TWO STAGE GASIFICATION : EFFECT OF HYDROPYROLYSIS CONDITIONS

G. Skodras and G.P. Sakellaropoulos
Departement of Chemical Engineering and
Chemical Process Engineering Research Institute
Aristotle University of Thessaloniki
Thessaloniki, Greece 54006

SUMMARY

Two-stage hydropyrolysis and CO_2 gasification has been investigated with Greek lignite at various temperatures and residence times in order to indentify optimal conditions for switching between the two steps. Optimality was based on carbon conversion and product formation. Such optimum conditions are obtained for hydrocharing at 900°C for 2 to 5 min and subsequent CO_2 gasification of the resulting chars at 900°C and 10 min.

INTRODUCTION

Hydrogasification is a relatively slow process [1,2], with most hydrocarbons formed in the ealry hydropyrolysis step [2,3]. Carbon dioxide gasification of chars is faster than hydrogasification and can improve conversion and carbon atom utilization. Char gasification in CO_2 has been investigated with respect to carbon reactivity [4,5], kinetic behavior [6], and promotion by catalysis[7]. However, most chars used in CO_2 gasification have been prepared, almost exclusively, in non-reactive atmospheres, such as N_2 or He [4-6]. Little is known about the effect of the initial charring step (pyrolysis or hydropyrolysis) on the reactivity in the second stage and on total carbon conversion and gaseous product formation.

In this work Greek lignite was gasified in a reactive hydrogen atmosphere and subsequently in CO_2, to explore lignite behavior under two stage, ambient pressure gasification. The effect of temperature and solids residence time in each stage on total carbon conversion and on gaseous product yields and selectivity was studied.

EXPERIMENTAL

Greek lignite from the Ptolemais reserve (4 10⁹ t) was used, with particles in the range of 150 to 250 μ. This lignite is high in calcium carbonate ash and humidity and has a volatiles content of 47.16% (on dry basis).

The gasification test reactor was equipped with gas and solids feeding controls and with product collection and analysis devices, Fig. 1. The U-shape reactor design permitted rapid quenching of the reactor, thus, hydropyrolysis or CO_2 gasification reactions could be interrupted at any desirable time.

Lignite samples were initially hydropyrolyzed (800°C or 900°C, at 2, 5 or 10 min) and the produced chars were gasified under a CO_2 atmosphere (800°C or 900°C, at up to 15 min). Gaseous products were collected in both stages, and were analyzed mainly for CH_4 and CO by G.C. (Varian Vista 6000). Chars obtained in the hydropyrolysis and the CO_2 gasification step were analyzed by a LECO C-H-N 800 analyzer, in order to determine elemental compositions and conversions in each step.

RESULTS AND DISCUSSION

During the first stage (hydropyrolysis), the devolatilization and hydrocracking reactions which take place [3,8] cause significant

weight loss. On a dry and ash free basis, weight losses are of the order of 62% at 800°C, reaching about 67% at 900°C and long residence times. Since the initial volatile matter of lignite is 47% w/w on a dry basis, devolatilization appears to be the main reaction during this first stage [3,8,9]. The heterogeneous carbon-hydrogen gas-solid reaction becomes significant only at longer solid residence times (>10 min).

Methane, CO and CO_2 are the main gaseous products during this first stage, Tables 1 and 2. Maximum CH_4 formation is observed at 900°C and 10 min, via the heterogeneous hydrogen-carbon gas-solid reaction. In contrast, $CO+CO_2$ yields are less affected by the hydropyrolysis residence time, since these are products of hydropyrolysis and hydrocracking reactions during the initial 2 min of pyrolysis. The yield of CO, however, increases appreciably (about 60%) with temperature, from 800°C to 900°C, while that of CO_2 drops to about one third, due to enhacement of the CO_2 reduction to CO in a H_2 atmosphere [3]. Other hydrocarbons (C_2H_4, C_2H_6 etc) are also produced in small quantities (1 to 12 cc/g lign. daf), Table 1 and 2.

In order to evaluate the significance of each product at the various conditions tested a "selectivity index" has been used, shown in Table 1 and 2. To calculate the selectivity of the gaseous products, other higher molecular weight products have been assumed to be insignificant compared to CO, CO_2, CH_4, C_2H_4 and C_2H_6. Increase of solid residence time at low hydropyrolysis temperature (800°C) almost doubles the CH_4 "selectivity index" (8.15% at 2 min, and 15.7% at 10 min), Table 1. Similar behavior is also exhibited by CO selectivity for both hydropyrolysis temperatures. In contrast, CO_2 selectivity decreases with an increase of hydropyrolysis time and temperature. This is particularly evident by the relative selectivity of CO and CO_2 expressed as the ratio CO/CO_2, Tables 1 and 2. Thus, high T and long times minimize CO_2 formation while total ($CO+CO_2$) selectivity decreases somewhat.

The elemental analyses of chars prepared at 800°C and 2,5 or 10 min show that elemental carbon conversion is rather low in this stage, Table 3. Increase of hydropyrolysis temperature to 900°C improves the elemental carbon conversion, which reaches 51.5% for 10 min solid residence time, Table 3. This improvement results from enhacement of the devolatilization and hydrocracking reactions with temperature. Elemental H and O conversions, are in all cases high (84-96% w/w), Table 3. Thus, during hydropyrolysis, cleavage of oxygen containing groups occurs. In the same period, cleavage and release of aliphatic and aromatic groups take place [8], resulting in high hydrogen conversion (84-96% w/w). The chars formed are, hence, rich in carbon and ash.

In the second stage, the carbon-carbon dioxide gas-solid reaction is practically the only one taking place, since the volatile matter has been almost completely removed during hydropyrolysis [8,9]. Traces of hydrocarbons detected in this stage, come from residual volatiles of the original lignite.

Conversion of organic matter (essentially C-conversion) in the second stage depends on the history of the char and on the conditions of CO_2 gasification, ie temparature and residence time. Increase of the solids residence time at low temperature (800°C) hydropyrolysis, increases conversion in the second stage, Fig 2. In contrast, at high

hydropyrolysis temperature (900°C) and solid residence time. conversion in CO_2 gasification decreases, Figs 2 and 3.Thus, chars prepared by hydropyrolysis at low T and residence time (800°C/2-5 min) yield 29% C-conversion when gasified in CO_2 at 800°C and 5 min, Fig 2.As the residence time in hydropyrolysis stage increases, more active sites are formed in the char, capable of further reaction with CO_2, thereby increasing C-conversion, Fig 2,3.For the same hydropyrolysis char, conversion increases by 20 to 30% with increasing residence time in CO_2 gasification.

Similar behavior is also exhibited by hydrochars prepared at 900°C However, CO_2-gasification of these chars yields lower conversions in the second stage, as compared with chars prepared at 800°C and 10 min, Fig 2,3.Conversion in CO_2 gasification decreases further with an increase in hydropyrolysis solid residence time, for chars prepared at 900°C, Fig 2.This is probably due to active site deactivation, occuring at high hydropyrolysis temperatures (900°C) and long residence times,[10-12] cf Fig 2,3 .

Formation of CH_4 and other hydrocarbons practically stops during CO_2 gasification of the chars.Hydropyrolysis chars react in the second stage according to the Boudouard reaction, and produce CO which is the main gaseous product, Figs 4 and 5.We should note here that second-stage product yields are presented per gram of initial lignite (daf), permiting direct comparison of yields between the two stages. Carbon monoxide formation in the second stage, improves with hydrochars obtained at 800°C and long residence time, Fig 4 and 5. However, chars prepared at 900°C and long residence times yield low CO product by CO_2 gasification, Fig 4 and 5, due to active site deactivation under such conditions.These results are in good agreement with the observed C-conversions discussed previously.Such agreement should be anticipated since CO is formed by char reaction with CO_2 in the second stage.

Elemental carbon conversion of CO_2 gasification chars at 800°C or 900°C and 5 min residence time, is rather low and incomplete (29 -46% w/w), Fig 6.The increase of second stage solid residence time improves elemental C-conversion for both CO_2-gasification temperatures (800°C & 900°C), Fig 6.It should be noted here that second stage elemental C-conversion values at 900°C are higher than at 800°C, Fig 6, due to enhacement of the Boudouard reaction rate with increasing temperature.

Similar to weight loss, elemental C-conversion in the second stage depends on the history of the char, ie hydropyrolysis temperature and residence time.Increase of the solid residence time at low temperature (800°C) hydropyrolysis, increases elemental carbon conversion in the second stage, Fig 6.In contrast, at high hydropyrolysis temperature (900°C), and long solid residence time, second stage elemental C-conversion decreases, Fig 6.This behavior is in agreement with the previously discussed active carbon deactivation at high hydropyrolysis temperatures and times.

From Figs 2-5 it is apparent that an optimum hydropyrolysis temperature and residence time should exist, which, combined with CO_2 gasification, leads to maximum carbon conversion.The optimum corresponds to hydrogasification at 900°C and 2 to 5 min.Thus, a hydropyrolysis char, obtained at 900°C/2 min, reacted with CO_2 at 800°C and 10 min, gives a maximum total carbon conversion of about

88%.For CO_2 gasification at 900°C and 10 min total C-conversion reaches 98%.At other temperatures and residene times, overall conversions are somewhat lower (84-95%), at longer times (15-20 min).

These results suggest that hydropyrolysis at 900°C and 2 to 5 min generates more active sites in the lignite matrix than hydropyrolysis at 800°C at the same residence time, resulting in higher second-stage char conversions.However, prolongation of the residence time (10 min) at lower hydropyrolysis temperature (800°C) improves C-conversion in the second stage, Fig 2.Thus, total C-conversion of hydrochars prepared at 800°C/10 min is comparable to that of chars obtained at 900°C/2 min.This indicates that similar amounts of active sites exist in the lignite matrix of these two chars, further supporting the notion of deactivation at high hydropyrolysis temperature and long time.

The above comments on optimality are based solely on total carbon conversion.However, selection of optimum operating conditions should also take into account the yields of gaseous products.Thus, maximum CH_4 production is observed for samples hydropyrolyzed at 900°C and 10 min. This maximum should be anticipated, since CH_4 formation via the heterogeneous carbon-hydrogen gas-solid reaction becomes significant for long hydropyrolysis times.Maximum CO production is observed for chars hydropyrolyzed at 900°C and 2 min and subsequently gasified in CO_2 at 900°C and 10 min (about 1700 cm^3 CO/g lignite daf).Maximum total carbon conversion (97.8% w/w) is also observed at these conditions.Thus, optimum conditions for carbon conversion coincide with these for CO formation.However, maximum CH_4 production appears at somewhat different conditions.

ACKNOWLEDGEMENT

The authors wish to thank the European Coal and Steel Community and the Chemical Process Engineering Research Institute for financial support of this work.

REFERENCES

1. Kokorotsikos,P.S.,Stavropoulos,G.G.,Sakellaropoulos,G.P, Proc. 1985 Int. Conf. Coal Science, Sydney, Oct. 1985,253.
2. Kokorotsikos,P.S.,Stavropoulos,G.G.,Sakellaropoulos,G.P., Proc. Int. Symp. on "Fundamentals of Catalytic Carbon and Coal Gasification", FUNCAT COGAS 86, Rolduc, The Netherlands, May 1986,327.
3. Sakellaropoulos,G.P., Kokorotsikos,P., Korili,S., Stavropoulos, G.,"Catalytic Gasification of Lignites for Synthetic Fuels", Final Report, Contr. No 7220,EC/701, Thes/niki, October 1987.
4. Adanez, J., Miranda, J.L. and Gavilan, J.M., Fuel, 1985, 64, 801.
5. Koening,P.C.,Squires,R.G. and Laurendeau,N.M., Fuel,1986,65, 412.
6. E. Hippo and D.L. Walker, Jr., Fuel, 1975, 54, 245.
7. Sams, D.A. and Shadman, F., AIChE J., 1986, 32, 1132.
8. Anthony, D. and Howard, J.B., AIChE J., 1976, 22, 625.
9. Gavalas, G.R., "Coal Pyrolysis", Elsevier, NY 1982.
10. Johnson,J.L.,"Kinetics of Coal Gasification",J.Wiley & Sons Inc, NY 1979.
11. P. Ehrburger, F. Louys and J. Lahaye, Carbon, 1989, 27, 389.
12. Elliot, M.A. "Chemistry of Coal Utilization", Second Supplementary Volume, J Wiley and Sons, NY 1981.

Table 1 : Total gaseous products during hydropyrolysis at 800°C

Product	cm^3 /g lignite d.a.f. *					
	800°C/2 min		800°C/5 min		800°C/10 min	
	Yield	Selectivity(%)	Yield	Selectivity(%)	Yield	Selectivity(%)
CH_4	26.6	8.2	42.5	11.8	68.4	15.7
C_2H_4	6.5	2.0	8.0	2.2	14.0	3.3
C_2H_6	1.5	0.5	2.0	0.6	2.3	0.5
CO	128.0	39.1	139.0	38.4	236.0	54.3
CO_2	164.0	50.3	170.0	47.1	114.0	26.2
$CO+CO_2$	292.0	89.4	309.0	85.5	350.0	80.5
CO/CO_2		0.8		0.8		2.1

Table 2 : Total gaseous products during hydropyrolysis at 900°C

Product	cm^3 /g lignite d.a.f. *					
	900°C/2 min		900°C/5 min		900°C/10 min	
	Yield	Selectivity(%)	Yield	Selectivity(%)	Yield	Selectivity(%)
CH_4	52.3	11.6	72.2	14.4	77.1	14.8
C_2H_4	11.8	2.6	12.0	2.4	12.7	2.4
C_2H_6	0.8	0.2	1.0	0.2	1.2	0.2
CO	306.0	67.7	337.0	67.2	378.0	72.4
CO_2	81.0	17.9	80.0	15.9	53.0	10.2
$CO+CO_2$	387.0	85.6	41.7	83.0	431.0	82.8
CO/CO_2		3.8		4.2		7.1

Table 3 : Composition and conversion of hydropyrolysis chars

Sample Code	Temp/Time (°C,min)	Weight loss (% w/w)	Char Composition (% w/w)					Elemental conversion (Ci)% w/w			
			C	H	N	ASH	O	C_c	C_H	C_N	C_O
TS1a	800/2	48.10	55.74	1.21	1.18	31.97	9.30	38.60	86.60	51.80	83.50
TS2a	800/5	49.20	57.80	0.93	1.19	32.69	8.92	37.90	89.90	52.40	88.00
TS3a	800/10	51.70	55.04	1.22	0.66	34.35	8.13	43.60	87.40	74.90	86.60
TS4a	900/2	54.10	54.21	0.42	1.27	36.15	7.35	47.20	95.90	54.10	88.50
TS5a	900/5	55.00	54.72	0.51	1.01	36.92	6.24	48.80	95.10	64.20	90.40
TS6a	900/10	56.70	52.84	0.44	1.15	38.33	6.24	51.50	95.90	60.80	90.20

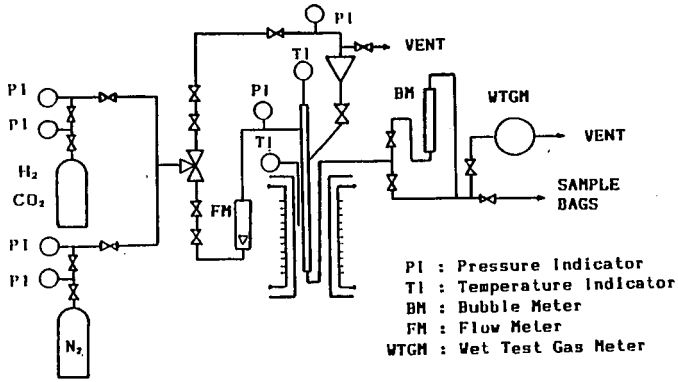

Figure 1 : Flow diagram of a rapid quenching gasification system.

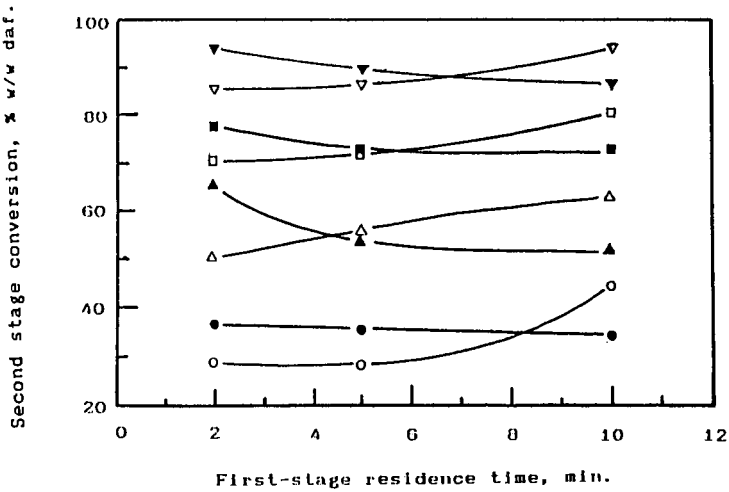

Figure 2 : Effect of hydropyrolysis temperature and residence time on weight loss during CO_2 gasification. Open points: hydropyrolysis at 800°C; closed points: hydropyrolysis at 900°C. CO_2 gasification: ○ ● : 800°C/5 min, △ ▲ :800°C/10 min, □ ■ : 900°C/5 min, ▽ ▼ : 900°C/10 min.

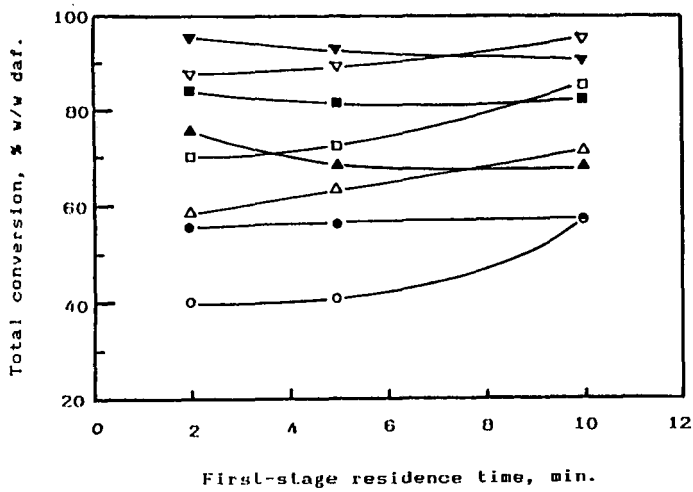

Figure 3 : Effect of hydropyrolysis temperature and residence time on total weight loss. Open points: hydropyrolysis at 800°C; closed points: hydropyrolysis at 900°C. CO_2 gasification: o ● : 800°C/5 min, △ ▲ : 800°C/10 min, □ ■ : 900°C/5 min, ▽ ▼ : 900°C/10 min.

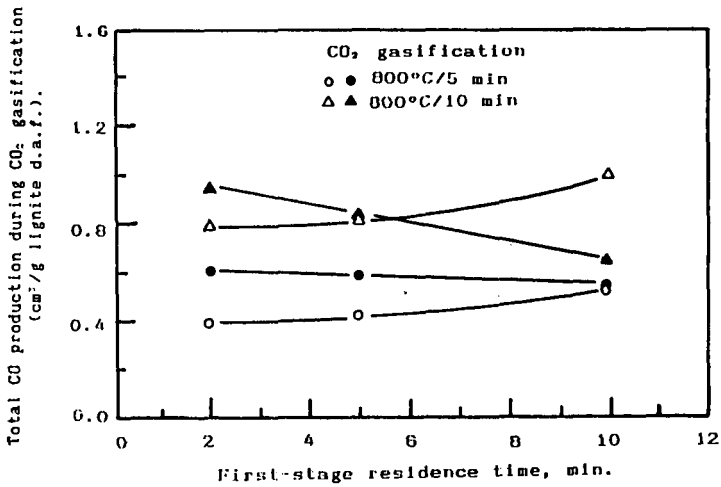

Figure 4 : Effect of hydropyrolysis temperature and residence time on total CO production, during CO_2 gasification at 800°C. Open points: hydropyrolysis at 800°C; closed points: hydropyrolysis at 900°C.

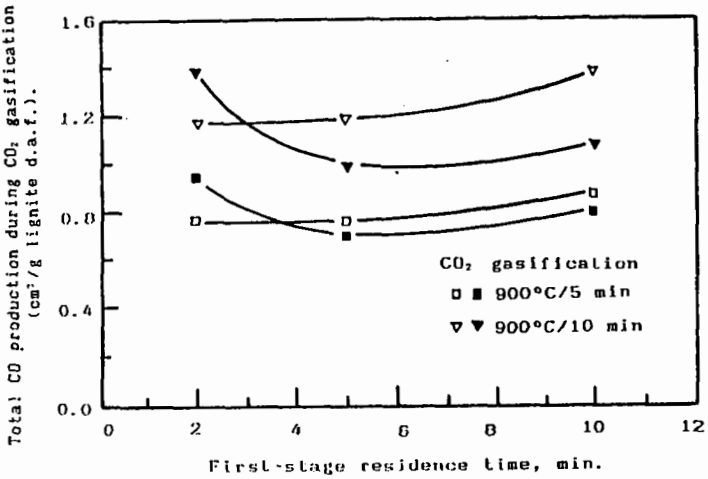

Figure 5 : Effect of hydropyrolysis temperature and residence time on total CO production, during CO_2 gasification at 900°C. Open points: hydropyrolysis at 800°C; closed points: hydropyrolysis at 900°C.

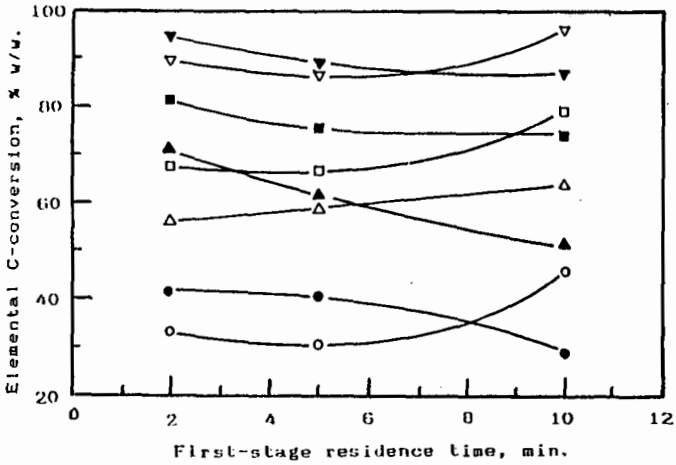

Figure 6 : Effect of hydropyrolysis temperature and residence time on elemental C-conversion during CO_2 gasification. Open points: hydropyrolysis at 800°C; closed points: hydropyrolysis at 900°C. CO_2 gasification: ○ ● : 800°C/5 min, △ ▲ :800°C/10 min, □ ■ : 900°C/5 min, ▽ ▼ : 900°C/10 min.