DDGS chars gasification with CO₂: a kinetic study using TG analysis

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Abstract Dry Distiller's Grains with Solubles (DDGS) is a by-product during ethanol production from cereals which is currently mainly used as feedstock for cattle. With the growth of the ethanol industry, the increasing supply of DDGS may saturate the livestock feed market; thus, its potential applications need to be explored. DDGS gasification in a 100-kW_{th} circulating fluidized bed (CFB) steam-O₂ blown gasifier has been studied. However, the modeling of DDGS gasification process encounters difficulties due to the unavailable knowledge of DDGS char gasification kinetics. Therefore, in this paper, gasification kinetics of DDGS char with CO₂ was investigated using thermogravimetric analysis (TGA). Two different types of char samples have been tested. Char type one (PYR-Char) was obtained after DDGS pyrolysis in a TGA at a final temperature of 750°C or 850°C for 20 min. Char type two (CFB-Char) was obtained after DDGS gasification in the 100-kW_{th} CFB gasifier within the temperature range of 790°C to 820°C with a steam/biomass mass ratio of 0.81 and oxygen to biomass stoichiometric ratio of approximately 0.38. The influences of pyrolysis temperature (750°C, 850°C), heating rate (10°C/min, 30°C/min, 50°C/min, 70°C/min), CO₂ concentration (10, 20, 30 vol.%), and gasification temperature (900°C, 1,000°C, 1,100°C) on the reaction rate of char-CO₂ reaction were determined. Two representative gas-solid reaction models, the volumetric reaction model (VRM) and the shrinking core model (SCM) were applied in order to determine kinetic parameters. It was found that the calculated activation energy (E_a) values using SCM

were slightly lower than those using VRM. The calculated E_a values for PYR-Char using both models were in the range of 100–165 kJ/mol, while the calculated E_a values for CFB-Char were in the range of 55–100 kJ/mol. It was observed by scanning electron microscopy (SEM) that CFB-Char was more fragile and PYR-Char obtained at lower heating rate had a less porous structure. Generally, the predicted results using both models showed a fairly good agreement with experimental results, and SCM model suited slightly suitable better for char gasification at high temperature.

Keywords Thermogravimetric analysis · Dry Distiller's Grains with Solubles · Char gasification · Volumetric reaction model · Shrinking core model

1 Introduction

Fossil fuels are non-renewable, and their massive utilization causes many environmental problems associated with CO₂ emission. Biomass fuels are a potential source of alternatives to increase energy independence and reduce environmental pollution. Biomass can be converted into more valuable energy via either biochemical (fermentation, hydrolysis) or thermochemical conversion (pyrolysis, combustion, and gasification) technologies [1, 2]. Biomass gasification has received the highest interest since it offers high system efficiency and increases options for combination with various power generation systems using gas engines, gas turbines, and fuel cells [3]. Char gasification reactions like the Boudouard reaction ($C + CO_2 = 2CO$) is the rate-limiting step during biomass gasification [4]. Therefore, a good understanding of char gasification kinetics is essential for the effective modeling and operation of gasification processes.

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Dry Distiller's Grains with Solubles (DDGS) is a non-fermentable byproduct of ethanol production. During the past decade, the global production of bioethanol increased from 17 billion liters in 2,000 to more than 46 billion liters in 2007, whereas in the USA alone, ethanol production increased from about 6.5 billion liters in 1999 to more than 39 billion liters in 2009 [5, 6]. The Renewable Fuels Association recently reported that the USA exported 397 million gallons of ethanol in 2010, which is nearly a 400% increase over 2009, and accompanied with the ethanol industry nine million metric tons of DDGS were also exported, which is a 60% increase over 2009 [7]. Driven by the mandate of the Renewable Fuels Standard II, ethanol and DDGS production will continue to grow until 2015 [8]. Currently, most of the DDGS is used primarily as a feed supplement and is an important product for the livestock and dairy industries. US Grains Council reported that the US domestic market demand for DDGS is becoming more and more saturated and needs to find potential for the export market to avoid the adverse effect on ethanol production [8]. Otherwise, as the supply for DDGS increases, ethanol plants must discount the price to persuade end-users to increase DDGS use for their cattle, swine, or poultry ratio. Therefore, the potential of DDGS for gasification to produce gaseous fuel has been investigated by Kumar et al. [1], Tavasoli et al. [9], and Meng et al. [10]. Liu et al. [11] studied the pyrolysis and oxidation kinetics of distiller's grains and solubles (DGS) using thermogravimetric analysis (TGA). They reported that DGS residue had similar drying characteristics in both N_2 and air. The determined activation energy (E_a) of DGS during dry pyrolysis in N_2 and oxidization in air were in the range of 18 to 36 and 10 to 60 kJ/mol. Giuntoli et al. [12] studied pyrolysis kinetics of DDGS and reported that DDGS mainly released NH_3 and HCN with a minor release of HNCO which mainly came from proteins.

Gasification kinetics of various biomass chars with CO_2 such as wood [13, 14], cotton wood [15], Douglas fir [15, 16], Eucalyptus wood [17], rice husk [18], olive residue [19], beech wood char and oil palm shell [20], olive husk and pine seed shells [21], and pine and birch [22] have been investigated. Various mathematical models like the random pore model (RPM), volumetric reaction model (VRM), and shrinking core model (SCM) as well as the Langmuir–Hinshelwood model (LHM) have been also applied in order to determine kinetic parameters. Bhat et al. [18] reported that VRM and SCM agreed well. Ollero et al. [19] reported that the LHM fitted well in the presence of CO . Lee and Kim [23] and Murillo et al. [24] studied gasification kinetics of waste tire char with CO_2 using the SCM, VRM, and the modified VRM models. Matsumoto et al. [25] investigated gasification kinetics of four Japanese wood chars with CO_2 using the RPM by considering surface porosity, constant particle size, and specific surface area. Seo et al. [26]

reported that RPM predicted the experimental data better than the SCM and VRM. Fierro et al. [27] reported that the LHM better fitted the reactivity data for char gasification at atmospheric and at elevated pressures. Kinetic parameters and gasification conditions of above-stated literature are summarized in Table 1, where it can be seen that there is a significant variation among kinetic parameters reported by different researchers depending on biomass fuel types, gasification conditions, and model types used.

Currently, only few data are available in the literature regarding gasification kinetics of DDGS char. In order to offer reliable kinetic data for the modeling DDGS gasification in a 100-kW_{th} circulating fluidized bed (CFB) steam- O_2 blown gasifier for syngas generation studies, the gasification reaction kinetics of DDGS chars with CO_2 have been investigated using TGA. The aims of this work are to study the influences of pyrolysis temperatures, heating rates, gasification temperature, and CO_2 concentrations on gasification kinetics of DDGS chars. As conversion models, VRM and SCM were applied to determine the kinetic parameters, since these two model can be easily coupled together with other reaction rates (e.g., homogenous reactions occurring during gasification) for further reactor modeling.

2 Experimental setup and char samples

2.1 Char samples preparation

ATA Instruments TGA Q600 apparatus has been employed to conduct all isothermal char gasification experiments. This apparatus is capable of providing a simultaneous measurement of heat flow and weight change on the same sample from ambient temperature ($\sim 20^\circ C$) to $1,500^\circ C$. A separate Inconel 600 tube permits introduction of reactive gases into the sample chamber [28]. DDGS used for this study was obtained from Lantmännen, Sweden. Two different types of char samples have been tested. Char type one (PYR-Char) was prepared under the following conditions: after the instrument was tarred to zero, around 20 mg ground DDGS was loaded into an alumina crucible, and then heated up using different heating rates (HR= $10^\circ C/min$, $30^\circ C/min$, $50^\circ C/min$, $70^\circ C/min$) and finally pyrolyzed at a temperature of $750^\circ C$ or $850^\circ C$ ($T_{Pyr}=750^\circ C$, $850^\circ C$) for 20 min in an N_2 inert atmosphere. Char type two (CFB-Char) was obtained after DDGS gasification in the 100-kW_{th} CFB steam- O_2 blown gasifier within the temperature range of $790^\circ C$ to $820^\circ C$ with a steam/biomass mass ratio of 0.81 and oxygen to biomass stoichiometric ratio of approximately 0.38. The particle size distribution of the char samples was performed by using a Microtrac S3500 series particle size analyzer. The particle size distribution was determined as well as proper images of very small particles to be seen. It was found that around

Table 1 The kinetic parameters and gasification conditions presented in the literature

Reference Number	Char type	Kinetic model	Kinetic parameters		Gasification condition	
			E_a (kJ/mol)	n	Temperature (°C)	Setup
13	Wood	A local volumetric rate model	217	0.6	800–1,100	Quarts container
14	Wood	SCM	210	0.71	900–1100	Tube furnace
15	Douglas Fir Cottonwood	VRM	220	0.6	700–900	Chamber furnace
			196	0.6		
16	Douglas Fir	RPM	–	–	700–1100	PTGA
17	Eucalyptus wood	–	230–261	–	775–850	TGA
18	Rice husk grain	VRM	200	1	750–900	TGA
	Rice husk power	VRM	197	1		
	Rice husk power	SCM	83	1		
19	Olive residue	<i>n</i> th order model	133	0.43	800–950	TGA
20	Beech wood	LHM	200	–	720–730	TGA
	Oil palm shell		300	–	730–780	
21	Olive husk	<i>n</i> th order model	230	0.5	750–910	TGA
	Pine seed shells		245	0.59		
	Wood chips		298	0.64		
22	Pine and birch	<i>n</i> th order model	262–263	0.4	600–1000	TGA
23	Waste tire	The modified VRM	238	0.68	850–1000	Thermo-balance reactor
24	Waste tire	VRM	191.79	0.7	850–1000	Thermo-balance reactor
		The modified VRM	191.40	0.5		
		SCM	197.45	1		
		RPM	197.70	1		
25	Japanese wood	RPM	94	0.22	900–1200	drop tube furnace
26	Pinus densiflora for Multicaulis	VRM	172	–	850–1050	Fixed bed reactor
		SCM	142	–		
		RPM	134	–		
27	Pinus elliotii	VRM	184	0.33	750–900	PTGA
		SCM	185			
		RPM	184			

30%, 50%, 70%, and 90% of the particles had a diameter below 0.13, 0.26, 0.5, and 0.9 mm, respectively. Some main properties of DDGS and char samples are listed in Table 2.

2.2 Char gasification procedures

A schematic diagram of the experiment setup is shown in Fig. 1. For PYR-Char, the experimental procedures used to perform char gasification in the TGA are as follows:

1. Under N_2 using a flow rate of ± 100 ml/min supplied via a primary gas supply line, the temperature was equilibrated at 35°C for 20 min.
2. In N_2 atmosphere, heating from 35°C to 750°C or 850°C at a constant rate of 10°C/min, 30°C/min, 50°C/min, or 70°C/min

3. Isothermal at 750°C or 850°C for 20 min to ensure that the sample was completely pyrolyzed
4. Introduction of pure CO_2 via a second gas supply line which was further mixed with N_2 from primary gas supply line to achieve different CO_2 concentrations ($CO_2=10, 20$, or 30 vol.%) and rapidly heated up to the desired gasification temperatures ($T_{Ga}=900^\circ C, 1,000^\circ C$, or $1,100^\circ C$)
5. Isothermal temperature at 900°C, 1,000°C, or 1,100°C for 20 min for char gasification

Since DDGS CFB-Char was released from the devolatilization and gasification process during DDGS gasification in the CFB gasifier to simulate this rapid heating up environment, a different temperature program has been

Table 2 DDGS and char sample properties

Types of fuel	Moisture (wt.% a.r.)	Volatile matters	Fixed carbon	Ash content
DDGS	12	67.2	15.5	4.82
CFB-Char	5–10	10–20	55–65	15–30
	C	H	O	N
DDGS	48.2	6.54	31.2	5.52
CFB-Char	66.5	–	18.8	–
	K ₂ O	Na ₂ O	MgO	CaO
DDGS-Ash	38.1	10	8.9	2.9

applied to DDGS CFB-Char. After around 10 mg char sample was loaded into an alumina crucible, the temperature was increased from ambient temperature (~20°C) to 850°C as fast as possible (around 4 min) under N₂ of a flow rate of ±100 ml/min and then the isothermal at a temperature of 850°C for 20 min to ensure that residual volatiles were completely released. The following steps were kept the same as PYR-Char (steps 4–5).

2.3 Kinetic models of data analysis

The VRM and SCM models were applied to DDGS char gasification with CO₂ to determine Arrhenius kinetic parameters. The VRM assumes that the char particle reacts homogeneously with CO₂ and that the particle size remains constant while the density decreases during the reaction [24]. The SCM assumes that the reaction initially occurs at the external surface of char and gradually CO₂ diffuses through the gas film and the ash layer and reacts on the unreacted core surface, which keeps on shrinking but always exists during the reaction progress [18, 23]. The overall reaction rates for VRM and SCM are expressed in Eqs. 1 and 2, where X , K_{VRM} and K_{SCM} , n , and C_{CO_2}

represent char reaction ratio (–), the reaction rate constant of VRM and SCM, the reaction order (–), and concentration of CO₂ (vol.%), respectively. K_{VRM}/K_{SCM} and X were calculated using Eqs. 3 and 4, where k_0 , E_a , R_g , and T represents the pre-exponential factor (s^{–1}), the activation energy (J/mol), universal gas constant (8.314 J/(mol·K)) and reaction temperature (K), and m_0 , m_t , and m_f represent the initial char weight, the char weight at time t , and the residue char weight, respectively.

$$\frac{dX}{dt} = K_{VRM}(1 - X)C_{CO_2}^n \quad (1)$$

$$\frac{dX}{dt} = 3K_{SCM}(1 - X)^{\frac{2}{3}}C_{CO_2}^n \quad (2)$$

$$K_{VRM}(\text{or } K_{SCM}) = k_0 \exp\left(\frac{-E_a}{R_g T}\right) \quad (3)$$

$$X = \frac{m_0 - m_t}{m_0 - m_f} \quad (4)$$

Fig. 1 Schematic diagram of the experiment equipment setup

3 Results and discussion

3.1 Effects of different parameters on conversion rate

Figure 2 shows the PYR-Char conversion rate versus time curves at different heating rates (10°C/min, 30°C/min, 50°C/min, 70°C/min) at two fixed gasification temperatures (900°C, 1,100°C) with 10 vol.% CO₂. It can be seen that a higher heating rate during pyrolysis generally enhanced PYR-Char conversion rate. When the heating rate was increased from 10°C/min to 70°C/min, the conversion rate of PYR-Char at 900°C within 20 min increased from 50% to 85%. These observations agreed with those obtained from willow PYR-Char [29]. However, an increase in the heating rate from 10°C/min to 30°C/min almost did not affect the conversion rate neither at 900°C nor at 1,100°C.

Fig. 2 Effects of different heating rates on PYR-Char conversion rate

From this, it can be seen that under similar conditions, DDGS PYR-Char was less reactive than willow PYR-Char, and also, its char reactivity was less affected by low range heating rate change.

Figure 3 shows the PYR-Char conversion rate versus time curves at different pyrolysis temperatures (750°C, 850°C) at two fixed heating rates (10°C/min, 70°C/min) with 10 vol.% CO₂. It can be seen that PYR-Char obtained at the pyrolysis temperature of 750°C was slightly more reactive than chars obtained at 850°C. However, the influence of pyrolysis temperature on the conversion rate became negligible for PYR-Char obtained at 70°C/min and further gasified at 1,100°C. From this observation, it can be derived that the char reactivity can be enhanced by lowering pyrolysis temperature or increasing heating rate.

Figure 4 shows the PYR-Char conversion rate versus time curves at different CO₂ concentrations (10, 20, and 30 vol.%)

Fig. 3 Effects of pyrolysis temperatures on PYR-Char conversion rate

Fig. 4 Effects of gasification temperatures and CO₂ concentrations on PYR-Char conversion rate

and different gasification temperatures (900°C, 1,000°C, 1,100°C) of a heating rate of 10°C/min. It can be seen that gasification temperature significantly affected PYR-Char conversion rate. No PYR-Char samples completely reacted at 900°C, but all PYR-Char samples reacted completely at 1,100°C even with 10 vol.% CO₂. With 10 vol.% CO₂, the PYR-Char conversion rate increased sharply from 50% to 100% with increasing temperature from 900°C to 1,100°C. Higher CO₂ concentration increased all PYR-Char conversion rate. When the CO₂ concentration was increased from 10 to 30 vol.%, the PYR-Char conversion rate gasified at 900°C increased sharply from 50% to more than 90%. Furthermore, from Fig. 4, it can be clearly seen that with higher CO₂ concentrations at higher temperature, DDGS PYR-Char firstly reacted very fast then slowed down, probably due to an increase of the ratio of ash to unreacted char sample. This observation was not found during willow PYR-Char gasification [29].

Fig. 5 Effects of gasification temperatures and CO₂ concentrations on CFB-Char conversion rate. a (50 μm) b (50 μm). c (100 μm) d (10 μm)

Fig. 6 SEM photographs of PYR-Char obtained from pyrolysis temperature of 850°C with 10°C/min (a) and 70°C/min (b), and CFB-Char (c, d)

The gasification temperature and CO₂ concentration had a similar influence on DDGS CFB-Char which can be seen in Fig. 5. CFB-Char was more reactive at lower temperature than PYR-Char and completely reacted under all reaction conditions. Scanning electron microscopy (SEM) photographs of PYR-Char obtained from pyrolysis temperature of 850°C with heating rate of 10°C/min and 70°C/min and CFB-Char are shown in Fig. 6. It can be seen that PYR-Char obtained at 10°C/min was less porous, while such char obtained at 70°C/min had some condensation on the surface and DDGS CFB-Char was very fragile and also observed condensation on char surface.

There were no results available in the literature to compare the results obtained from this work. Since DDGS is one kind of agriculture residue, its char gasification behavior can be explained by the results obtained from biomass derived char gasification. According to Di Blasi [4], the char conversion rate is critically determined by several fundamental factors, represented by surface area, surface accessibility, carbon

active sites, and catalytic active sites created by indigenous or added inorganic matter and the local gaseous reactant concentration. Therefore, an enhancement in the char conversion rate is ultimately due to an improvement of these factors. Standish and Tanjung [14] reported that incomplete char reaction at lower CO₂ concentration was due to possible reduction of active site density by available N₂ high concentration around. Feroso et al. [27], Ashu et al. [30], Kumar and Gupta [31, 32], and Lu et al. [33] reported that an increase in pyrolysis temperature substantially decreased the char reactivity because char structures such as amorphous concentration, aromaticity, and crystallite size became more ordered at higher temperatures thus lowering the concentration of reaction sites. Okumura et al. [16], Chen et al. [34], Cetin et al. [35], Guerrero et al. [36], Kurosaki et al. [37], and Mermoud et al. [38] reported that char obtained at high heating rate possessed higher reactivity than chars obtained at low heating rate, which is because chars obtained at high heating rate during pyrolysis generally had sparse, large

Table 3 The calculated values for estimating possible limitation effects of mass and heat transfer

	PYR-Char (VRM)	PYR-Char (SCM)	CFB-Char (VRM)	CFB-Char (SCM)
C_{wp}	9.25E-03	6.81E-03	6.64E-03	4.98E-03
k_{ex}	9.01E-03	4.89E-03	4.65E-03	2.61E-03
k_{heat}	2.61E-05	1.37E-05	8.67E-06	4.74E-06

Fig. 7 $-\ln(1-X)$ versus time for PYR-Char at different temperatures and CO_2 concentrations

internal cavities, and macropores structure and/or a higher concentration of active sites. Fushimi et al. [39] reported that the increase in the maximum rate of weight loss and volatile yield observed at high heating rate during pyrolysis also shortened tar vapors residence time in the pores, thus reducing the activity of condensation reactions and preventing char agglomeration and condensation of fragments on the char surface. Furthermore, DDGS ash is rich in alkali (K and Na) and alkaline earth (Ca and Mg), which are the most commonly used catalysts; thus, these elements present in char samples could also affect char reactivity under different cases [40].

3.2 External and internal mass transfer limitation

According to Di Blasi [4], both the mass and heat transfer effects could become more prominent at higher temperatures and higher reactant partial pressure. In this paper, several criteria were applied in order to estimate effects of mass and heat during char gasification. Mears criterion [41] was used to estimate effects of external mass transfer (Eq. 5) and intraphase heat transfer (Eq. 7). Weisz–Pater criterion [42] was used to determine effect of internal mass transfer (Eq. 6). When Eqs. 5–7 are satisfied, it means that effects of external mass transfer, internal mass transfer, and intraphase heat transfer effects can be neglected.

$$k_{\text{ex}} = \frac{-r'_A \rho_c (1 - \varepsilon) R_p n}{k_g C_{\text{Ab}}} < 0.15 \quad (5)$$

$$C_{\text{wp}} = \eta \phi_1^2 = 3(\phi_1 \coth \phi_1 - 1) \ll 1 \quad (6)$$

$$k_{\text{heat}} = \left| \frac{-\Delta H_{\text{RX}} (-r'_A) \rho_c (1 - \varepsilon) R_p E_a}{h T^2 R_g} \right| < 0.15 \quad (7)$$

$$\phi_n = R_p \sqrt{\frac{k_n \rho_c S_a C_{\text{As}}^{n-1}}{D_e}} \quad (8)$$

Where

Items	Meanings	Reference
C_{Ab}	Bulk fluid gas concentration (kmol/m^3)	This work
C_{AS}	Surface fluid gas concentration (kmol/m^3)	This work
D_e	Effective diffusivity (m^2/s)	Calculated [42, 43]
d_p	Solid particle diameter (m), $d_p = 2R_p$	This work
h	Heat transfer coefficient, ($\text{kJ/m}^2 \cdot \text{s} \cdot \text{K}$)	This work
k_g	Mass transfer coefficient (m/s)	This work
k_n	n -order specific reaction rate constant ($(\text{m}^3/\text{kmol})^{n-1} \times (\text{m} \times \text{s}^{-1})$)	This work
n	Reaction order	This work
r'_A	Reaction rate per unit mass of solid particle ($\text{kmol/kg} \cdot \text{s}$)	This work
R_p	Solid particle radius (m)	This work
S_a	Surface area of the solid particle (m^2/kg)	This work
ρ_c	Density of the solid particle (kg/m^3)	This work
ε	Bed porosity (–)	This work
ΔH_{RX}	Heat of reaction (kJ/kmol)	[44]
ϕ_n	Thiele modulus (–)	This work
η	Internal effectiveness factor (–)	This work

From Eqs. 5 to 8, it can be seen that many parameters are required in order to determine mass and heat transfer limitations. Among them, effective diffusivity (D_e) was calculated using gases molecular diffusivity (D_{AB}) and Knudsen diffusivity (D_{KA}). Mass transfer coefficient (K_g) was calculated based on estimation of Reynolds (Re) number and Sherwood (Sh) number. Most parameters were

Fig. 8 $1-(1-X)^{1/3}$ versus time for PYR-Char at different temperatures and CO_2 concentrations

Fig. 9 E_a values for all PYR-Char obtained from pyrolysis temperature of 850°C with different heating rates and for CFB-Char

measured and calculated from experimental data, while some parameters ΔH_{RX} , D_{AB} , and D_{KA} were obtained from different literatures [42–44]. One type of PYR-Char (DH70_T850_T1100_0.3) and one type of CFB char (CFB D_T1100_0.3), which showed the highest reaction rate were chosen for calculation. DH70_T850_T1100_0.3 means PYR-Char obtained at pyrolysis temperature 850°C, heating rate 70°C/min and further gasified at 1100°C with 30 vol.% CO₂ and CFB D_T1100_0.3 means CFB-Char pyrolyzed at 850°C and further gasified at 1,100°C with 30 vol.% CO₂. The final calculation results are shown in Table 3. From Table 3, it can be seen that effects of mass and heat transfer both can be neglected during PYR-Char and CFB-Char gasification.

3.3 Determination of conversion kinetics

Figures 7 and 8 show the plots of $-\ln(1-X)$ and $1-(1-X)^{1/3}$ versus time for PYR-Char at different temperatures and CO₂ concentrations, respectively. It can be seen that generally, the conversion rates of PYR-Char present a linear correlation with time at different gasification temperatures and different CO₂ concentrations. Figures 9 and 10 show the calculated E_a values for PYR-Char and CFB-Char. From these two figures, it can be seen that for almost experimental conditions, the calculated E_a value using the SCM was slightly lower than that using VRM and increased sharply with increasing CO₂ concentration. The calculated E_a values for PYR-Char using SCM and VRM were both in the range of 100–165 kJ/mol,

Fig. 10 E_a values for all PYR-Char obtained from pyrolysis temperature of 750°C with different heating rates

while the calculated E_a values for CFB-Char were in the range of 55–100 kJ/mol, which were in the comparable E_a value ranges obtained from willow char samples [29] and the results reported by other researchers [18, 25, 26]. From Fig. 9, it can be seen that an increase in the heating rate did not significantly affect the E_a values of PYR-Char. CFB-Char showed much lower E_a values than PYR-Char under all conditions. From Fig. 10, it can be seen that the averaged E_a values of PYR-Char obtained at pyrolysis temperature of 750°C were slightly lower than those obtained at pyrolysis temperature 850°C. However, fairly high E_a values were observed for all PYR-Char obtained at a heating rate of 30°C/min and gasified with 20 vol.% CO₂. CO₂ concentration significantly affected E_a values of all char samples and E_a values increased with increasing CO₂ concentration. According to Di Blasi [4], the E_a values for CO₂ gasification generally varied between 88 and 250 kJ/mol. In this way, DDGS CFB-Char had fairly low E_a values when they were gasified with low CO₂ concentration. The influences of different factors (e.g., pyrolysis temperature, heating rate, etc.) on E_a have been discussed also by other researchers. According to Kumar and Gupta [31, 32], the E_a values obtained during wood char CO₂ gasification increased with increasing pyrolysis temperature and/or decreasing heating rate.

3.4 Recalculated TG

The weight loss (TG) curve was recalculated using the calculated Arrhenius parameters and compared with experimental ones to verify the models. Figure 11 shows the recalculated weight loss for PYR-Char at different CO₂ concentrations, where PYR-Char was obtained at pyrolysis temperature of 850°C, heat rate of 10°C/min, and gasified at 900°C. Figure 12 shows the recalculated weight loss for CFB-Char at different CO₂ concentrations, where CFB-Char was obtained at pyrolysis temperature of 850°C and gasified at 1,100°C. From these two figures, it can be seen that the calculated TG values for all char samples showed a fairly good fitting with the experimental results. At low gasification temperature of 900°C, almost no differences were observed between the predicted values from VRM and SCM models. However, at high gasification temperature of 1,100°C, SCM seemed to be more suitable than VRM model. From above observations, it was confirmed that VRM and SCM were suitable here to determine kinetic parameters of char gasification. However, since effects of mass and heat transfer could be enhanced with increasing temperature, for char gasification at high temperature with high reactant partial pressure, their effects need to be checked before applying the conversion models.

Fig. 11 The recalculated weight loss at 900°C for PYR-Char at different CO₂ concentrations

4 Conclusion

Gasification kinetics of DDGS PYR-Char and CFB-Char with CO₂ was investigated using a TGA. It was found that char reaction rate increased with increasing gasification temperature, CO₂ concentration, and heating rate but decreased with increasing pyrolysis temperature. Generally, the calculated E_a values using SCM were slightly lower than those using VRM. The calculated E_a values for PYR-Char using both models were in the range of 100–165 kJ/mol, while the calculated E_a values for CFB-Char were in the range of 55–100 kJ/mol. The predicted results using both models showed a good agreement with experimental results in particular with those obtained at lower gasification temperature and lower CO₂ concentration. According to observation from SEM, CFB-Char was more fragile, while PYR-Char obtained at lower heating rate had a less porous structure.

Fig. 12 The recalculated weight loss at 1,100°C for CFB-Char at different CO₂ concentrations

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