

PAPER • OPEN ACCESS

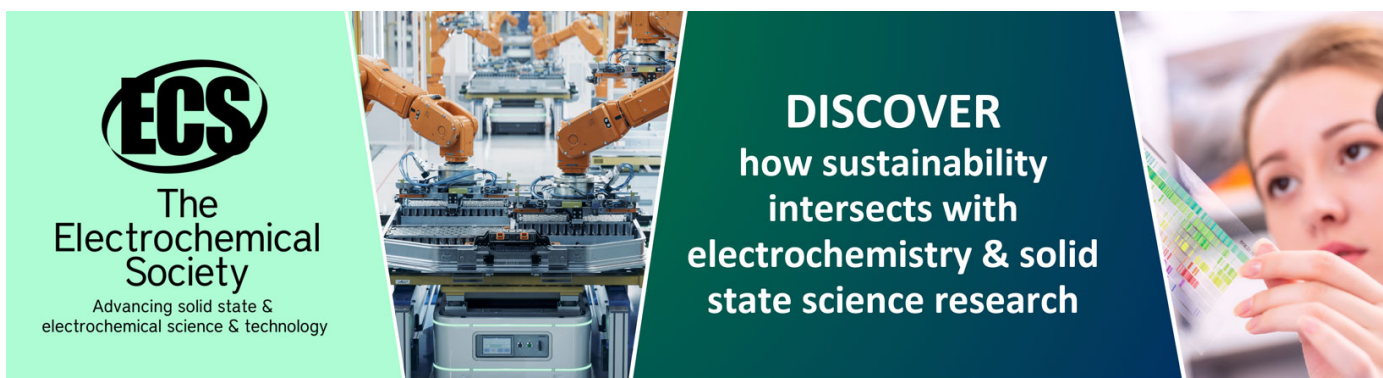
Kinetic analysis of waste tire-char CO₂ gasification

To cite this article: Douglas Hungwe *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **265** 012004

View the [article online](#) for updates and enhancements.

You may also like

- [A laser-based sensor system for tire tread deformation measurement](#)
Yi Xiong and Ari Tuononen
- [Automatic pixel-level detection of tire defects based on a lightweight Transformer architecture](#)
Yingwei Sun, Xiyu Liu, Xiaodi Zhai et al.
- [Wear resistance and wet skid resistance of composite bionic tire tread compounds with pit structure](#)
Chunyu Mao, Yunhai Ma, Siyang Wu et al.



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Kinetic analysis of waste tire-char CO₂ gasification

Douglas Hungwe*, Sarutt Thepitak and Kunio Yoshikawa

Tokyo Institute of Technology, Department of Transdisciplinary Science and Engineering, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan

* corresponding author: hungwe.d.aa@m.titech.ac.jp

Abstract. This work reports a kinetic analysis of tire tread and sidewall char in a thermogravimetric analyzer between 850°C and 1100°C to determine intrinsic kinetic parameters between 10 and 60% conversion. Experimental data was modeled using the volumetric, grain and random pore model, the random pore model described the reactions best and activation energy was found to be 116 and 130kJ/mol for tire tread and sidewall respectively. The onset for diffusion control was observed at 925-950°C for both samples. An increase in tire proportion was shown to decrease coal reactivity during co-gasification at different tire proportion and it was demonstrated that tire tread and sidewall are similar in gasification behavior save the inhibition effect caused by residual ash on tread at high conversions. The reactivity of both tire tread and side wall was lower than that of coal but almost equal therefore, this does not justify separation of tire components prior to gasification.

1. Introduction

The advent of the automobile industry coupled with great strides in economic growth, triggered the large production of tires from both natural and synthetic rubber, consequently large volumes of end of life tire is generated only to meet inadequate tire disposal systems. Traditionally, waste tires are disposed of in landfills or simply uncontrolled burning, both of which exacerbate an already dire environmental concern, the former consumes more volume than most waste and contributes to the shortening of landfill life while the later disperses particulate matter and noxious gases into the atmosphere and fails to harness potential heat energy [1-3]. In keeping with green waste management policies, thermal disposal methods such as incineration, pyrolysis and gasification have received much attention [1]. Chief among the advantages of these technologies is the ability to recover tire components from pyrolysis or gasification and energy harvesting from incineration while posing little to no harm to the environment. Realizing that tires have a high carbon content and are difficult to dispose of, gasification and other thermal valorization methods have received much attention from researchers around the world. Numerous studies have established that there is potential for gasification of tire individually and as an adjunct to biomass or coal based technology [4].

Strata and Bucko (2009) reported that the heating value of syngas increased by 3% when tire and lignite are co-gasified at a ratio of 20% tire and 80% coal where air was used as a gasifying agent in a commercial scale Lurgi gasifier [5]. They recommended that the proportion of tire be reduced to an optimal value of 10% for feed ratio so as to reduce sulfur containing gases in syngas. To corroborate this work, Talab et al (2010) carried out numerical modelling of coal tire-shred co-gasification and concluded that tire proportion up to 20% had no effect on CO mass fraction in syngas but increased H₂ and H₂S mass fraction while NH₃ proportion decreased [6]. Sanchez et al (2013) investigated syngas



production using TGA and two atmospheres; oxygen and steam, they reported that increasing gas pressure on waste tire char derived from distillation increased HHV as well as the yield of H_2 and CO in syngas [7]. In work done by Gonzalez et al (2006), it was reported that activated carbon produced from steam gasification had a higher porosity and surface compared to CO_2 , thus it was concluded steam gasification reactivity was higher than the latter [8]. Wiess and Castaldi (2006) developed a model from TGA data and carried out a preliminary techno-economic rate of reaction of 19% was a possibility for an annual tire production of 4 million could be converted to 18MW of CO and H_2 [9]. Co-gasification of waste tires has also been carried out with biomass, plastics, sludge and coal [4]. Lahijani et al (2013) studied co-gasification of tire and biomass in the a TGA and they found out that palm empty fruit bunch and almond shells lowered activation energy from 250 kJ/mol to 203 and 187kJ/mol respectively[10]. At 50% blend ratio, the conversion rate increased by a factor of 10 for palm fruit bunch and 5 for almond shell, however within the temperature range 850-1000°C, pure tire char transition from chemical to pore diffusion regime was not observed. Li et al (2001) also reported that CO_2 gasification of tire char produced in a rotary kiln, they estimated that activation energy ranged between 248kJ/mol and 348kJ/mol [11].

The gasification performance of separate tire components, tire tread and sidewall has not received much attention; differences in their reactivity may give an insight on how to effectively use them. Bituminous coal (BC) is known to have intrinsic within its structure, alkaline and alkali earth metals which are key in catalyzing the gasification reactions. Therefore co-gasification of tire and coal char is expected to have a positive influence on the reactivity of pyrolytic tire char. It is with this background that a comparative study of tire tread (TT) and side wall (SW) gasification reactivity is done coupled with the effect thereof on bituminous coals reactivity. The aim is to determine whether TT and SW are distinct enough in reaction behavior to justify separation of tire components prior co-gasification. Another objective is to investigate the effect of tire char proportion and temperature on the reactivity of coal.

2. Methodology

2.1. Sample preparation

Coal samples were pulverized to a size of less than 106 μ m and charged into fixed bed glass reactor details of which are reported by Hardi et al (2018) [12]. The 3g sample was pyrolyzed at 800°C and the residence time was 30 minutes with argon as the purging gas at a flow rate of 600ml/min so as to maintain an inert atmosphere and inhibit any reactions with air. To avoid thermal shock of the glass tube the heater was switched off after 30mins and allowed to cool, during this time the argon supply was still on. Waste tire was separated into two parts namely the tire tread and side wall and were charged separately into a pyrolysis reactor under the same conditions. The vaporized volatiles were condensed and collected for analysis.

2.2. Sample analysis

The isothermal rate of char- CO_2 gasification reactions was carried out between the temperature range 850°C and 1100°C. A lower temperature of 850°C was chosen because of the limitation of the TG Analyzer which can only run experiments of up 999 minutes at most. This temperature range is apt to distinguish chemical control and diffusion control regime by identifying the break in linearity in the Arrhenius plot. The experimental procedure started by loading a thin layer of mass 10 mg of sample in an Al_2O_3 crucible so as to minimize temperature lag and gas diffusion effects. Temperature was raised from ambient to 150°C at 10°C/min and held at 10 minutes to drive out residual or absorbed moisture after which the heating rate was increased and maintained at 25°C/min until target temperature was reached under high purity N_2 at 150ml/min. Then the sample was held at target temperature for 5 minutes to avoid temperature lag after which the N_2 gas was switched to reagent gas (CO_2) at the same flow rate. The flow rate was chosen to ensure that all product gas is purged and does into inhibit reactions. All experiments were done in duplicates and blank corrected to produce accurate and

repeatable experiments within particle range 90-106 μm . All samples were subjected to fundamental chemical analysis including GCMS analysis of pyrolytic oil to determine their composition.

3. Results and discussion

The pyrolysis process mass balance showed that sidewall produced more oil, char and gas compared to tire tread. Of note is that sidewall produces 5% more oil compared to tire tread which produced 35%, this was expected since sidewall contains less reinforcement material compared to tire tread. Proximate and ultimate analysis had complimentary results in which TT contained more than twice the amount of ash but both samples had a very low N_2 content (0.425% average). One concern of using tire char as a fuel source is the high sulfur content associated reported at an average of 2.08% compared to 0.29% found in coal char. This ultimate analysis result also reflects that during tire pyrolysis a greater percentage of sulfur is retained in the char. The summary of results is in table.1. It can be concluded that tire derived oil irrespective of origin has similar elemental content as can be seen from the ultimate analysis, which suggests that if oil is the main product of interest, then tire separation as pre-treatment would not be necessary.

Table 1. Chemical analysis of samples

Sample	Ultimate Analysis /dry wt%					Proximate/dry wt%		
	C	H	N	S	Cl	Ash	FC	VM
TT Char	72.97	1.15	0.41	2.15	0.21	18.03	76.84	5.13
SW Char	85.16	0.98	0.44	2.01	0.22	7.65	85.79	6.56
Coal Char	81.41	1.12	0.87	0.29	—	6.29	93.71	—
SW Oil	86.07	6.11	0.65	1.23	0.13			
TT Oil	86.12	9.24	0.70	1.33	0.15			

The analysis of tire derived oil using GCMS showed that it is complex mixture of a wide range of compounds, so for brevity the list of compounds was classified into 6 categories and only compounds with similarity indices greater than 90% were considered and represented graphically as shown in figure below. The classes of compounds include mono-aromatics, naphthalenes, phenyls, fluorines and their alkanated derivatives.

It was observed that the tire-tread oil and side wall oil are similar in composition taking into account the randomness of polymer degradation. Sidewall produced more compounds compared to tire tread save the compounds classified as others. Sulfur and nitrogen compounds were identified in the form of benzothiazole and its derivatives in both samples, this is of interest because such compounds decrease the quality of oil produced since these compounds contain elements that are not environmentally friendly. These partially polar compounds are slightly soluble in water therefore there is a possibility of using water for their removal from tire derived oils.

3.1. Gasification model fitting

Thermogravimetric mass loss data was converted to conversion-time data on ash-free basis according to the equation

$$x = \frac{m_0 - m_t}{m_0} \quad (1)$$

Char- gas interaction at any time during gasification can be expressed as

$$\frac{dx}{dt} = k(C_g, T_p)f(x) \quad (2)$$

$k(C_g, T_p)$ is the intrinsic surface reaction rate that is a function of gas concentration and temperature while m_0 and m_t are initial and final mass at any time, respectively. Considering the endothermic nature of gasification reactions, it increases with temperature and $f(x)$ represents the

physico-chemical evolution of char particles as the reaction proceeds from zero conversion to completion. There are three models that are used to describe $f(x)$: volumetric model (VM), grain (GM) or shrinking core model and random pore model (RPM). The difference in the models stems from fundamental assumptions made to assign a mathematical representation to char chemical and physical reactions.

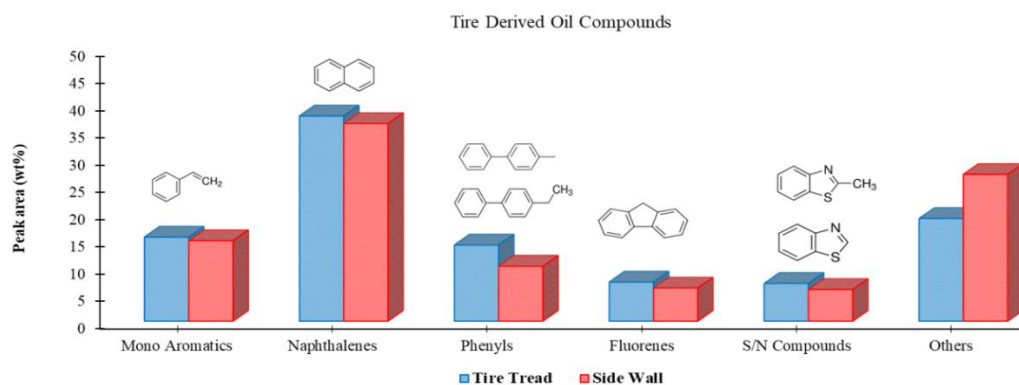


Figure 1. Summary of GCMS analysis of sidewall and tire tread oil.

Table 2. Summary of char conversion models [14].

Model	Separable form	Linear form
Volumetric model (VM)	$\frac{dX}{dt} = k_{VM}(1 - X)$	$k_{VM}t = -\ln(1 - X)$
Grain model (GM)	$\frac{dX}{dt} = k_{GM}(1 - X)^{\frac{2}{3}}$	$k_{GM}t = 3 \left[1 - (1 - X)^{\frac{1}{3}} \right]$
Random pre model (RPM)	$\frac{dX}{dt} = k_{RPM} \sqrt{1 - \phi \ln(1 - X)}$	$k_{RPM}t = \frac{2}{\phi} \left[\sqrt{1 - \phi \ln(1 - X)} - 1 \right]$

The volumetric model assumes that the reaction occurs simultaneously at all points in the particle and the random pore model assumes that char particles have an intricate porous structure that changes due to reaction such that solid-gas interaction is characterized by pore growth and coalescence. The grain or shrinking core model assumes that the reaction proceeds from the surface of a solid sphere and it moves its way inwards towards the center leaving ash behind. The mathematical representation of these models is shown in table 2.

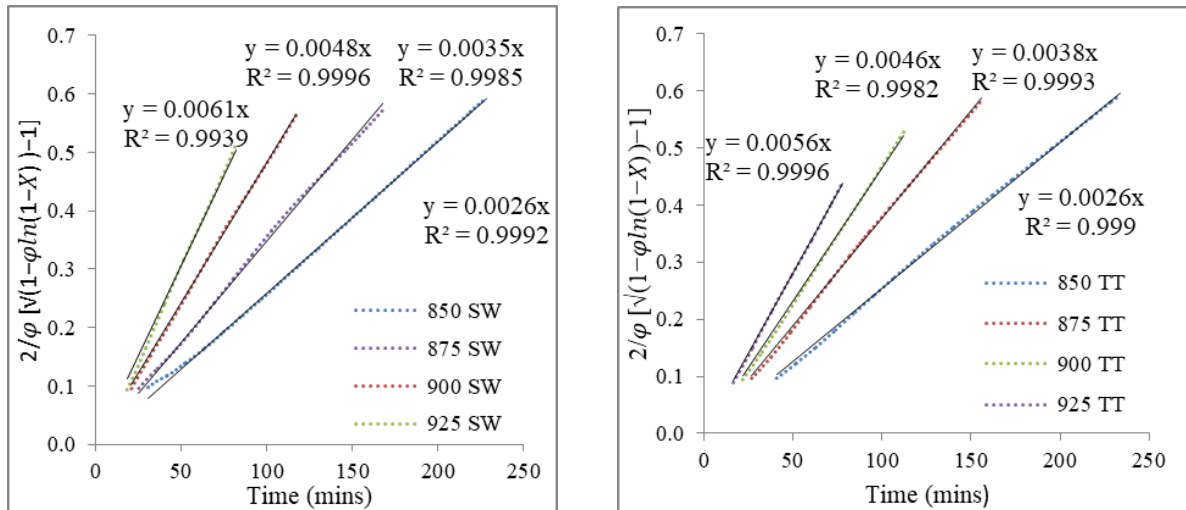
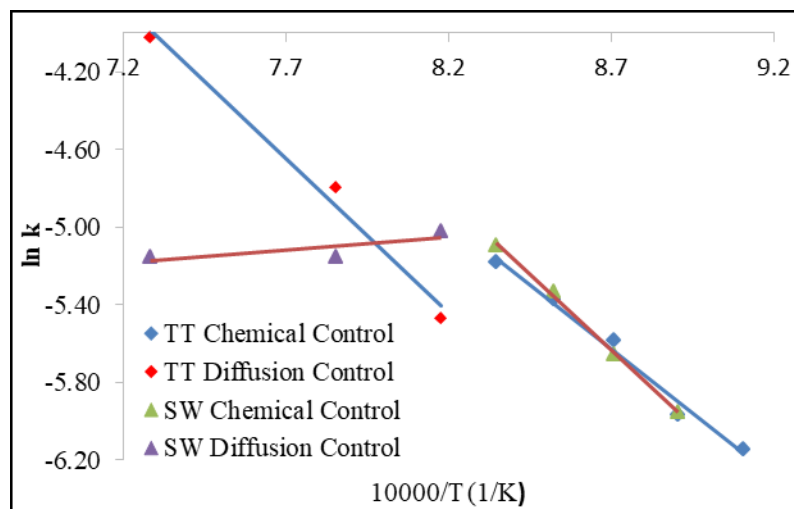
The conversion- time data considered in modeling was within the conversion 0.1 and 0.6, the lower limit was chosen to eliminate the false maximum caused by change in atmosphere and the upper limit was chosen to eliminate the effect of annealing, large morphological changes and ash diffusion effects which makes models deviate from ideality[13,14]. The elimination of the data below $x = 0.1$ improves all fits making the difference between the widely used random pore model and other models very small. Data from all experiments was used to determine the activation energy, the pre-exponential factor and the regime transition temperature according to the Arrhenius relationship:

$$k = A_0 \exp \left(-\frac{E_a}{RT} \right) \quad (3)$$

The summary of modeling results is shown in the table 3 and a comprehensive mathematical manipulation associated with these results is discussed elsewhere [14]. The random pore model correlated well with experimental data and the results are shown in figure 2, all experiments within the chemical reaction regime have an R^2 factor of at least 0.99. The resultant Arrhenius plot is shown in figure 3, the break in linearity was used to determine the onset of diffusion control.

Table 3. Kinetic parameters from random pore model.

Model	E_a (kJ/mol)	A_0 (s^{-1})	Transition($^{\circ}C$)
RPM (TT)	116	$2.90E+03$	925-950
RPM (SW)	130	$2.90E+03$	925-950

**Figure 2.** Correlation of random pore model with experimental data for SW and TT.**Figure 3.** Arrhenius plots showing the temperature dependence of SW and TT

It can be observed that conversion-time profiles of TT and SW are distinct, with tire tread exhibiting an inhibition effect at high carbon conversion while sidewall does not as demonstrated in figure 4. This can be explained in light of the presence of non-catalytic ash inherent in tire char and its associated char to ash transition process. The non-catalytic nature of the ash is reflected by the inability of the char reactivity to change by a factor greater than unit when the ash content in tire tread is more than twice that of sidewall. In the case of tire tread char as the gasification reaction proceeds there is accumulation of residual ash, consequently there is significant diffusion resistance at high conversions and coupled with char structural defects which become less and less as the reaction progresses this has a decelerating effect on the reaction rate.

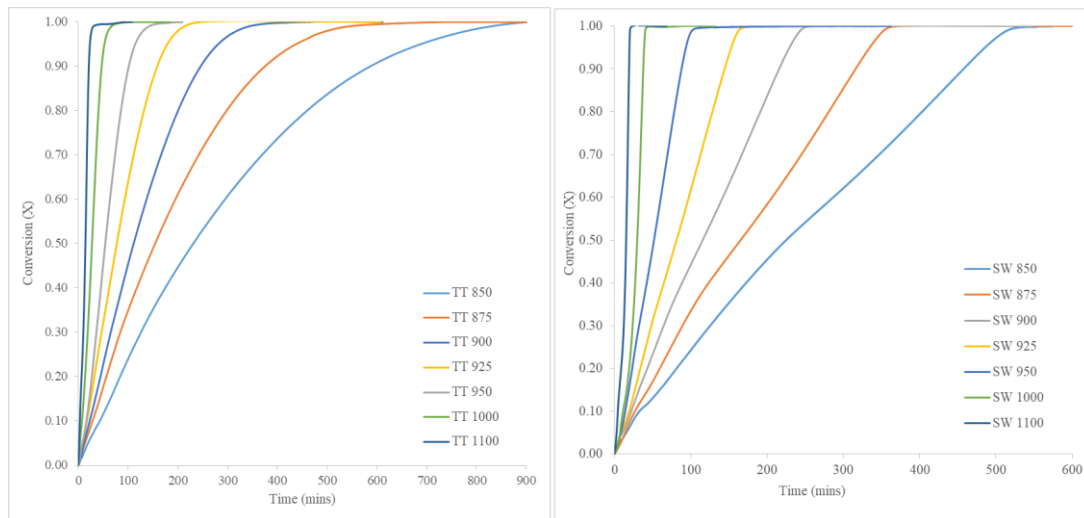


Figure 4. (a) Tire tread conversion time graph and (b) Side wall conversion time relationship

The two regimes of particle transformation that are used to describe the way in which particles change from char to ash are the shrinking particle and the shrinking core pattern [15]. The distinctions between the aforementioned patterns are described by how the ash affects the mode of particle morphological transformation and interaction as the reaction progresses among other factors. If the ash is finely dispersed in the carbon matrix such that its amount is not equal or more than the threshold amount that may result in a coherent skeleton structure that remains unchanged in the course of the reaction but it fragments instead, then char particles are said to react in the shrinking particle pattern. However, if the amount of ash is such that it forms a coherent skeleton structure that remains unchanged during the reaction, then the most likely pattern is the shrinking core regime in which the diffusion effect becomes more and more pronounced as the reaction reaches high conversion.

Tire tread char transformation could reasonably be reacting in the shrinking core pattern, the high percentage of ash in the tire tread char which inevitably impedes gas diffusion into the unconverted carbon. It is also reasonable to speculate that in the case of side wall char, the ash percentage does not reach the threshold amount to support the formation of an external structure, rather as the reaction progresses the particles fragment and are exposed to the gas for reaction with residual offering insignificant diffusion resistance.

3.2. Effect of tire char on coal gasification reactivity

The reactivity index [15] was used to represent the overall char gasification reactivity and its formula is;

$$R_{0.9} = \frac{0.9}{t_{0.9}} \quad (4)$$

Bituminous coal was blended with 25%, 50% and 75% tire proportion to investigate the effect of tire proportion on coal reactivity. A summary of results is shown graphically by the conversion-time data in figure 5. It is observed that coal reactivity is higher than that of tire tread and side wall. Reactivity indices are shown in the figure 4 and it was found that the reactivity trend at the same temperature is BC>BC: SW_3:1>BC: TT_3:1>BC: SW_1:1>BC: TT_1:1, with the exception of 900°C in which blends at 3:1 switch places, however it is of note that the differences may be considered inconsequential given that they are of the order of 2.6% on average.

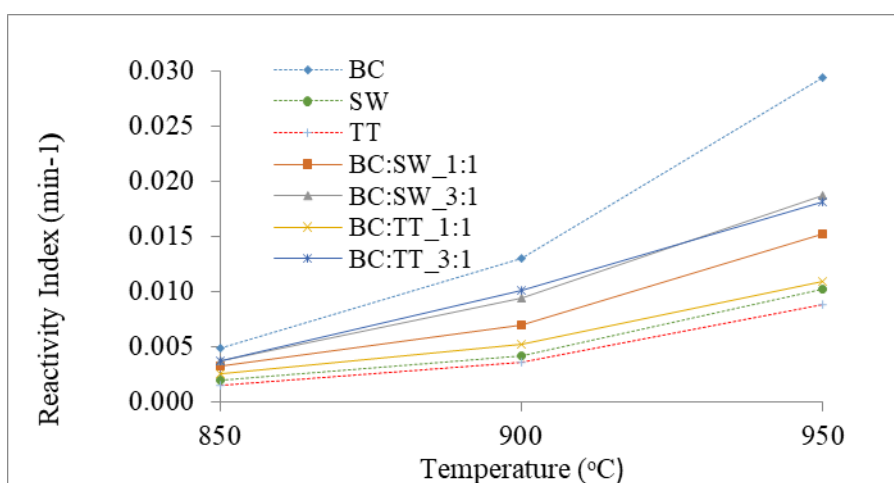


Figure 5. The relationship between reactivity and temperature between Bituminous coal, tire tread, sidewall and their blends at 25, 50 and 75% proportion.

It can be reasoned that at low waste tire char proportion the effect of ash content from either sidewall or tire tread is similar in extent. Comparing the reactivity indices of bituminous coal and the blends from the figure 5 confirms that high temperature promotes reactivity as should be expected from endothermic reactions. The lower reactivity associated with tire char may be as a result of a less developed pore structure than that of the coal char. An increase in tire proportion has a detrimental effect on coal gasification reactivity due to the inhibiting nature of the ash inherent in tires as previously reported by Strata and Bucko (2009). Practical consequences of co-gasification with tire may result in an increased proportion of unreacted char in the ash expelled from coal gasification reactor, this however can be averted by carefully monitoring the proportions of tire char charged with the coal and adopting higher operational temperatures.

4. Conclusion

Side wall has a slightly higher reactivity compared to tire tread mainly due to the inhibition effect of ash in tire tread. The inhibition effect is more notable at high conversions in tire tread. The activation energy of SW and TT is 116 and 130 kJ/mol, and reaction behavior can be described by the random pore model. Regime change from chemical to diffusion control was observed between 925 and 950°C for both samples. Oil analysis showed that differences in composition are not significant. High tire proportion reduces coal reactivity to a greater extent hence co-gasification with coal requires low proportions of tire. The aforementioned discussion suggests that it may not be necessary to separate tire components prior to gasification.

References

- [1] Machin E.A, Pedroso D.T., Carvahlo J.2017, *Renew. Sustain. Energy Rev.* **68** 306–315.
- [2] United States Enviomental Protection Agency (US. EPA), *Wastes-Resource-Conservation-Common Waste and Materials-Scrap Tires*, US EPA, Washington D.C, 2012.
- [3] Europeran Commision-Environment, *Landfill of Waste*, European Commission, Brussels, Belguim, 2014.
- [4] Oboirien B.O., North B.C 2017 *Journal of Environmental Chemical Engineering* **5** 5169–5178
- [5] Straka, P., Bucko, Z., 2009. *Fuel Process. Technol.* **90**, 1202–1206
- [6] Ilham Talab, Zaki Al-Nahari, Rana Qudaih, Isam Janajreh 2010 *Jordan Journal of Mechanical and Industrial Engineering* **4** 155- 162
- [7] Sanchez D., Paez M., Sierra R., Gordillo G.2013 *ASME Turbo Expo 2013: Turbine Technical Conference and Exposition* 7.

- [8] González J.F., Encinar J.M, González-García C.M., E. Sabio, A. Ramiro, J.L. Canito 2006 *Appl. Surf. Sci.* **252** **17** 5999–6004.
- [9] Wiess B., Castaldi M.J. 2006 *25th Annual International Conference on Incineration and Thermal Treatment Technologies, IT3*, 15 May 2006 through 19 May 2006,
- [10] Lahijani P., Zainal Z.A., Mohamed A.R., Mohammadi M. 2013 *Bioresour. Technol.* **138** 124–130.
- [11] Li R., Yan J., Li S., Chi Y., Huang J., Wang L.2001 *J. Fuel Chem. Technol.* **29** (4) 318.
- [12] Hardi F., Imai A., Theppitak S. , Kirtania K., Furusjö E., Umeki K. and Yoshikawa K. 2018 *Energy Fuels* **32**, 5999–6007
- [13] Tanner J. and Bhattacharya S. 2016 *Chemical Engineering Journal* **285** 331-340
- [14] Gomez A., Silbermann R.and Mahinpey N. 2014 *Applied Energy* **124** 73-81
- [15] Ding L., Dai Z., Guo Q and Yu G. 2017 *Applied Energy* **187** C 627-639