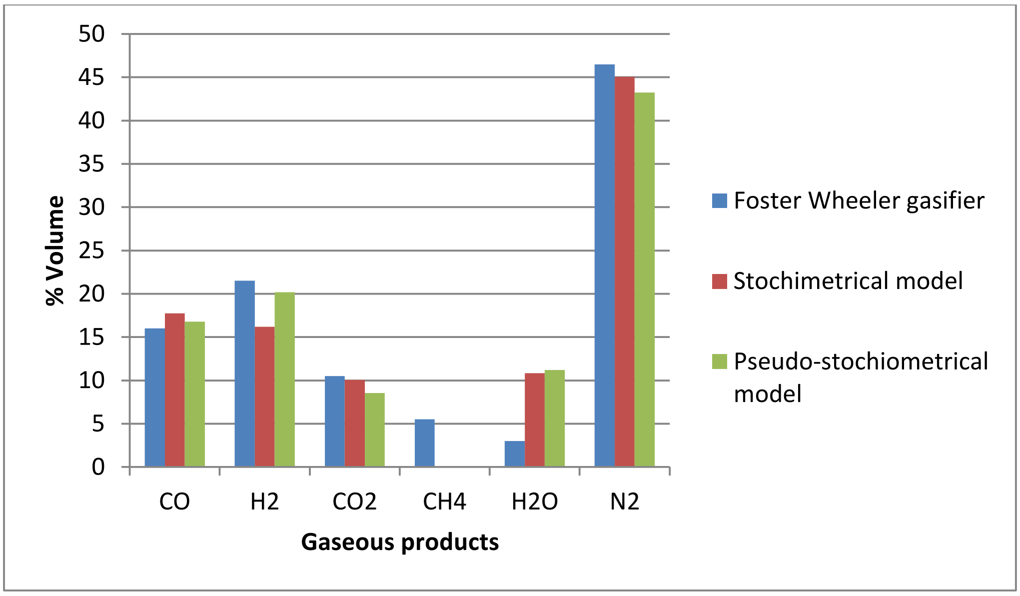


Figure 6.5 Volume concentration for different gaseous products for air gasification

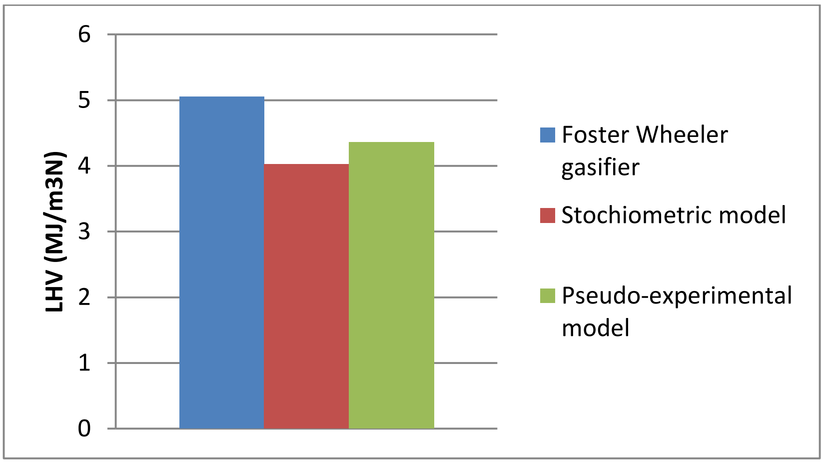


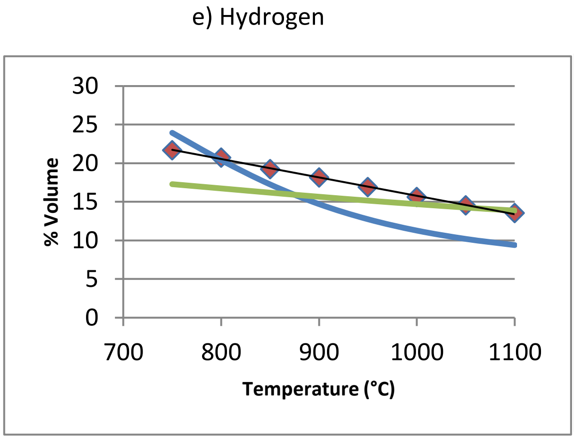
Figure 6.6 LHV (MJ/m3N) for air gasification

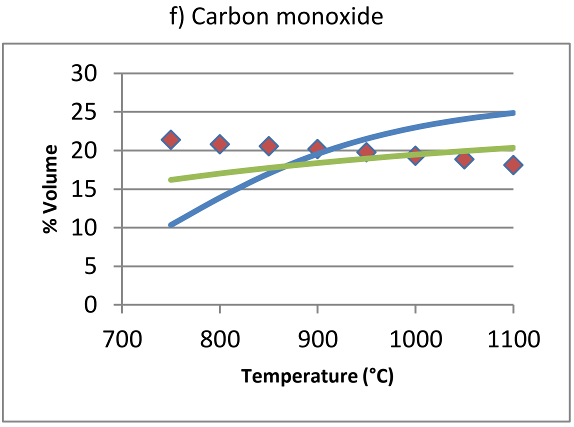
It can be seen that for air gasification, both mathematical models provide similar results to experimental ones. The most salient differences, is that both models assumes the near-absence of methane and water content is higher than in the plant, but concerning the main products (CO, $H_2$ and $CO_2$), the results are quite accurate.

As regards Lower heating value, mathematical models are close between them, although there is a slight difference with the Foster Wheeler gasifier. This fact is essentially due to the information provided about the experiment plant: there, not exactly value of LHV is given, but a range between 4.3 and 5.8.

### *6.1.2.2 Variation of parameters*

#### **Temperature**





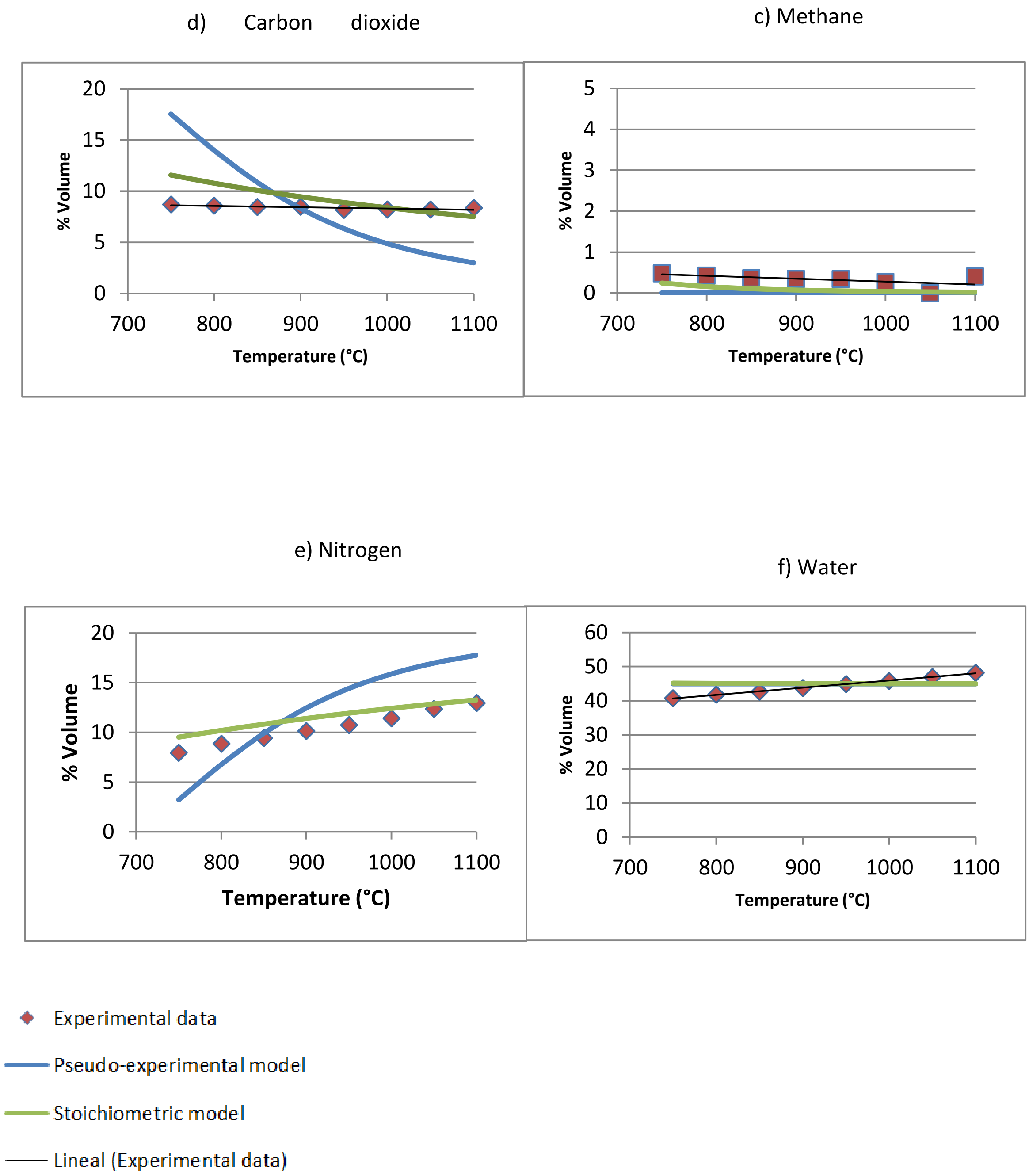


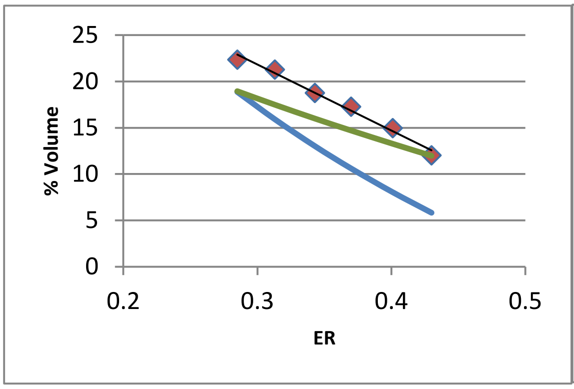
Figure 6.7 Volume percentage vs temperature of gaseous products for pseudo-experimental and stoichiometric models and experimental data **(8)** for air gasification.

Experimental data came from the paper “Energy and exergy analysis of biomass gasification at different temperatures”, (8) written by Rade and Vladan Karamarkovic. The paper presents a chemical equilibrium model for air gasification. Biomass feed is represented by the formula $CH_{1.4}O_{0.59}N_{0.017}$, which is similar to the working biomass. This report focuses on analysis of biomass with different moisture at different temperatures, specifically analysis in a range from 900 to 1373 K of biomass with 0% moisture and 30% were carried out. Due to the fact that working biomass in the present project has 16.4% of moisture, experimental points taken were an average between 0 and 30 moisture percentage.

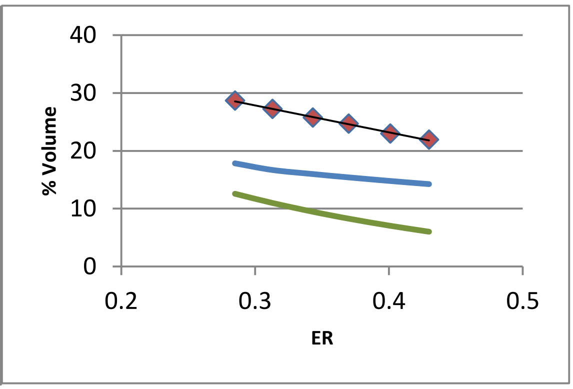
In this case, stoichiometric model provides better results compared to pseudo-experimental model. Results from the first model are very close to the experimental ones. The most significant divergence concerns to carbon monoxide: experimental points have a down gradient, while points from both models have an up gradient. However, as with parameter variations in steam gasification, in temperature ranges with which plants usually work (800-900°C), results provide from the models fit very well with experimental ones.

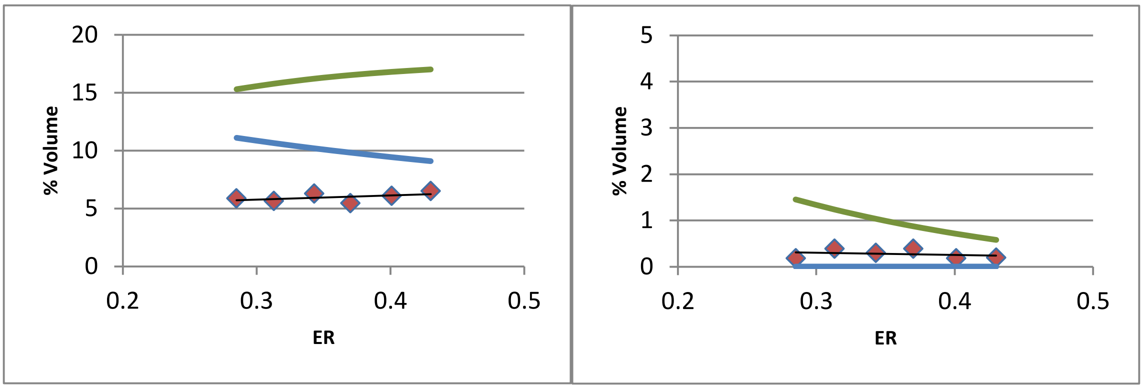
## ER ratio

g) Hydrogen



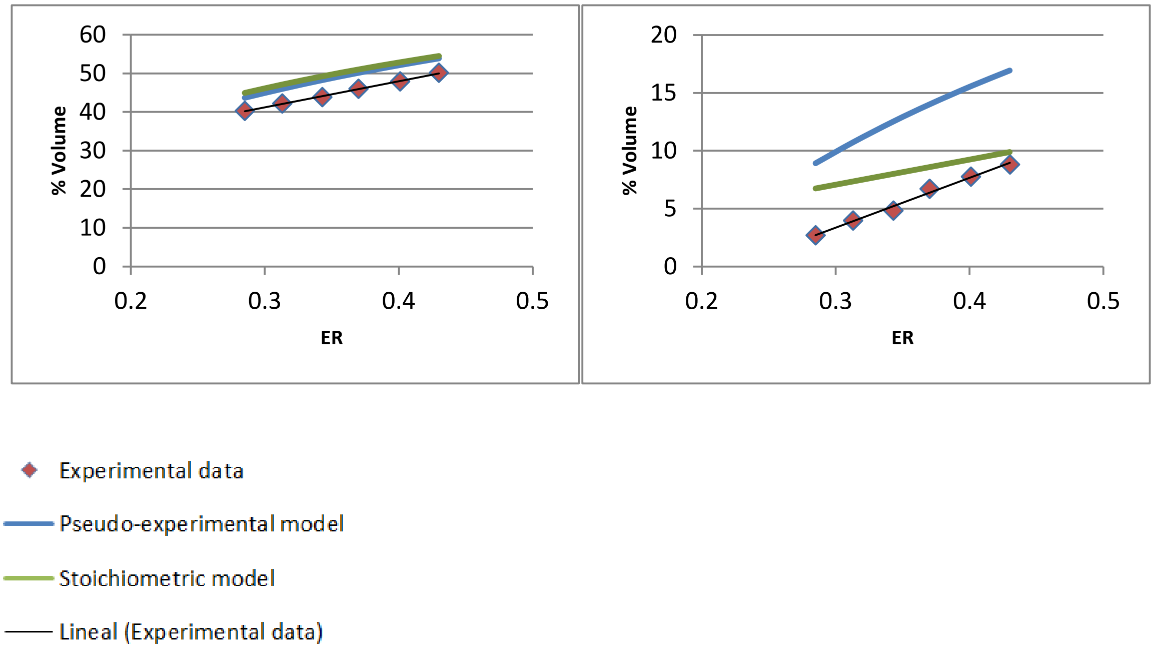
h) Carbon monoxide





d) Carbon dioxide

c) Methane



e) Nitrogen

f) Water

Figure 6.8 Volume percentage vs ER of gaseous products for pseudo-experimental and stoichiometric models and experimental data **(8)**

In figure Figure 6.8 Volume percentage vs ER of gaseous products for pseudo-experimental and stoichiometric models and experimental data , experimental data has been obtained from the same reference as in. In this case, volume concentrations are referred for ER values that are usually used for gasification. Above these ER values, it is suppose that combustion process takes place instead of gasification one.

In the same way as in steam gasification, mathematical models provide worst results in the case of ER variation than in the case of temperature variation. The mayor differences come from carbon dioxide and monoxide. Although the trends of the points are similar in both models as well as in experimental data, the ranges where points are located differ considerably. The reasons for these divergences have been widely explained.

Concerning water, differences of model results with experimental ones are not so sizeable, but they are still appreciable. For the rest of the gaseous products, models predict quite accurately experimental points.

For ER ratio variation, pseudo-experimental model fits a little better to experiments results than stoichiometric model. However, for temperature variation, stoichiometric model predicts much better results than the first one. Thereby, stoichiometric model will be selected for further studies concerning air gasification as well as oxygen gasification.

In conclusion, both models provide quite accurate results when temperature and gasification agent/biomass ratio is set. However, these models present several divergences with experiments (or other theoretical models) when volume composition dependence on these above parameters is analyzed.

## *6.2 ANALYSIS OF THE INFLUENCE OF THE OPERATION PARAMETERS*

This second section includes the analysis of the influence of the main operation parameters, which are temperature, gasification agent/biomass ratio and moisture content in biomass. We will focus this study on the volume composition and the Lower Heating Value. After having study this influence, these parameters will be optimized for a SNG production and an electricity production plants.

### 6.2.1 GASIFICATION AGENT/BIOMASS RATIO

The first parameter to be studied is gasification agent/biomass ratio. During these simulations for steam, air and oxygen gasification, temperature has been set at 850°C, which is a typical value for gasification plants.

For steam gasification, this parameter is known as steam/biomass ratio and it is defined according to the formula represented by equation 5.11.

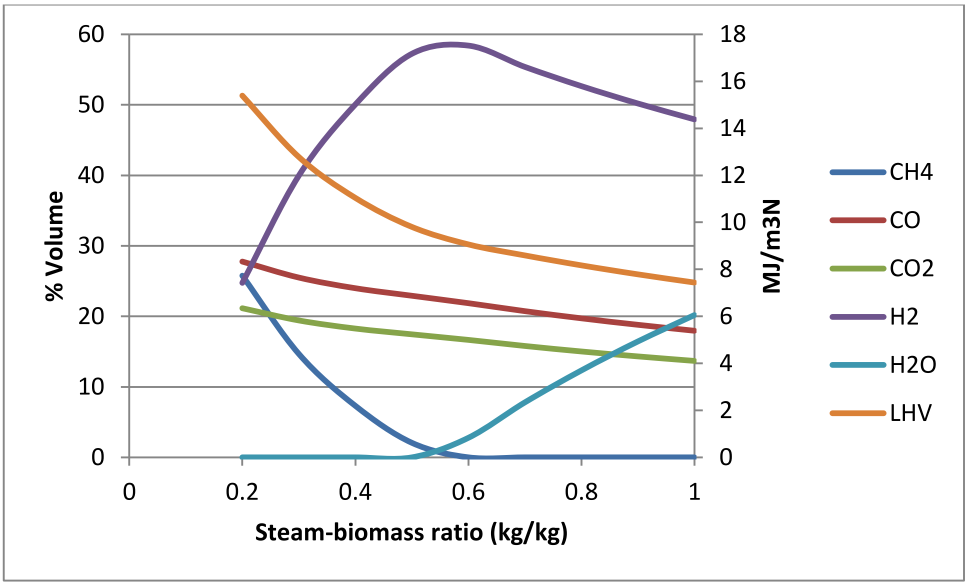


Figure 6.9 Volume composition and LHV vs. steam-biomass ratio

As it has already said in the above section, this model presents some problems when varying steam-biomass ratio. Anyway, we will explain the real trends of the products with S-B variation.

Firstly, it should be said that steam-biomass ratio has a weak effect on volume composition. In real experiments, there is only a smoothly increase in $CO_2$ and $H_2$ and a slightly decrease in CO composition. Methane remains almost constant.

The reason for the $CO_2$ and $H_2$increase and the opposite trend of CO can be found in water-gas shift reaction (eq. 3.5). According to Le Chatelier´s principle, an increase in one of the reactants leads to promote the reaction toward the right direction, i.e., $CO_2$ and $H_2$ increase while CO diminishes.

However, this growth reaches a maximum for a steam/biomass ratio of 0.55 approximately. Above this ratio, hydrogen yield begins to decrease. This reason is attributed to the decrease of carbon conversion of the biomass in the gasifier, due to the greater need of heat for higher gasification temperature and the greater amount of heat that steam needs to absorb to reach bed-temperature. Unfortunately carbon combustion in the combustion chamber (we are supposing a FICB gasifier, which is the most common for large-scale plants) cannot supply enough heat to heat up the steam to take part in the water-gas shift reaction. Therefore, after the maximum ratio, there is an increasing amount of unreacted steam and carbon that leads to a decrease in hydrogen production.

Concerning oxygen and air gasification, the above parameter is known as ER and it is defined as follows according eq. 5.12.

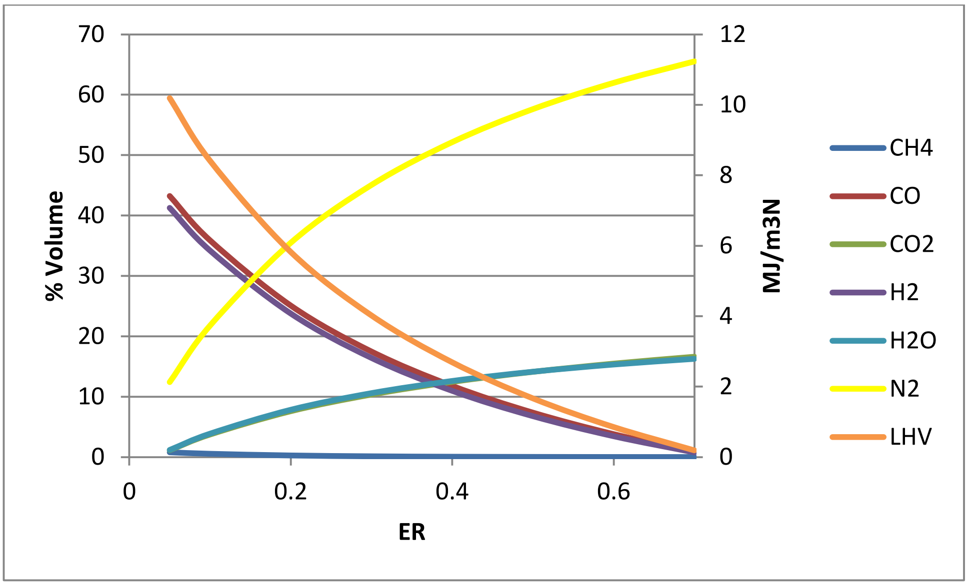


Figure 6.10 Volume composition and LHV vs. ER (air gasification)

First of all, it should be said that for air gasification, ER is the most influential parameter. In fact, other parameters, such as temperature, rely on it. An increase in ER encourages combustion reactions, which are exothermic, and it leads to a higher bed temperature.

Secondly, influence of ER on tar, char and gas conversion should be commented: during the gasification process, biomass is firstly converted into gas, tar and char. Tars are decomposed to light and heavy hydrocarbons, as well as carbon monoxide and dioxide and hydrogen. Heavy hydrocarbons are broken into light hydrocarbons and hydrogen. And finally, char is converted into CO, $CO_2$, $H_2$ and a solid residual. Higher bed temperature will promote, at first, gas composition in the initial pyrolysis. Furthermore, tars cracking reactions are also favored. Finally, char gasification are enhanced at higher temperature, by the Boudouard and water shift reactions, given their endothermicity.

Lastly, ER is a decisive factor in syngas composition. It influences directly as a reactant, displacing the equilibrium to the right direction. Increasing ER leads to promote combustion reactions of hydrogen, methane and carbon monoxide, instead of gasification reactions. As a consequence, burning products (steam and carbon dioxide) increase with ER. Moreover, the drop in syngas products ($H_2$, CO and $CH_4$) provokes a sharp decrease of the Lower Heating Value until a near-zero value, where the product gas is only composed of steam, carbon dioxide and nitrogen.

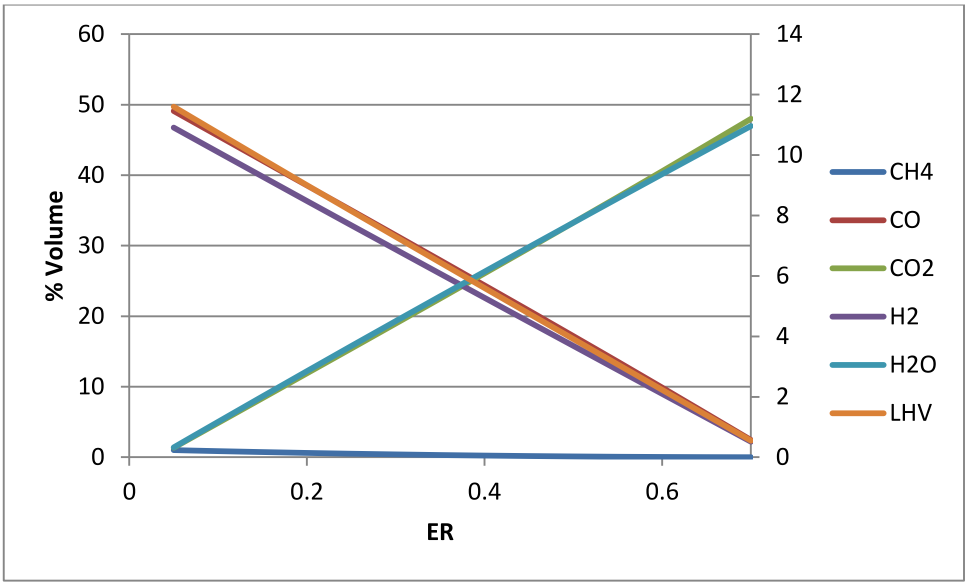


Figure 6.11 Volume composition and LHV vs. ER (oxygen gasification)

The influences of ER on syngas composition, as well as on tar, char and gas conversion is the same for oxygen and for air gasification. The absence of nitrogen let higher bed temperature with less ER. Therefore, not only the composition, but also the Lower Heating Value is higher in the case of oxygen gasification.

### 6.2.2 TEMPERATURE

Once we have analyzed the first parameter, the following one is the temperature. We will study the influence of it on composition of the product gas as well as on LHV. Reaching the desired temperature in the bed is performed by adding external heat (indirect gasifiers) or more commonly, by oxidation of the unconverted carbon in a secondary chamber (combustion chamber).

For this simulation, steam/biomass ratio has been set at 0.3.

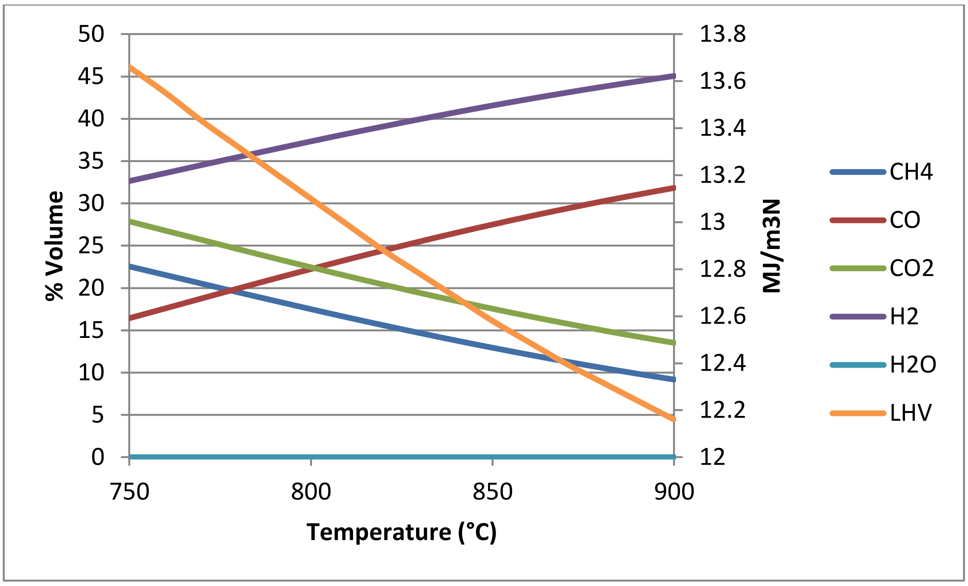


Figure 6.12 Volume composition and LHV vs. temperature (steam gasification)

Although in this simulation the trends are more pronounced than real ones, we could say that temperature does not have a strong effect on the composition of the syngas and on the LHV. Char, tar and gas conversion have not been taken account in the model. Therefore, it cannot be seen the main influence of the temperature on the process. In the same way as for air and oxygen gasification, temperature leads to a decrease in tars, char and, therefore, it results in a higher gas conversion.

For steam gasification, the main reactions that take place inside the gasifier are the Boudouard reaction (eq. 3.2), steam gasification reaction (eq. 3.1), steam-methane reforming reaction (eq. 3.4), water-gas shift reaction (eq. 3.5) and methanation reaction. If we consider this system of reactions, we can see that the first three reactions are endothermic and the last two are endothermic. An increase of temperature, according Le Chaterlier´s principle, will provoke a displacing of the equilibrium to the products in endothermic reactions, and to the reactants in exothermic reactions. Carbon monoxide will increase, due to Boudouard, water-gas shift and steam-methane reforming reactions. Carbon dioxide concentration will also diminish according to Boudouard and water-gas shift reaction. However, understanding the hydrogen and methane trends is not so easy: they are involved in several reactions, and in some of them they are a product and in some other they are a reactant. To understand why hydrogen increases and methane decreases with temperature, we have to look at the heat of reaction. The higher heat of reaction (positive or negative), the greater influence temperature has on this reaction. Therefore, the equilibrium is shifter the higher heat of reaction. In the reactions with high heat of reaction, the equilibrium is shifted toward hydrogen formation, and methane is present as a reactant (steam-methane reforming and water-gas). These reactions dominate over the ones with low heating value. This makes hydrogen increases and methane decreases, although it is a smoothly variation.

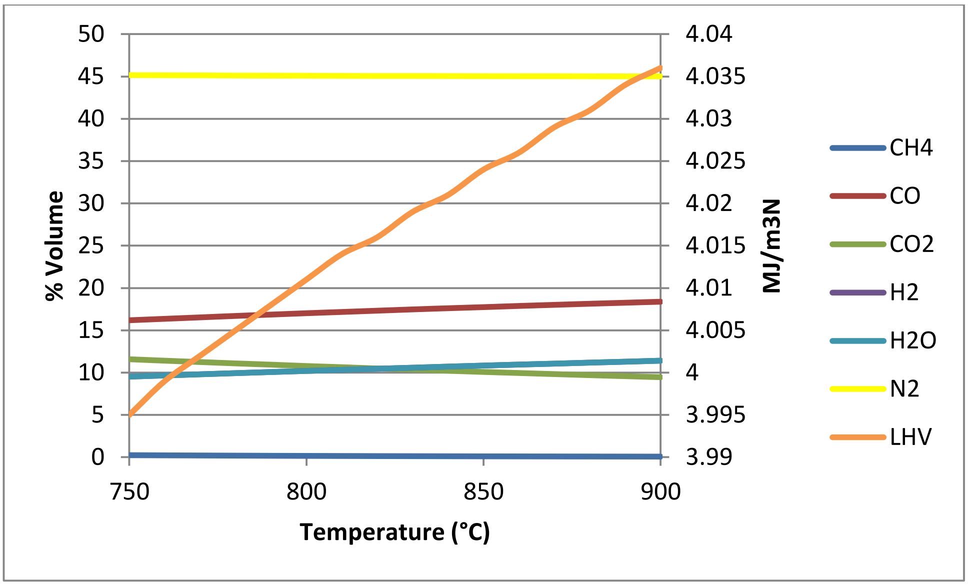


Figure 6.13 Volume composition and LHV vs. temperature (air gasification)

As regards air and oxygen gasification Figure 6.13 and Figure 6.14 Volume composition and LHV vs. temperature (oxygen gasification) show the same behavior inside the gasifier as for steam gasification. Temperature is not the main parameter concerning volume concentration, although it has great importance for tar and char conversion.

A slight increase in CO, $H_2$ and $H_2O$ concentration is observed as well a smooth decrease in $CH_4$ and $CO_2$. The reasons for these changes are the same as in steam gasification: temperature affects the equilibrium, according Le Chatelier's principle and it promotes Boudouard reaction, water-gas reaction and steam refoming reactions.

There are several authors that have discuss the temperature influence in experiments, such as Emami Taba and Faisal Irfan (51),Jinsong Zhou and Qing Chen (5),Jin-Won Kim and Tae-Young Mun (52), among other.

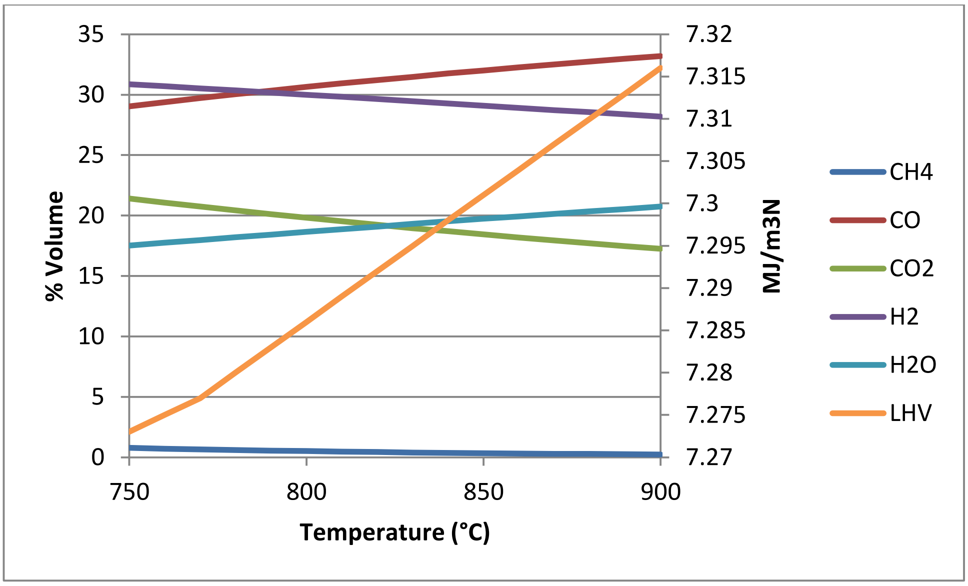


Figure 6.14 Volume composition and LHV vs. temperature (oxygen gasification)

### 6.2.3 MOISTURE

The last parameter to be studied is moisture content in biomass. The following figures represent volume composition and LHV versus moisture content for steam, air and oxygen gasification. Although there are some divergences between them, especially concerning steam gasification model, there is a conclusion that can be drawn in gasifiers when moisture is varied:

$CO_2$ and $H_2$ compositions increase, while CO and $CH_4$ ones decrease.  The reason is, one more time, the equilibrium shifting. Increasing the moisture content leads to increases the concentration of one of one of the reactants ($H_2O$) of water-gas shift and steam-methane reforming reactions. It results in an increase of carbon dioxide and hydrogen and a decrease of carbon monoxide and methane.

Lower Heating Value, for most experiments, suffers a decline with increasing moisture. This is largely due to high water content in product gas.

Moisture also affects to chemical efficiency. It also goes down due to, firstly, the drop in LHV and, secondly, to increased heat required to evaporate the higher amount of water.

The influence of moisture in gasification process has been studied in several researchs: Plis and Wilk studied air gasification process in a fixed bed gasifier (53);G. Schuster and G. Löffler proposed a thermodynamic model based in equilibrium for steam gasification (54)

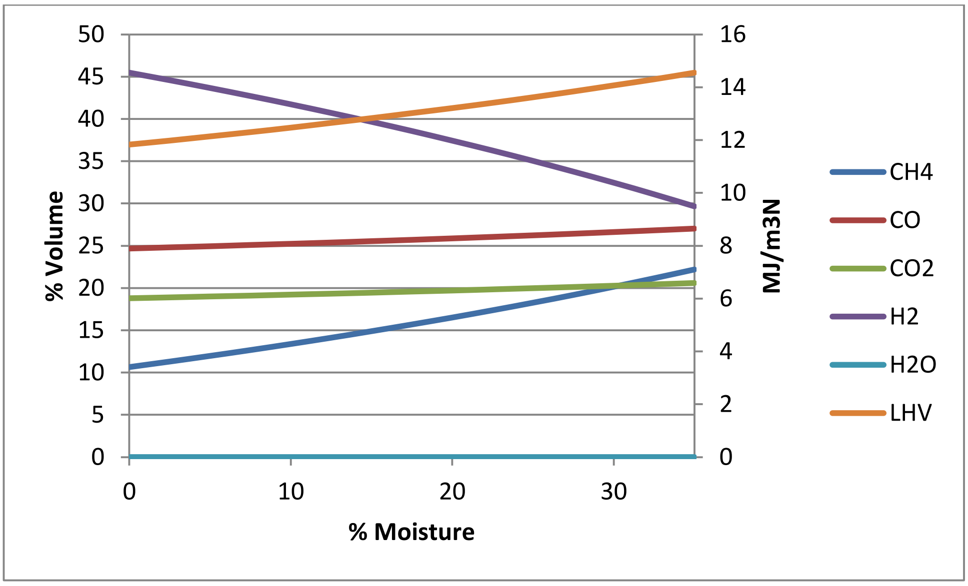


Figure 6.15 Volume composition and LHV vs. moisture (steam gasification)

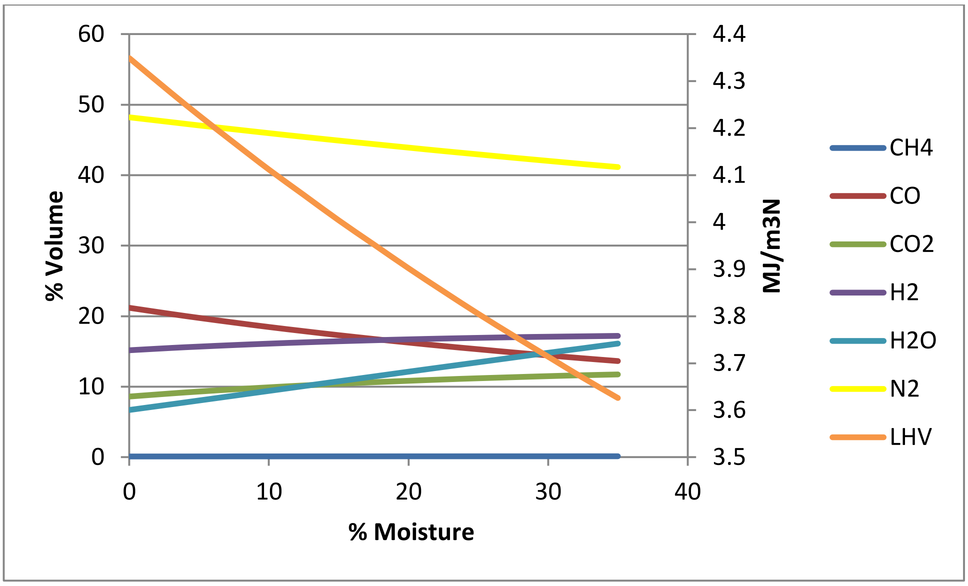


Figure 6.16 Volume composition and LHV vs. moisture (air gasification)

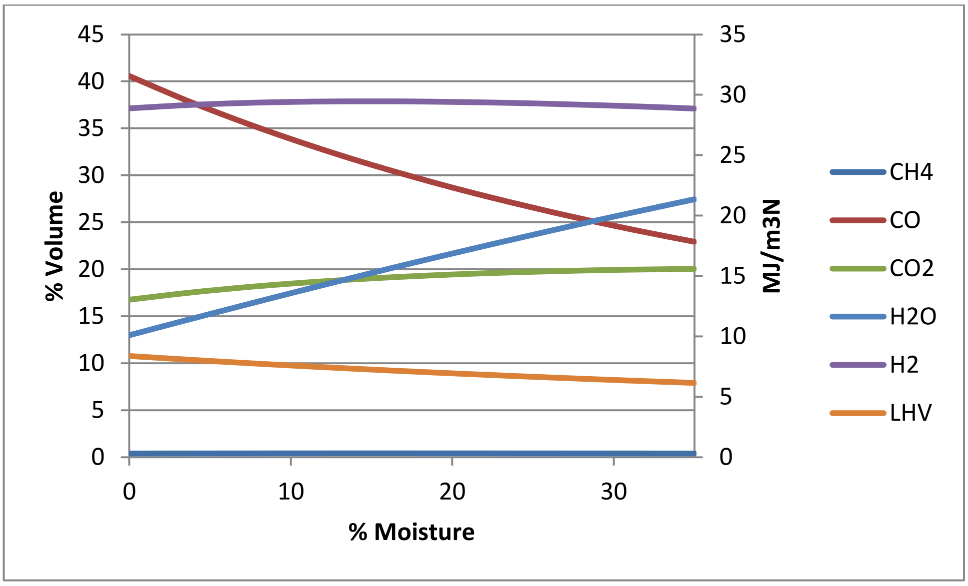


Figure 6.17 Volume composition and LHV vs. moisture (oxygen gasification)

## *6.3 OPTIMIZATION OF OPERATION PARAMETERS FOR A SYNGAS PRODUCTION PROCESS AND AN ELECTRICITY GENERATION PROCESS.*

Syngas from gasification process, as it has already said, has two main applications: it can be converted into bio-methane and then be added into natural gas grid, and also it can be burnt to produce energy and heat.

The following section pretends to study the different operation parameters for each process and select the best option for each one.

### 6.3.1 Bio-SNG PRODUCTION PROCESS

Syngas coming from gasification process is composed mainly by carbon monoxide and hydrogen. Further steps to produce bio-methane include gas conditioning, where particles and other impurities are removed, methanation process, that converts CO and $H_2$ into $CH_4$ and gas upgrading, where $CO_2$ and $H_2O$ are removed from the gas.

In order to add bio-methane into natural gas grid, gas composition has to be composed mainly by methane (98% approximately). Therefore, it is important to obtain a gas composition from the gasifier that enables to reach this composition.

The critical factor to know if the resulting gas composition is suitable for bio-SNG production is $H_2/CO$ relation. According to methanation reactions, this relation should be between 3 and 4, which would be stoichiometric relation, according to reverse reforming reactions.

### Gasification agent

The first parameter to be optimized is the gasification agent. Obtained results, as well as operating conditions are represented in the figures below.

Table 6.1 Operation conditions for optimization of gasification agent (bio-SNG production)

| Gasification Agent | T(°C) | Gasification agent/ biomass ratio | $H_2$/CO ratio |
|---|---|---|---|
| STEAM | 830 | 0,6 | 2,67 |
| AIR | 830 | 0,2 | 0,95 |
| OXYGEN | 830 | 0,2 | 0,94 |

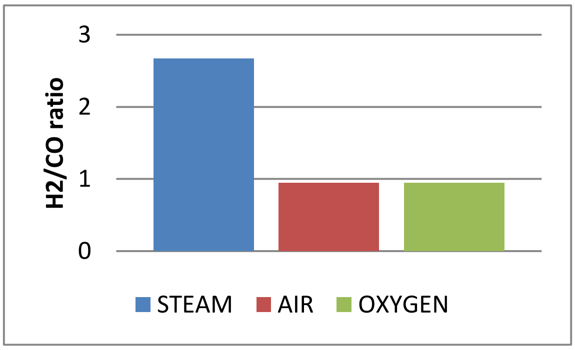


Figure 6.18 $H_2$/CO ratio for steam, air and oxygen gasification (gasification optimization for bio-SNG production)

It can be seen that steam gasification results in higher $H_2$/CO relation. Working with steam lets to obtain a relation close to the stoichiometric one. In fact air and oxygen are rarely used for bio-SNG production.

### Temperature

Once steam has been chosen as gasification agent, next parameter to be optimized is temperature.

Steam/biomass ratio has been set at 0.6 kg steam/kg biomass.

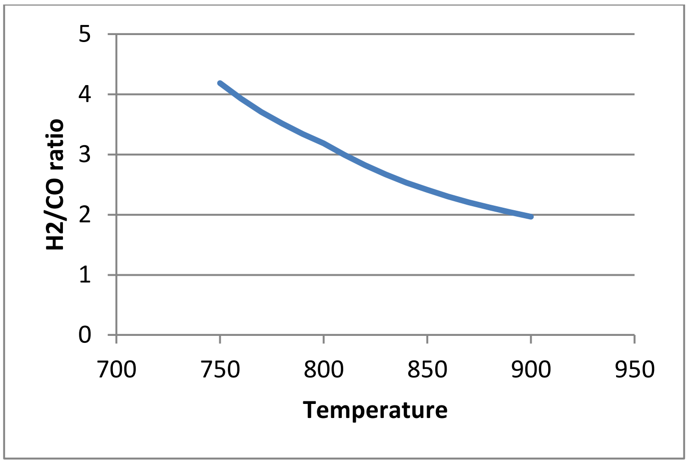


Figure 6.19 $H_2$/CO ratio vs. temperature (optimization of temperature for bio-SNG production)

Although in the first instance may interest lower temperatures because it leads to higher ratio, it should be remember that higher temperatures are required to reach low tar and char content. On the other hand, higher temperatures could produce ash melting in downdraft and updraft fixed bed gasifiers. This can be avoided by keeping the temperature below the melting temperature of the ash. (55)

Therefore, there is not an optimum point, but an optimal range, which could be set approximately from 850 to 900 °C, which is the range in which gasification plants usually work.

### Steam/biomass ratio

Steam/biomass ratio is the last parameter included in this study.

Gasifier temperature has been set at 850 °C.

As the figure 23 shows, steam gasification reaches a maximum of $H_2$/CO ratio when increasing steam/biomass ratio. After the maximum, there is no more hydrogen and carbon monoxide production, but there is a growth in unconverted steam. Moreover, it does not make sense to spend more money feeding more steam if there will not be better results.

Then, the optimum ratio would be approximately 0.6. However, current gasification plants work with higher ratio, between 1-1.3 approximately.

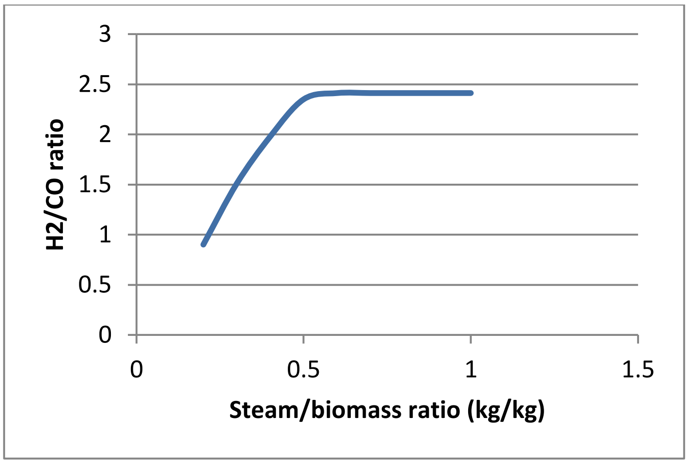


Figure 6.20 $H_2$/CO ratio vs. steam/biomass ratio (optimization of steam/biomass ratio for bio-SNG production)

### 6.3.2 ENERGY PRODUCTION PROCESS

In this case, $H_2$/CO ratio is not the main factor. Energy production plants focus on the Heating Value of syngas, because the more heating value the gas possesses, the more energy can be extracted. However, composition is still something important, because Heating Value depends on the composition. In particular, it depends on methane, hydrogen and carbon monoxide composition. Usually high methane compositions are more interesting because it is the compound with higher heating value.

## Gasification agent

Table 6.2 Operation conditions for optimization of gasification agent (energy production process)

| Gasification Agent | T(°C) | Gasification agent/ biomass ratio | LHV (MJ/m3N) |
|---|---|---|---|
| STEAM | 830 | 0,3 | 12,58 |
| AIR | 830 | 0,2 | 5,82 |
| OXYGEN | 830 | 0,2 | 9,00 |

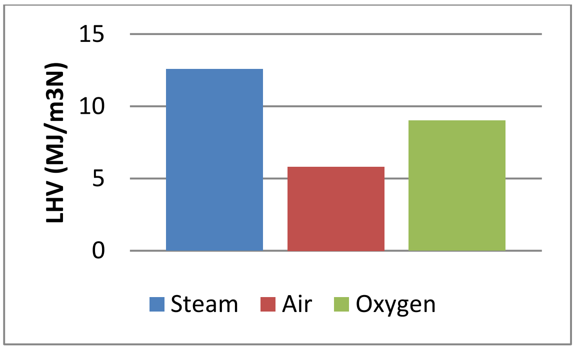


Figure 6.21 LHV for steam, air and oxygen gasification (optimization of gasification agent for energy production process)

Steam gasification produces a medium calorific value gaseous fuel (10-14 MJ/m$^3$N) with high $H_2$ content. Air, by contrast, produces a gas with low calorific value and it contains high nitrogen composition (around 50%). Gas from oxygen gasification has a calorific value that falls between steam and air, due to the lack of nitrogen. [17]

Theoretically steam would be the best option, although air is more widely used nowadays, compared to steam, because of its extensive low-cost availability.

There is another advantage of air against steam: air gasification is an exothermic process, while steam gasification is an endothermic process which requires heat input because heat releases from the partial combustion of the feedstock is not enough to cover the required heat for the gasification process. This means that although steam leads to produce a higher calorific value gas compared to air, it needs extra energy during the process.

Oxygen is rarely used alone, due to its high price, and it is more commonly used together with air or steam. It lets obtain a lower nitrogen content gas in the case of air, and it allows achieve an autothermal gasification process in the case of steam, by adding the required heat through the combustion of unconverted char.

Both cases are going to be studied: air and oxygen (enriched air) and steam and oxygen:

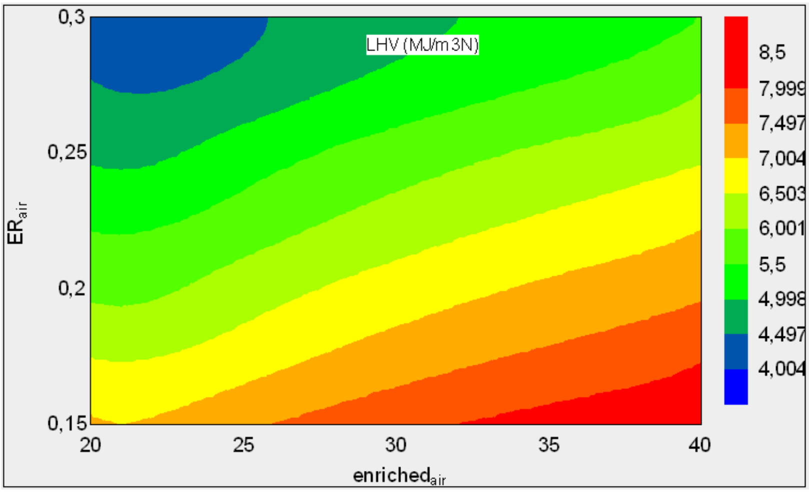


Figure 6.22 LHV vs. ER (air) and %oxygen-enriched air (air-oxygen gasification) (energy production process)

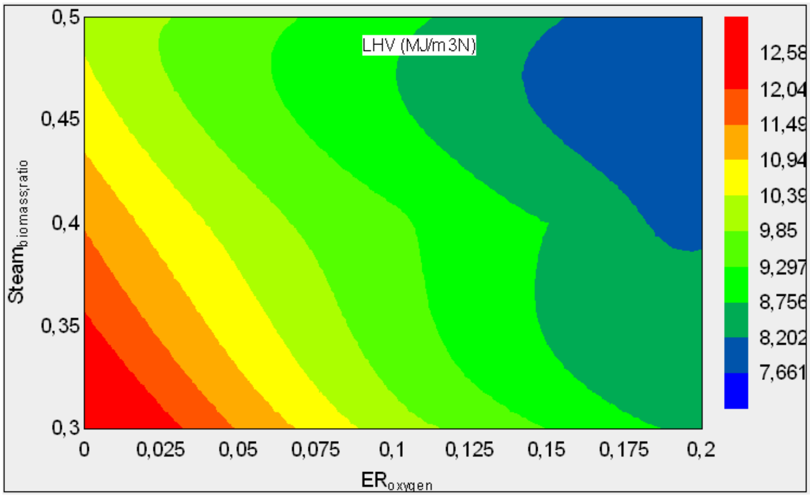


Figure 6.23 LHV vs. steam/biomass ratio and ER (oxygen) (steam-oxygen gasification) (energy production process)

As Figure 6.22 and Figure 6.23 show, the highest value is reached in steam-oxygen gasification. This value is reached with lower amount of oxygen, what means that increases on oxygen leads to a gas with lower heating value. However, the real influence of oxygen on steam gasification is not reflected in the figure, which is the reduction of heat that is required to supply to the gasifier.

On the other hand, oxygen has a positive influence on lower heating value for air gasification. In fact, high contents of oxygen in the air let produce a medium heating value gas (around 8 MJ/m$^3$N).

In order to find the best solution, an economic analysis is required, where initial investment (air or steam and amount of oxygen) and final benefit are taking account to find the optimal solution.

Anyway, oxygen-air gasification has a greater diffusion, so probably it would be the best solution, mainly due to its low price and because it is a simpler process, compared to the steam one.

Once air-oxygen gasification has been chosen, best combination of ER (air) and % of oxygen enriched- air must be found. Equivalence ratio normally varies between 0.2-0.4 for gasification processes. A suitable solution would be the lowest-possible ER values, between 0.2-0.25, and a high percentage of oxygen, around 35-40%, which results in higher calorific value gas.

As regards temperature, no figure is represented because the model does not reflect the real influence of temperature on the process. It supposes that temperature has a weak effect on calorific value gas, which is not correct, mainly because temperature has a strong effect on tar and char conversion, and, as it has already said, these aspects are not considered in the model. Anyway, best choice for bed temperature will be discuss theoretically.

Most plants that use fluidized bed reactor maintain temperature in a range between 850 and 900°C. As it has already explained above, higher temperatures reduce tar content, but they also need more combustion, leaving less material to be gasified. This makes a reduction in the calorific value of the produced gas. Moreover, increasing temperatures may cause problems related with sintering, build-up, erosion, corrosion. Alkaline metals such as potassium may give rise to alkaline silicates and sulfates, which have low melting points, and they may become attached to the reactor walls forming deposits that reduce process efficiency. Furthermore, the presence of these compounds in the syngas may cause problems in the electricity conversion equipment.

# 7. CONCLUSIONS

The global goal of the present project is the study of biomass gasification. Firstly, a study of biomass (characteristics, advantages and disadvantages), gasification technologies available and biomass gasification process has been carried out.

Second part of the project has been the development of the mathematical models. Two thermodynamic models have been built: stoichiometric and pseudo-experimental model. The first one, based solely on reaction constants and mass balance, supposes that thermodynamic equilibrium is reached. The second one has been developed from mass balance and a correlation of $CO/CO_2$ relation, which has been taken from experimental results. Through the introduction of this correlation, the model pretends to obtain results closer to the experimental ones.

Next section corresponds to results. It has been divided in three parts. The first one, comparison of thermodynamic models, aims to choose which model is the best option for a steam gasification process and an air gasification process. For this purpose, both models have been compared, at first, in specific conditions, with results from a steam gasification plant and an air gasification plant, and then, varying operation parameters (temperature and gasification agent/biomass ratio). This first part reflects better results of pseudo-experimental models in the case of steam gasification and better ones of stoichiometric model in the case of air gasification.

Second part of results corresponds to the analysis of the influence of the operation parameters. Temperature, gasification agent/biomass ratio and moisture content in feedstock have been studied.

In the case of steam gasification, increasing steam/biomass ratio, leads to higher $CO_2$ and $H_2$ concentration and lower CO and $CH_4$. In the case of air and oxygen gasification, an increase in ER ratio results in higher $CO_2$ and $H_2O$ concentration, while $CH_4$, CO and $H_2$ concentrations decrease.

Temperature affects in the same way to steam gasification as well as to air and oxygen gasification: higher temperatures provoke a growth in CO and $H_2$, and a reduction in $CH_4$ and $CO_2$.

Last parameter, moisture content in biomass, also has the same impact in both types of gasification (steam, air and oxygen): higher moisture contents lead to higher $CO_2$ and lower CO, $H_2$ and $CH_4$ concentrations. It also affects significantly to Lower Heating Value and chemical efficiency, resulting a decrease in both of them.

Last section is the optimization of operation parameters for a bio-SNG production process and an energy production process.

The main parameter in a bio-SNG production process is the $H_2/CO$ ratio. It has to be maximized to produce high concentration of methane. For this purpose, steam gasification is the best choice. Suitable range of temperatures are between 850 and 900°C, because high temperatures are preferred in order to produce higher $H_2/CO$ ratios and lower tar and char contents, but too high temperature might produce ash melting. Steam/Biomass ratio chosen is 0.6 because it is the lower ratio that let obtaining the highest $H_2/CO$ ratio.

In an energy production process, Lower Heating Value is the parameter that needs to be maximized. In this case, a mixture of air-oxygen gasification is the best choice, with an ER ratio between 0.2 and 0.25 and an oxygen percentage in the air around 35%. Bed temperature is the same as for bio-SNG production process due to the same reasons.

Developed models led to results closer to the experimental ones, especially in typical operation conditions. Future improvement concerning pseudo-experimental model are related with $CO/CO_2$ correlation. It only considers temperature, so an introduction of gasification agent parameter would lead to a significant improvement of the results. As regards stoichiometric model, an introduction of any experimental aspect should be carried out in order to get away from its definition purely theoretical.