Southern pines char gasification with CO₂ - Kinetics and effect of alkali and alkaline earth metals

Narendra Sadhwani ^{a, b}, Sushil Adhikari ^b, Mario R. Eden ^a, Zhouhong Wang ^b, Ryan Baker ^b

^aDepartment of Chemical Engineering and ^bDepartment of Biosystems Engineering, Auburn University, Auburn, AL 36849, USA

Abstract

Carbon dioxide gasification of southern pine char was carried out in a fixed bed reactor at temperatures in the range of 800°C – 975°C. Evolution of carbon monoxide was used as the basis for conversion. The conversion versus time data were fitted to three different solid- gas reaction models: volume reaction model (VRM); non-reactive core model (NRC) and random pore model (RPM). Regression analysis showed that the RPM was the best at predicting experimental data. The measured change in char surface area was in agreement with the change in surface area predicted by the RPM. Furthermore, the RPM was used to predict the kinetic parameters of gasification of chars that were loaded with alkali and alkaline earth metals such as Na, Mg, K and Ca. The reduction in activation energy and hence increase in gasification reactivity was highest for potassium followed by calcium, sodium and magnesium. The pore structure parameter was highest for sodium implying a significant change in surface area of the char with initial conversion.

Keywords: Biomass, CO₂, gasification, southern pine, random pore model (RPM), alkali and alkaline earth metals

1. Introduction

Biomass can be converted to biofuels through various pathways. Syngas produced from biomass gasification can be used for power generation by combustion in power plants, production of chemicals and fuels through Fischer Tropsch and methanol synthesis[1] and as a fuel like natural gas. Gasification is considered as one of the more promising pathways for biofuel production due to high carbon conversion and energy efficiency[2]. Air, steam, oxygen and carbon dioxide can be used as oxidizing agents during the gasification process [3],[4],[5],[6]. However, gasification using CO₂ has not been studied to the same extent as gasification using other oxidizing agents.

CO₂ is a pollutant from almost every big industry sector. It is a major cause of global warming[7] and also leads to various health issues. Hence, using CO₂ for gasification serves a dual purpose i.e. reducing pollution and generating syngas. A major drawback of this process is that an external source of heat is constantly required to maintain the gasification temperature because the heat is not supplied by partial combustion of biomass as in the case of air or oxygen gasification[8]. This could be one of the primary

reasons that CO₂ has not been an attractive option for gasification studies. However, the CO₂ gasification process can be coupled with a power plant or a conventional gasification unit to utilize the flue gas CO₂. Additionally, incentives for reducing carbon footprint can make this process an attractive option for energy producers.

Conversion of char is the rate – limiting step when CO₂ is used as a gasifying agent [9]. Therefore, it is of vital importance to study the kinetics of the reaction of char with CO₂. Several studies have tried to quantify the kinetic parameters using different methods. Ollero et al.[10] used an n^{th} order model and Langmuir-Hinshelwood model to understand the gasification reactivity of olive residue in a TGA in absence and presence of CO inhibition, respectively. Marculescu et al.[11] studied the effects of pyrolysis factors such as temperature and residence time and concluded that gasification kinetics of municipal solid wastes was not a function of the pyrolysis residence time. Khalil et al.[12] studied the CO₂ gasification of pine and birch chars using a thermogravimetric analyzer (TGA) at pressures of 51 and 101 kPa and proposed a three parameter empirical model to examine the dependence of gasification reactivity on conversion. Mani et al.[13] studied the kinetics of CO₂ gasification of wheat straw char using a TGA. The effects of temperature and particle size were studied using the 50% conversion (r_{50}) technique. Bhat et al.[14] used the volume reaction model (VRM) and shrinking core model (SCM) to study steam and CO₂ gasification kinetics of rice husk char in a TGA at 750°C to 900°C and found the activation energy to be 197 kJ/mol and 180 kJ/mol for the models. Cetin et al.[15] used the VRM with pine char as the feedstock and found the activation energy to be 224 kJ/mol.

Some studies have looked into the intra-particle diffusional effects in CO₂ gasification of biomass. Van Dan Aarsen et al.[16] studied two step pyrolysis and CO₂ –gasification of beech wood particles in a fluidized bed. The value of the Thiele modulus was found to be less than 0.3 implying that the influence of internal mass transfer could be neglected. Mani and Mahinpey[13] studied the gasification kinetics of wheat straw char with CO₂ at various particle sizes from 60 micron to 925 micron. The study reported that the change in particle size did not increase the value of Thiele modulus high enough to consider strong pore diffusion in the char gasification and the process was chemically controlled. Lee and Kim[17] studied waste tire char gasification with CO₂ and determined that gasification rate was independent of particle size for sizes less than 650 micron. A review of biomass - CO₂ gasification by Lahijani et al.[18] mentioned a few other studies that have concluded that at lower particle sizes, the diffusional effects are not prominent and the process is chemically controlled. However, Rapagna and Latif[19] attributed the effect of particle size on the steam gasification of ground almond shells to the extra and/or intraparticle heat transfer limitations. Various endothermic reactions occurring inside the biomass particles during CO₂

gasification lead to a temperature difference between the particle temperature and the temperature of the gasifying agent.

Another important aspect to address in the reaction of char with CO_2 is that it leads to a change in the pore structure and surface area of the solid during conversion. Hence, the changing surface area needs to be taken into account while studying the kinetics of this reaction. Fermoso et al.[20] used a pressurized TGA setup with slash pine heartwood chars prepared at different temperatures. VRM, SCM and Random pore Model (RPM) which considers surface area changes with conversion, were used to study the kinetics of the system and all three models yielded the same value of the activation energy (185 kJ/mol). Seo et al.[21] obtained char conversion data using a real time gas analyzer. Kinetic data was fitted using VRM, SCM and RPM and kinetic parameters were calculated. The RPM pore structure parameter was determined using measured Brunauer–Emmett–Teller (BET) surface area of the char particle. Sircar et al.[22] investigated the CO_2 gasification of pine char between 725°C and 900°C using the aforementioned three models. In addition, a study by Zhang et al.[23] looked into the gasification of 14 different biomass chars and proposed a semi-empirical modified RPM to explain the behavior of all the chars.

Since the reaction of carbon and CO_2 is the slowest step, various catalysts have been used to increase the reaction rates. Meng et al.[24] studied the catalytic effect of carbonates of alkali metals on the CO_2 gasification of Pingshuo coal and found that all three catalysts (Li, Na, K) lead to increased activity with lithium being the highest. A review paper by Irfan et al.[25] cites a number of studies using metal catalysts to enhance the CO_2 gasification reactivity of coal. A study by Hurley et al.[26] studied the effects of impregnated Fe, Co, Ni and Ru metal ion on woody biomass CO_2 gasification and discovered that the amount of char and tar reduced and syngas yield increased significantly. All these studies show the importance of metal catalysts in char- CO_2 gasification. However, it is important to quantify the effect of these metals and show the resultant change in kinetic parameters.

Studying the kinetics of the rate limiting step in CO_2 gasification and identifying the appropriate catalyst to speed up the conversion could be a milestone in using this process on a larger scale. Also, many of these metals are present in biomass and in char so understanding the role of these metals in CO_2 gasification is important. The current study focuses on identifying a kinetic model for the southern pine char – CO_2 gasification from the models mentioned above; and using the model to quantify the effect of alkali and alkaline earth catalysts on the process by calculating the change in kinetic parameters for each catalyst. The models and catalysts identified here may be applicable to a broader range of biomass chars undergoing the CO_2 gasification process.

2. Methodology

2.1 Feedstock preparation: Pine wood chips were obtained from a local plant in Opelika, Alabama. The wood chips were dried in open air for a few days and ground using a hammer mill that was fitted with 1 inch screen size and sieved using 0.8 mm (1/32 inch) screen. 100 grams of ground pine was placed in a large tubular reactor which was heated at 10°C/min up to 800°C and held there for 60 minutes step to ensure that all the volatile matter from the biomass is released. Nitrogen was flowing continuously through the reactor at 7 l/min. Each run yielded around 25 grams of char. After a few runs, all the char was mixed and subjected to the same treatment again to achieve uniformity. Ultimate and proximate analyses were carried out in accordance with ASTM standards. CHNS/O elemental analyzer (Perkin Elmer, Model 2400, Waltham, MA) was used to perform the ultimate analysis. The HHV of the char sample was determined using an oxygen calorimeter (IKA Bomb calorimeter, Model C-200, Wilmington, NC). Particle density was calculated from volume measurements using a gas pycnometer (Micromeritics AccuPyc 1340, Norcross, GA). A camsizer was used to determine the particle size distribution of the char sample. Surface area measurements were done using Brunauer–Emmett–Teller (BET) surface area and porosity analyzer (Micromeritics, TriStar II, Norcross, GA). The char samples were degassed at 300°C with a continuous flow of helium for 16 hours. The samples were then placed in the analyzer and Nitrogen was used as the adsorbate gas to measure the surface area. Char for experiments was kept in an air-tight container and stored in a controlled environment until it was used for carbon dioxide gasification.

2.2 Loading of metal catalysts: Four different metal catalysts (Na, Mg, K and Ca) were impregnated onto the pine char. The maximum amount of loading targeted was 0.1 gram metal per gram carbon in the char. In accordance with this target, a calculated amount of metal acetate was dissolved in ultrapure water and stirred using a magnetic stirrer until complete miscibility was achieved. 30 grams of char was added to this aqueous solution and placed on a temperature controlled shaker (New Brunswick scientific, Excella E24, Edison, NJ) at 25°C for 48 hours. This mixture was allowed to stand for another 24 hours. The wet loaded char was filtered and spread out in an aluminum tray and placed in an oven to dry at 105°C for 24 hours. The initial and final weights of char were noted and approximate amount of loading was determined. An ICP MS with an octopole reaction/ collision cell (Agilent 7900 ICP MS, Santa Clara, CA) was used to measure the exact amount of catalyst loading on the char. The images of loaded char samples were taken using a scanning electron microscope (ZEISS EVO50 SEM, Jena, Germany) and SEM-EDS was used study the distribution of the metals on the char surface.

2.3 Fixed bed experimental setup: Figure 1 depicts the experimental setup used for the CO₂ gasification of pine char. The setup consists of a stainless steel tubular reactor (i.d. =0.5 in.) mounted vertically inside a furnace (Thermo scientific, Lindberg Blue M). A known amount (2.5 ± 0.2 g) of char was placed

between two quartz wool plugs inside the reactor to make a fixed bed. A thermocouple passes through the bed indicating the temperature of the bed throughout the process. Nitrogen was flown through the reactor at 0.3 ± 0.05 l/min when the reactor is being heated. Once the gasification temperature was reached, CO₂ flow was switched on at 1.2 l/min. The gases escaping the reactor were passed through ice-cooled iso - dodecane and a bed of activated carbon to prevent any unwanted compounds from entering the gas analyzer. The gas mixture (N₂, CO and CO₂) is analyzed using a micro GC (Agilent 3000A, Santa Clara, CA) which analyzes a sample every 3 minutes.

Figure 1. Schematic of fixed bed char gasification setup. 1. Tubular reactor; 2. Furnace; 3. Temperature indicator; 4. Condenser; 5. Heated line; 6. Activated carbon; 7. Gas Analyzer; 8. Flow meter

The Boudouard reaction or char – CO₂ reaction is a highly endothermic reaction which takes place at high temperatures[27] (Equation 1). Since the Boudouard reaction is the only reaction taking place, the conversion of char can be easily estimated using the evolution of CO as basis. The yield of CO (g/min) at any time is calculated by comparing nitrogen input flow rate and its concentration in the output. Conversion can thus be measured as the ratio of amount of CO evolved up to time t to the total amount of CO released as shown in Equation 2.

$$\text{Conversion [X] at time } t = \frac{\text{cumulative amount of CO produced until time } t}{\text{Total amount of CO produced}} \quad [2]$$

All the samples were gasified until complete conversion. This was adjudged by the diminishing concentration and finally absence of CO in the output gas. The time taken for complete conversion varied from 220 minutes at 800°C to 50 minutes at 975°C. Alternatively, for the purpose of surface area

measurements at various conversion levels, the flow of CO₂ was turned off and the furnace is shut down at a predetermined point to achieve the desired conversion. After the run was completed, the reactor was allowed to cool down with N₂ still flowing.

2.4 Reaction models and kinetic parameters: Three different solid-gas reaction models viz. volume reaction model (VRM), non-reactive core model (NRC) and random pore model (RPM) are used to interpret the conversion profiles obtained at each temperature. These models were chosen because they assume different mechanisms for the solid-gas reactions. The VRM speculates that the reaction is occurring homogenously throughout the volume of the particle. The conversion of the solid particle with respect to time is described as:

$$X = 1 - \exp(-k t) \quad [3]$$

where k and t are rate constant and reaction time respectively. The NRC hypothesizes that the solid-gas reaction initially occurs at the surface and gradually penetrates into the particle. This leaves a constantly shrinking non-reactive core at the center of the particle.

$$X = 1 - (1 - k t)^3 \quad [4]$$

The RPM proposed by Bhatia and Perlmutter [28], assumes that the structure of the pores in the solid and hence the surface area available for reaction is constantly changing during the course of the reaction. It considers the effect of enlargement of pores to yield more surface area in the initial stages of conversion, and the coalescence of these enlarged pores leading to a reduction in reactive surface area and thereby decreasing the reactivity of the solid particle in the later stages of conversion.

$$X = 1 - \exp\left(-k t \left[1 + k t \frac{\Psi}{4}\right]\right) \quad [5]$$

The pore structure parameter Ψ relates to the initial pore structure of the solid and is an indicator of the amount of change in specific surface area as the reaction progresses. It can be calculated using the initial pore surface area per unit volume S_0 , the initial pore length L_0 and the particle porosity ϵ_0 .

$$\Psi = \frac{4\pi L_0 (1 - \epsilon_0)}{S_0^2} \quad [6]$$

In this study, Ψ is treated as a parameter obtained by fitting and optimizing the RPM with the experimental data. The other kinetic parameters were determined using the Arrhenius rate law.

$$k = A \exp(-E_a/RT) \quad [7]$$

3. Results and discussion

3.1. Char properties: The physical properties and ultimate analysis of char are shown in Table 1. The higher heating value (HHV) of the char appears to be much higher than that of raw pine (HHV = 20.81

MJ/kg). This is due to the higher amount of carbon and consequently lower amount of oxygen in the char. The BET surface area for char appears to be in agreement with the study by Sircar et al.[22], which was 218 m²/g.

Table 1: Physical properties and ultimate analysis of unloaded char

Physical properties	
Ash content (wt %, d. b.)	2.8 ± 0.31
Bulk Density, (g/cm ³)	2.18 ± 0.6
Particle density, (g/cm ³)	2.32 ± 0.35
Particle size range, (microns)	150 - 600
BET surface area, (m ² /g)	197.6 ± 7.3
Higher Heating Value (MJ/kg)	32.65 ± 0.35
Elemental Analysis (wt. % d. b.)	
C	84.67 ± 0.95
H	2.56 ± 0.08
N	0.04 ± 0
O (by difference)	9.96 ± 0.73

d. b. = dry basis

3.2. CO yield and char conversion: The instantaneous CO yield (g/min) was calculated by quantifying the amount of nitrogen entering and leaving the reactor. The conversion of char during the process is calculated based on the evolution of CO using Equation 2. Figures 2(a) and 2(b) show the CO yield and char conversion with time. The initial CO yields for 900°C, 850°C and 800°C are considerably lower than 975°C and 945°C. Also, the plots for 975°C, 850°C and 800°C show constant declining yields whereas profiles for 900°C and 945°C show an increase in the yield in the middle and initial phases of conversion respectively. This shows the importance of the kinetics of the process which leads to many variations in such a narrow range of temperature. Char conversion profiles show the variation in times taken to achieve complete conversion; which are in the range of 50-90 minutes for the four higher temperatures and 220 minutes for 800°C.

Boudouard reaction is a highly endothermic reaction occurring inside the char particles during char-CO₂ gasification. This may lead to a temperature difference between the particle temperature and the temperature of the gasifying agent. The calculation of the heat transfer between bulk gas and reacting particle is shown in Appendix A. The particle temperature correction was calculated between 0.85°C to 7°C at different reaction temperatures.

Figure 2. Variation of (a) instantaneous CO yield with time

(b) char conversion with time

3.3. Model fitting: The conversion time plot was used to fit all three reaction models described above. The models are fitted using statistical software (SAS) which uses a non-linear Gauss Newton method to find the parameter values. The software also performs a lack-of-fit test to judge if the model fits the data. The fits for each model are shown in Figures 3 (a), (b), and (c).

Figure 3. Experimental data fitted with (a) VRM, (b) NRC and (c) RPM

A visual evaluation of the fits reveals that VRM and NRC show good agreement for profiles at lower temperatures but are off when predicting the data at 900°C and 945°C. However, the fits for RPM appear

to be efficiently predicting the conversion profiles at all temperatures. For better judgment, the experimental and predicted conversion profiles for each temperature and model were subjected to general regression in Minitab software. The R^2 values obtained from the regression confirm that of the three models, RPM was best at predicting the experimental data. The R-square values averaged over temperature for each model are shown in Table 2.

Table 2: R^2 values for various models averaged over temperature

Model	Average R^2 value (%)
VRM	97.81
NRC	98.93
RPM	99.71

Also, kinetic rate constants obtained for each temperature in all three models were used in Equation 7. The natural log of the rate constant ($\ln K$) was plotted against the inverse of temperature ($1/T$) to determine the values of the kinetic parameters. These values were then compared to values from similar studies in literature and Table 3 shows the comparison.

Table 3: Comparison of kinetic parameters from current study with literature

Study	Model	E_a (kJ/mol)	$\ln A$	Ψ (avg.)	Temp. ($^{\circ}\text{C}$)
Current study	VRM	280 ± 32	7.94 ± 0.4	-	800 - 945
	NRC	248 ± 14	6.03 ± 1	-	800 - 945
	RPM	219 ± 16	5.13 ± 1	9.88	800 - 945
Sircar et al.[22] (2014)	VRM	217	15.4	-	725 - 900
	NRC	186	10.7	-	725 - 900
	RPM	125	5.0	5.5	725 - 900
Yuan et al.[29] (2011)	RPM	248.5	6.75	50.01	850 - 1050
Fermoso et al.[20] (2009)	VRM	184	14.36	-	750 - 900
	NRC	185	14.2	-	750 - 900
	RPM	184	14.22	0.7	750 - 900

The value of Ψ obtained from RPM fits increased with increase in temperature. This correlates well with reports in literature.[22],[30] RPM predicts that the surface area of the particle increases during the initial

conversion phase due to the expansion of pores. The surface area of the particle can be correlated to conversion using Equation 8.

$$S = S_0(1 - X)\sqrt{1 - \Psi \ln(1 - X)} \quad [8]$$

S is the volumetric surface area (m^2/cm^3) of the particle and S_0 is its initial value. S can be converted into specific surface area (SSA, m^2/g) by dividing it with the density of the particle. The measured values of specific surface area through BET measurements are then compared to the calculated values by plotting against conversion. Table 4 shows the measured values of BET surface area at different conversion values for 850°C .

Table 4: Variation of measured surface area with conversion at 850°C

Conversion [X]	SSA (m^2/g)
0.1	290.41
0.2	393.88
0.45	533.74
0.85	562.24
0.93	705.24

To account for the reduction in amount of char due to conversion, the value of SSA is multiplied with $(1 - X)$. Figure 4 shows the comparison between measured and calculated surface area plotted against conversion.

Figure 4: Comparison of change in measured and calculated surface area plotted against conversion.

The trend of the measured points and their proximity to the predicted values validate the use of RPM to predict experimental data. On the other hand, some studies^[21] do it the other way, i.e. use the measured BET area data to calculate the value of Ψ .

3.4 Effect of metal catalysts:

The exact amount of catalyst loading onto the char is shown in Table 5. The bold values are the concentration values of the metals that are loaded. The amount of catalyst impregnated on char is measured in wt %. Figure 5 illustrates the SEM images of the loaded char samples and there is no difference in char samples loaded with different metals. The metal analysis using EDS on the chunks showed that they contained more metals (wt.%) than when analyzing the larger area of the particles. The loaded char was subjected to the same CO₂ gasification procedure as discussed above at four temperatures: 800°C, 850°C, 900°C and 945°C. RPM was used to predict the conversion vs time behavior for each catalyst. Figure 6 shows the RPM plots for each catalyst. Visual evaluation of the plots suggest that the fits for calcium, potassium and magnesium appear to be better than the fits for sodium which was confirmed by general regression performed on the predicted and experimental data.

Table 5. Metal catalyst loading on char

Sample	Actual loading (wt. %)			
	Na	Mg	K	Ca
Unloaded char	0.52	0.02	1.02	1.05
Na – char	1.24	0.11	0.80	0.42
Mg – char	0.31	1.00	0.71	0.35
K – char	0.75	0.16	1.95	0.80
Ca - char	0.16	0.06	0.66	1.85

Figure 5. SEM images: (a) Na- char, (b) Mg – char, (c) Ca – char, (d) K - char

Figure 6: RPM fits for (a) Na- char, (b) Mg – char, (c) Ca – char, (d) K - char

Values of pore structure parameter Ψ and kinetic parameters E_a and $\ln A$ are shown in Table 6. As compared to the unloaded char, the time required for complete conversion reduced with the addition of metal catalysts. The mechanism used to describe the CO_2 gasification is a widely accepted oxygen-exchange mechanism proposed by Ergun[18] as shown in equations [9] and [10]:

where C_f denotes the free carbon active site and $\text{C}(\text{O})$ represents the carbon-oxygen surface complex. The presence of metal aids in the extraction of oxygen from CO_2 ; the formation of an intermediate metal-carbon-oxygen complex and its decomposition. This leads to a faster utilization of surface active sites and conversion from CO_2 to CO . All four metal catalysts were successful in lowering the activation energy of the process. However, the catalytic effect was highest for potassium as it managed to lower the activation energy by 114 kJ/mol followed by calcium (102 kJ/mol), sodium (75 kJ/mol) and magnesium (74 kJ/mol). The data obtained in this study is in agreement with the data by Lahijani et al.[30] where the activation energy for CO_2 gasification of pistachio nut shell char with 5% Na loaded was 151.46 kJ/mol.

Table 6: RPM kinetic parameters for all catalysts

Catalyst	E_a (kJ/mol)	$\ln A$	$\Psi(\text{avg})$
Na	142.4 ± 17	11.4 ± 3	21.2 ± 8
Mg	143.4 ± 37	14.4 ± 3	4.9 ± 2
K	104.2 ± 24	8.3 ± 1	11.7 ± 9
Ca	115.8 ± 58	8.3 ± 5	8.7 ± 2

4. Conclusions: Three solid-gas reaction models were used to interpret the kinetics of pine char gasification with CO_2 in a fixed bed reactor. Regression analysis and char surface area measurements suggested that the random pore model (RPM) was best suited to predict the experimental data. Values of pore structure parameter, activation energy and frequency factor were calculated and compared with literature. Chars impregnated with four different metal catalysts were gasified and the random pore model was used to calculate the activation energy for each catalyst. The reactivity of the loaded chars was found to be in the order of: K-char > Ca –char > Na –char >= Mg –char. The pore structure parameter was the highest for sodium implying that change in surface area with conversion is highest for sodium.

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Appendix A: Heat transfer limitations between bulk phase and particle

A heat balance between the particle and surrounding medium at the particle surface can be written as:

$$h * A_p * (T - T_s) = \Delta H * R_r \quad [A.1]$$

Where h is the heat transfer coefficient ($\text{W/m}^2\text{K}$), A_p is the surface area of the particle (m^2), T and T_s are the temperatures (K) of the surrounding medium and the particle respectively, ΔH is the heat of reaction (kJ/mol) taking place inside the particle and R_r is the rate of reaction (mol/s). The value of h is determined using the correlation A.2 for forced convection at low Re values.

$$\text{Nu} = 0.3 \text{Re}^{1.3} \quad [A.2]$$

Parameters in this study:

d_p (biomass) = $275 \times 10^{-6} \text{ m}$; $u = 0.11 \text{ m/s}$; Viscosity = $1.53 \times 10^{-5} \text{ Pa s}$; $\rho_g = 1.842 \text{ kg/m}^3$; $K = 0.015 \text{ W/mK}$

The value of h obtained from this correlation [A.2] = $76.4 \text{ W/m}^2\text{K}$

For Boudouard reaction, $\Delta H = 172 \text{ kJ/mol}$. Using equation [A.1] and values of reaction rates at different temperatures, the difference between particle and bulk temperature are obtained as shown in table A.1.

Table A. 1 Temperature correction for particles at different temperatures

Temperature ($^{\circ}\text{C}$)	$T - T_s$ ($^{\circ}\text{C}$)
800	0.85
850	2.6
900	3.4
945	5.2
975	6.9

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Graphical Abstract