

# Pyrolysis of Coal for Fuel Production: A Review of the Effect of Various Parameters on the Pyrolysis Behavior of Coal

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**ABSTRACT:** *Alternative energy and renewable sources received considerable attention from many researchers because fossil fuel has intermediate products during the conversion of coal. Intermediate products such as synthesis gas, biochar, and condensable vapors are directly influenced by the production of energy to mitigate the barrier to future energy demand. The present review deals with the pyrolysis of coal and the results of pyrolysis of coal investigated by the parameters affecting product distribution such as type of reactor, feedstock composition, temperature, heating rate, particle size, and sweeping gas flow rate. Intermediate products such as charcoal obtained at 300 to 400°C usually the product of a slow pyrolysis process because coal has a large content of un-burnt inorganic compounds in the form of NO<sub>x</sub>, SO<sub>x</sub> and ash, bio-oil depend on volatile matters and obtained at temperature range 410 to 460°C as a product of fast and flash pyrolysis process because of high heating rate but during slow pyrolysis limited fraction obtained, gas formation observed when secondary cracking of coal at a temperature relatively higher to 500°C. Environmental effects and part of the potential scope of coal pyrolysis-based studies is also discussed in this review. Therefore, in the future utilization of coal will be interesting to optimize the products.*

**KEYWORDS:** *Pyrolysis; Coal; Thermo-Gravimetric Analysis (TGA); Reactors; Particle size.*

## INTRODUCTION

Coal is a fossil fuel, hard rock used as a combustible source. The majority of coal contents are variants highly dependent on the location and aging. Formation of coal is a time-consuming process maturity level of coal raised

with time and other parameters influenced directly its burning quality. Most of the coal consists are hydrocarbons, which is why the organic part is extracted and proceeded by further improvement for a useful source in the chemical

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1021-9986/2022/11/3852-3867

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Table 1: Process of Conversion of Coal.

Material	Partial process	Main chemical reactions
Decaying		
Vegetation	Peatification	Bacterial and fungal life cycles
Peat	Lignitification	Air oxidation, followed by decarboxylation and dehydration
Lignite	Bituminization	Decarboxylation and hydrogen disproportioning
Bituminous Coal	Preanthracitization	Condensation to small aromatic ring systems
Semianthracite	Anthracitization	Condensation of small aromatic ring systems to larger ones; dehydrogenation
Anthracite	Graphitization	Complete carbonification

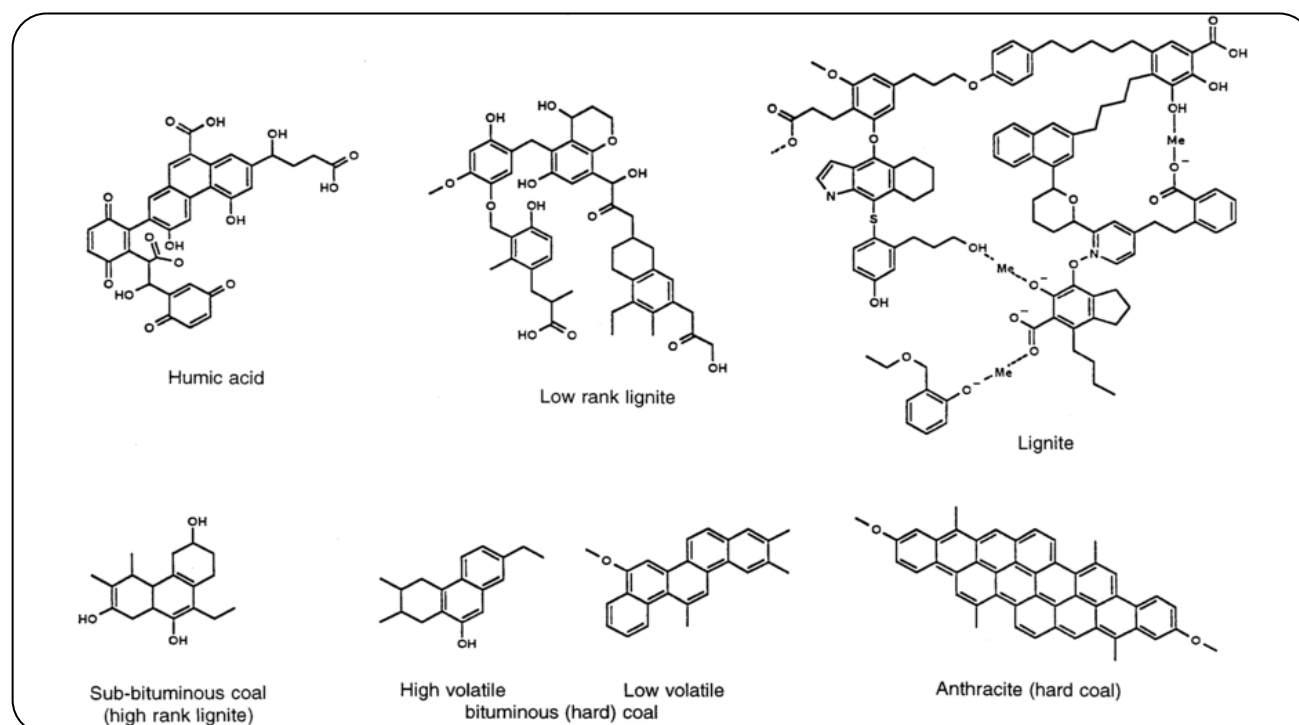


Fig. 1: Typical structure of different ranks of coal [1].

and petrochemical industry. In the United States coal is considered the amplest fossil fuel, as well as the world. World contains 1083000 reserves which 274000 million short tons of United States. On the basis of oil-corresponding, in this world, the coal reserves are two times higher than oil and natural gas. Economically coal has a large impact on energy development in the future. Coalification: the formation of immature coal to mature coal by the processing of dead plant in presence of control parameters following the process as shown in Table 1. Fig. 1 demonstrates the structure of different ranks of coal. In Fig. 1 ample space are large within the ring structure and relevantly decreases from lignite to anthracite.

Carbon to hydrogen ratio relatively higher from lignite to anthracite highly recommended for energy-efficient process. That's why the calorific value is determined on a mineral matter and moist-free basis [1]

Observe that the calorific value rises by raising coal rank but commences to lessen for semi-anthracitic and higher rank coals. A significant lessen in volatile matters represents a decrease in calorific value. In Table 2 different samples of coal were collected and done the proximate and elemental analyses. Proximate analysis of the lignite source Morwell Australia gave a maximum value of fixed carbon, ultimately having high heating value for this lignite source. In case of lignin, hydrogen to carbon ratio

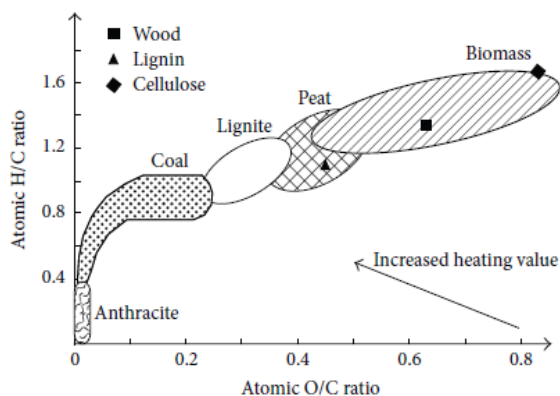


Fig. 2: H/C vs O/C ratio in low rank coal and biomass [2].

high in Western Australia sample that leads to high energy efficient yield. On the other side, oxygen to carbon ratio high in Pingzhuang, China sample that leads to the combustible products and cause of corrosion. In case of sub bituminous coal Taiheiyo, Japan has highest H/C ratio and favorable for combustible process. Meanwhile, O/C ratio high in Indian sub bituminous coal. The heating analysis provided useful information about H/C and O/C ratio as shown in Fig. 2.

On several different bases the analytical data can be estimated to consider the composition of feedstock as dried, as received, dried by air or by free ash, or by mineral free and dry basis. As received (ar) basis as shown in Fig. 3: feedstock composition is expressed as percentages of the moisture contents within the coal. Dry basis (db): feedstock composition is expressed when percentage of the water contents has been removed from the source; ash free and dry (afd): feedstock composition is expressed in percentage after the removal of water contents and ash from coal; mineral free and dry: in this analysis the feedstock is free from moisture and mineral matters which is include in a coal, and the calculations are a measure only the basis of organic portion of the coal; Moist ash free: in this analysis of feedstock preparation the coal contains moisture but don't have any ash particles. Moist mineral matter free: in this feedstock preparation an analysis the coal is to be free of mineral matter but still have a moisture contents [3, 4]. Internationally coal classified into two broad categories, hard and brown coal. Both are classified on the basis of calorific value. **Hard coal**: if coal has greater than 5700kcal/kg gross calorific value on a basis of free ash but moist present and means random reflectance

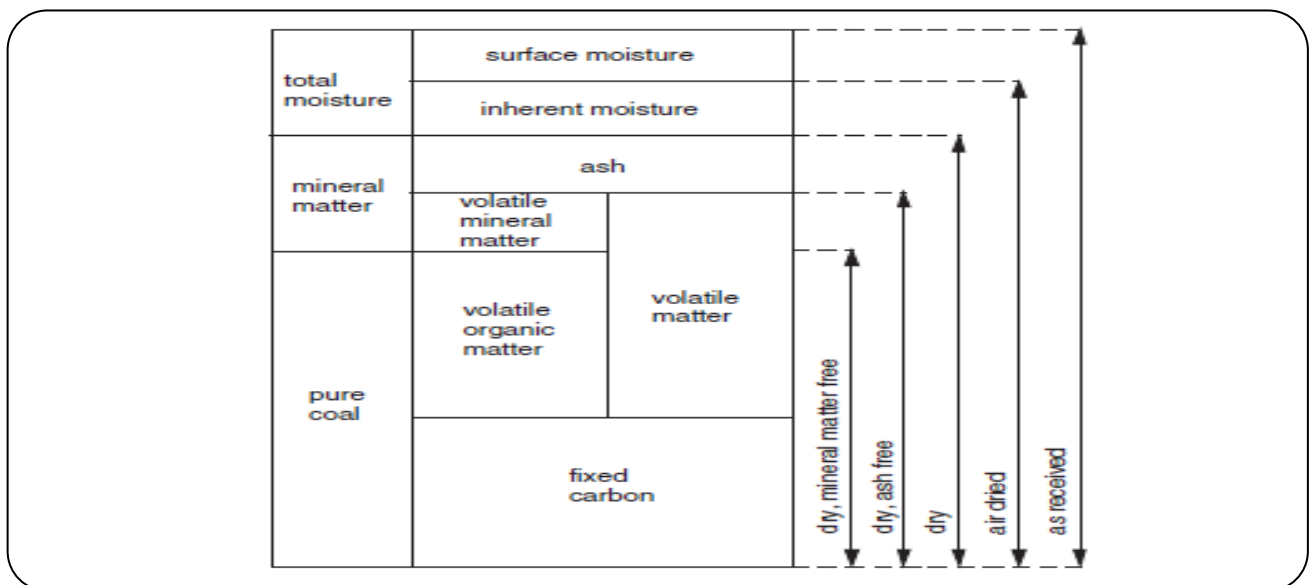
of vitrinite of at least 0.6. **Brown coal**: if coal is non-agglomerating and has a gross calorific value less than 5700kcal/kg containing more than 31% volatile matter on a dry mineral matter free basis. Hard coal is a combination of coking coal (allows the production of coke) and steam coal (produced low grade products). Brown coal is a combination of sub-bituminous having a gross heating value in a range of 4165 kcal/kg to 5700 kcal/kg and lignite coal having a gross heating value below 4165 kcal/kg. Coal Derived Products: rock-solid fuels are mainly produced as of the modification of hard and brown coal with the introduction of supplementary materials.

**Patent Fuel**: This type of fuel is made by adding some kind of binding agent into coal such as pitch. **Coke Oven**: Solid coke yield is formed when carbonization of coal is done at high temperatures. When the same process is revised at low temperature then semi coke is obtained. **Gas Coke**: Gas released from the carbonization process as a by-product is used as a town gas for domestic and heating purposes. **Coal Tar**: Low-temperature carbonization of coal in the absence of air produced a liquid yield also called bio-oil which is further processed for separation of various organic compounds used as a feedstock in petrochemical industries like benzene, toluene, and naphthalene. **Brown Coal Briquettes (BKB)**: This type of fuel is formed by crushing the brown coal into desired size and then molded at high pressure to convert into desired shape. **Coke Oven Gas**: This type of gas is formed by a gasification and carbonization process of solid fuel which is further used as a heating medium for iron and steel industries. **Blast Gas**: Blast gas is obtained when operating the refractories, it can be recycled when removed from the stack used partly in the same process and some part used for other steel industry in the burning process. **Other Fuels** such as Combustible Renewable and Wastes, Oil, Gas and Heat, and Electricity.

In the present study, a general review of the pyrolysis of coal was conferred. The target is to focus on the different products obtained from the pyrolysis process of coal. The effects of feedstock composition, temperature, heating rate, particle size, and sweep gas flow rate to investigate the product under the reaction performing conditions. Moreover, the scope of how to utilize the coal in process industry for demanding energy consumption, environmental issues how to mitigate acid gas removal were also presented.

**Table 2: Proximate and Ultimate Analysis of Low Rank Coal (M= Moisture, A= Ash, V= Volatile Matters, FC= Fixed Carbon).**

Categories	Source	Proximate Analysis (wt%)			Ultimate Analysis (wt% dry ash-free basis)									Ref.
		M	A	V	FC	C	H	N	S	O	H/C	O/C		
Lignite	Western, Australia	64.9	3.1	52.6	44.3	66.4	5.1	0.48	0.21	25.5	0.0768	0.384	[5]	
	Morwell, Australia	15.3	5.4	35.3	59.3	74.85	4.96	1.11	0.80	18.28	0.06	0.244	[6]	
	Indonesia	32.70	7.56	48.83	43.60	58.09	3.39	0.46	0.17	13.90	0.05	0.239	[7]	
	Schleenhain, Germany	15.5	11.6	52.4	36.0	70.6	5.1	-	4.3	20.0	0.072	0.283	[8]	
	Xialongtan, China	14.04	10.42	45.14	44.44	53.86	3.65	1.41	1.27	39.81	0.067	0.724	[9]	
	Pingzhuang, China	10.91	29.08	30.56	40.36	46.24	2.78	0.68	1.20	49.1	0.060	1.061	[10]	
	Thar, Pakistan	41.5	7.6	29.4	24.7	60.9	4.5	0.5	1.01	33.09	0.073	0.543	[11]	
	Sub-bituminous Coal	Indonesia	12.41	9.58	42.06	48.36	72.13	6.67	1.4	0.22	19.58	0.092	0.271	[12]
Diyarbakir-Hazro, Turkey		132	43.80	25.71	30.49	70.40	5.63	0.68	7.12	16.15	0.079	0.229	[13]	
India		4.57	13.49	38.67	47.84	60.12	6.84	1.47	0.46	31.11	0.113	0.517	[14]	
Shenfu, China		5.24	6.95	29.65	63.40	79.38	4.78	1.71	0.36	13.77	0.060	0.173	[15]	
Hongliulin, China		10.60	9.45	32.65	57.90	80.45	4.83	1.09	0.40	13.26	0.060	0.164	[16]	
Zhundong, China		8.79	5.68	32.96	61.36	75.23	3.18	0.70	0.53	20.36	0.042	0.270	[1]	
Taiheiyo, Japan		5.12	8.00	48.88	43.12	65.57	5.99	1.00	0.07	17.37	0.091	0.264	[17]	
Witbank, South Africa		2.01	7.88	32.14	59.58	76.65	4.96	1.90	0.59	8.02	0.064	0.104	[18]	
Curragh, Ireland		0.90	7.04	22.15	70.81	82.04	4.60	1.86	0.48	3.98	0.056	0.048	[19]	
Salt Range, Pakistan		4.8	17.8	38.5	39.5	55.5	4.8	7.8	4.5	26.4	0.086	0.475	[20]	



**Fig. 3: Coal components relates with feedstock composition [3].**

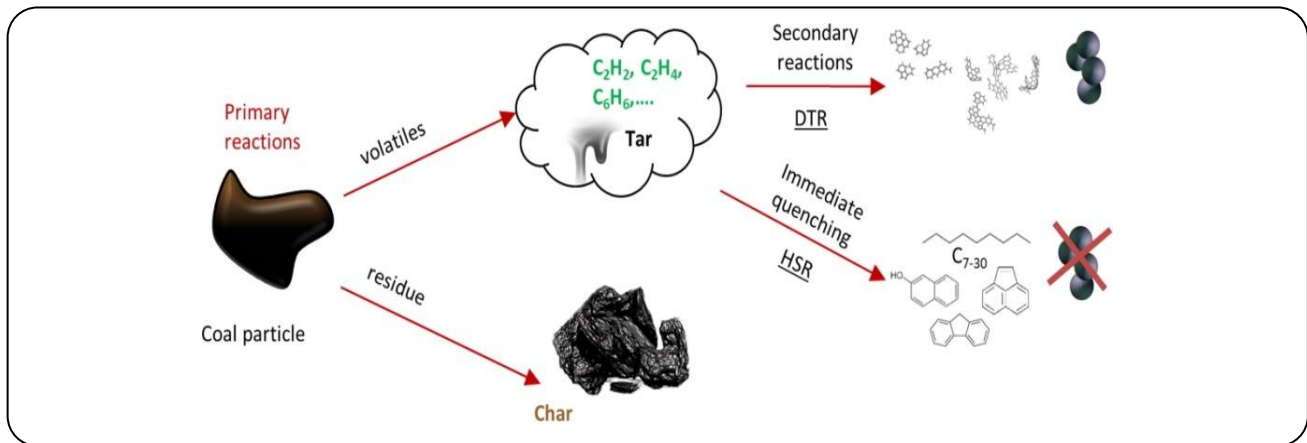


Fig. 4: Overview of Pyrolysis Process [22].

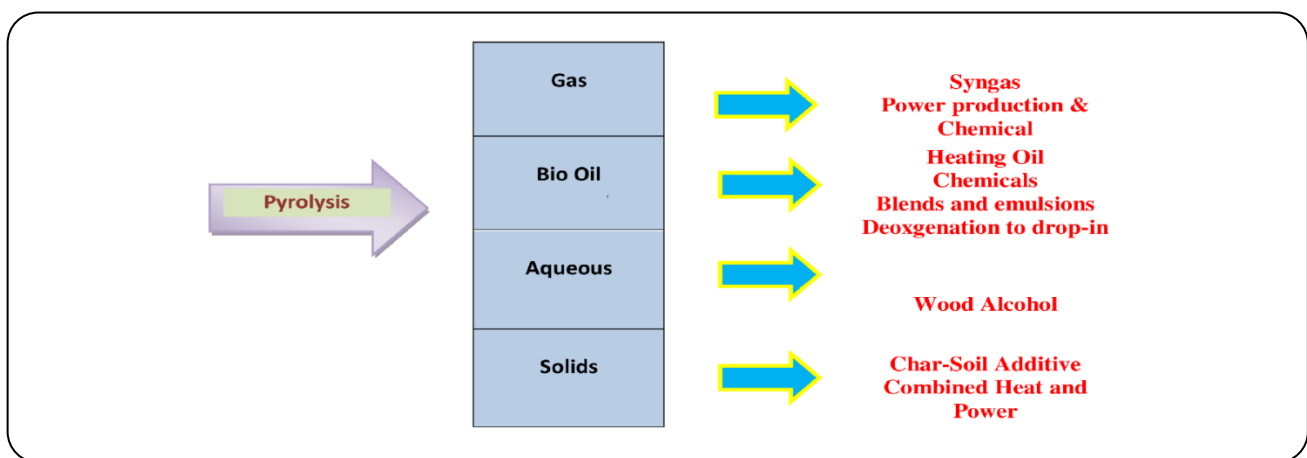


Fig. 5: Mechanics of Pyrolysis.

## PYROLYSIS

Pyrolysis is a process of thermal decomposition of feedstock to get a valuable product. As shown in Figs. 4 & 5, the coal converted to product by performing primary reaction still converted to secondary reaction by incessant supply of heat to get desire product, but its highly temperature dependent [21]. Later scientists started studying in recycling of flue gases to enhance the yield of pyrolysis process as shown in Figs. 4 & 5.

### Pyrolysis process techniques

Pyrolysis techniques exist in different framework, there are different pyrolysis processes depending upon the environment and process conditions.

#### Fast or flash pyrolysis

In this fast pyrolysis technique, high temperature about 500 to 1000°C achieved in very short time by adjusting very

high supply of heating rate as 1000 to 10000°C/s. This technique is useful for small scale production and quality of the product optimized by various analytical approaches. Mostly liquid phase product obtained and used as a fuel. Table 3 shows the operating parameters for different pyrolysis process.

#### Slow pyrolysis

This technique is helpful to get a solid product, required high rate of heat supply 1°C/min to 10°C/min operated to approximately 400°C, for large particle size. As above Table 3, shows the range of operating parameters for different pyrolysis techniques.

Its shows when particle size high than solid is product in case of slow pyrolysis. In fast pyrolysis particle size less than 1mm lead to the formation of oil yield. Flash pyrolysis has very high heating rate and particle size usually less than 0.2 mm resulting towards the formation of high percentage of oil yield [23].

**Table 3: Operating parameters for different pyrolysis process.**

Process	Time (s)	Rate (K/s)	Size (mm)	Temp. (K)	Oil Yield	Char Yield	Gas Yield
Slow	450-550	0.1-1	5-50	550-950	30	35	35
Fast	0.5-10	10-200	<1	850-1250	50	20	30
Flash	<0.5	>1000	<0.2	1050-1300	75	12	13

**Table 4: Different pyrolysis process techniques [25-27]**

Process (Developed by)	Toscoal (Tosco Corp.)	COED (FMC Corp.)	CSIRO (CSIRO, Australia)	ORC (Garrett/Occidental)	Lurgi-Ruhrgas (Lurgi-Ruhrgas)
Reactor type	Rotary kiln	Fluidized bed	Fluidized bed	Entrained bed	Moving bed (mixing bed)
Development period	1970s	1970s	1984-1985	1976-1978	1963
Development scale	25 t/d	36 t/d	0.5 t/d	4 t/d	Commercialized
Description	Conversion of oil shale carbonization process; 500 °C low-temperature carbonization by ceramic ball heated by combustion of product gas	Four fluidized beds at different temperature levels; Partial oxidation of char by oxygen; Movement and heat supply of hot char to upstream fluidized beds	Two fluidized beds; Generation of hot char by combustion of char in one fluidized bed; Circulation of hot char	Heating of char by combustion, separation of hot char in hot cyclone, and recycle of hot char to reactor. Ratio of recycled char to coal is about 10:1	Mixing and pyrolysis of char heated by combustion and coal in double shaft mixer; Another reaction in mixing bed
Feature Problem	Oil yield of 10% or less; Improvement of low-grade coal	Complex process with multiple fluidized beds; Low yield	Smooth hot charge movement between two fluidized beds	Uniform heating and dispersion of coal in recycle char are problems to be solved before scale-up	Lignite upgrading process; Low liquid yield

### Vacuum pyrolysis

In vacuum pyrolysis vacuum condition is applied usually at industrial level it is not preferred because of complexity in its construction and hard to maintain its process condition. However, vacuum pyrolysis process is extensively used at lab scale to study its safety limits and temperature conditions. Since in vacuum pyrolysis make sure the reactor pressure should be lesser than outside, in case of any accidents the risky fumes don't exit immediately making it safer to operate [24].

## RESULTS AND DISCUSSION

Pyrolysis of coal in different kind of reactor studied to observe the effect of yield by varying the studied parameters. Reactor type also takes part in product distribution. Numerous researchers have research on the limitations of studied variables on pyrolysis yield; some are given below.

### Classification of reactors/ influence on the reactor type

From the beginning of pyrolysis process different types of reactors have been formed for more active and environmental reliable operations. Various researchers in

past couple of decades have been researched on several reactors. Certain of the familiar reactors used in pyrolysis process are enumerated below. According to particles and bed movement, **class-1** during pyrolysis solid does not have any movement in a reactor e.g. batch reactors. **Class-2:** Moving bed e.g. shaft furnaces. **Class-3:** some of the mechanical forces used to cause the movement in the reactor e.g. rotary kiln, rotating screw etc. **Class-4:** in this reactor, movement which is produced by flow of the inert specie. Mostly charcoal creation is placed on class-1 and class-2 reactors; in developing countries mostly class-1 reactors are used. According to the heat is supplied to coal: **Class-1:** in this type of reactor part of the feedstock burns and the heat of reaction utilize to carbonize the further feedstock material. **Class-2:** flue gases during combustion of one or more or any other fuel in Table 4.

Operating parameters of different pyrolysis processes outside the reactor produced which provides direct transfer of heat. Class-3: directly heat is transferred from inert hot materials. Class-4: this type of reactor provides indirectly heat through the walls of the reactor i.e. heat is provided through extraneous source because of the combustion of

one or more pyrolysis products. Homogeneous and heterogeneous reactors: these are the two main categories of chemical reactors; differentiate on the basis of phase. Batch reactor: It is easy to control and used for small scale production [28]. The cripple enzyme and reactants are set in a close cylinder. Some external agency is introduced for better mixing and agitation. Numerous modifications have been done in these reactors to enhance the product quality and low consumption of feedstock by reuse of byproducts. Primary cracking lead towards the liquid yield and in case of incessant increase in temperature shifted to the secondary cracking formed gas yield. Rotary kiln reactor: this type of reactor is most widely used as a pyrolysis reactor at industrial and pilot plant, can be operated continuously and simple to fabricate [29]. Fluidized bed reactor is shown in Figs. 6 & 7: studied material is fluidized by external inert fluid which is provided through the bottom of the reactor. The kinetic study will help how to control the operating parameters and design structure of reactor. Basic characteristics properties of fluidized bed reactor below: Immensely high surface area contacts between fluid and solid per unit bed volume, fluid and the discrete solid phase having lofty relative velocities, Intermixing of the particulate phase at high levels and continual particle to particle and particle to wall collisions. Fluidized bed types classified on the basis of their flow behavior, including: Stationary fluidized beds, solid material is relatively static under fluidization condition and few of the fine particles being extracted. Circulating fluidized beds, solid particles suspended when fluidization takes place because of high kinetic velocity of inert fluid. These particles which are separated from circulating bed can be recycling to bed based on the particle size and identified by a cyclone separator. Flow dynamics described by various flow systems which involves: Slugging bed: Air bubbles covered the complete cross section of the reactor and bed divided into several layers. Boiling bed: Fluid particles and inert gas which is used for fluidization are approximately the same size in a reactor. Channeling bed: channels are formed during which the majority of the air is passed. Spouting bed: air flow from single opening and some of the particles are flow outside the bed. Circulating fluidized bed reactor is less used for pyrolysis process because it produces gas which contain less contaminate or impurities as shown in Table 5. This reactor having the cyclone separator after the bed which

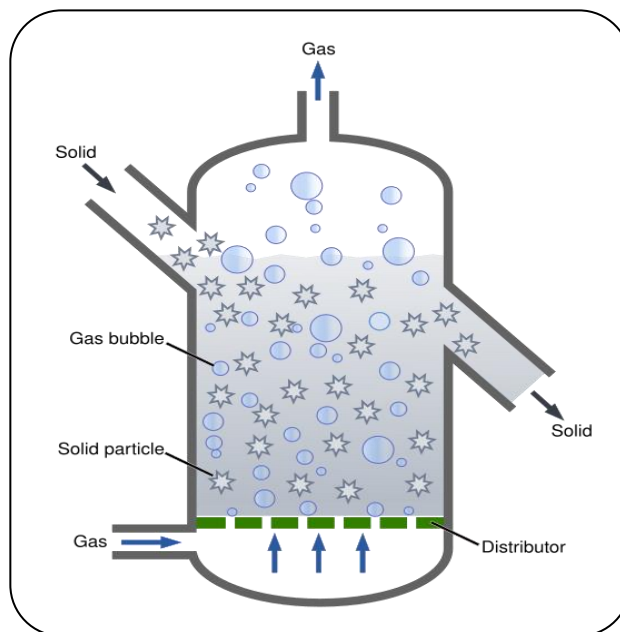


Fig. 6: Fluidized Bed Reactor.

formed the looped many times before removed the particulate and impurities

#### **Feedstock composition**

Components of coals are studied; it was observed these components have various fractions and these various fractions effects on the distribution of product of pyrolysis. Heated up to designed pyrolysis temperature the main components contribute to the pyrolysis yield. By primary decomposition of coal formed vapors and secondary reactions take place in gas phase forming soot, where secondary char is formed. Dry feed required in fast pyrolysis around 10% moisture contents. Moisture contents are directly effect on energy requirement water produced in product of pyrolysis directly affect the properties of pyrolysis products [30]

#### **Limitation of temperature**

Numerous scholars have observed that the coal pyrolysis exist in the range 300°C to 600°C. Researcher studied the pyrolysis of brown coal in fixed bed reactor and reported the oxides of sulfur and nitrogen formed during pyrolysis of brown coal. Thermal stability results have shown that two types of organic sulfur present in coal with dissimilar thermal stability [32]. The first type of sulfur converted to H<sub>2</sub>S at temperature below 600°C. The other type of sulfur remained stable up to 1000°C [33].

Table 5: Pyrolysis reactors comparison [31].

Pyrolyser	Status (units)	Liquid Yield (wt%)	Functional Complexity	Feed Size	Feed Variability	Scale-Up	Sweeping Gas Flow Rate
Fixed bed	Pilot(=1), lab (>1)	75	Medium	Large	High	Difficult	Low
Fluidized bed	Demo (>1), lab (>1)	75	Medium	Small	Low	Simple	High
Circulating bed	Pilot (>1), lab (>1)	75	Large	Medium	Low	Difficult	High
Rotating cone	Demo (=1)	70	Medium	Medium	High	Medium	Low
Ablative	Pilot (=1), lab >1)	75	Large	Large	High	Difficult	Low
Screw/auger reactor	Pilot (>1), lab (>1)	70	Small	Medium	High	Simple	Low
Vacuum	Pilot (=1), lab (<1)	60	Large	Large	Medium	Difficult	Low

Single=1, Few=<1, Multiple=>1

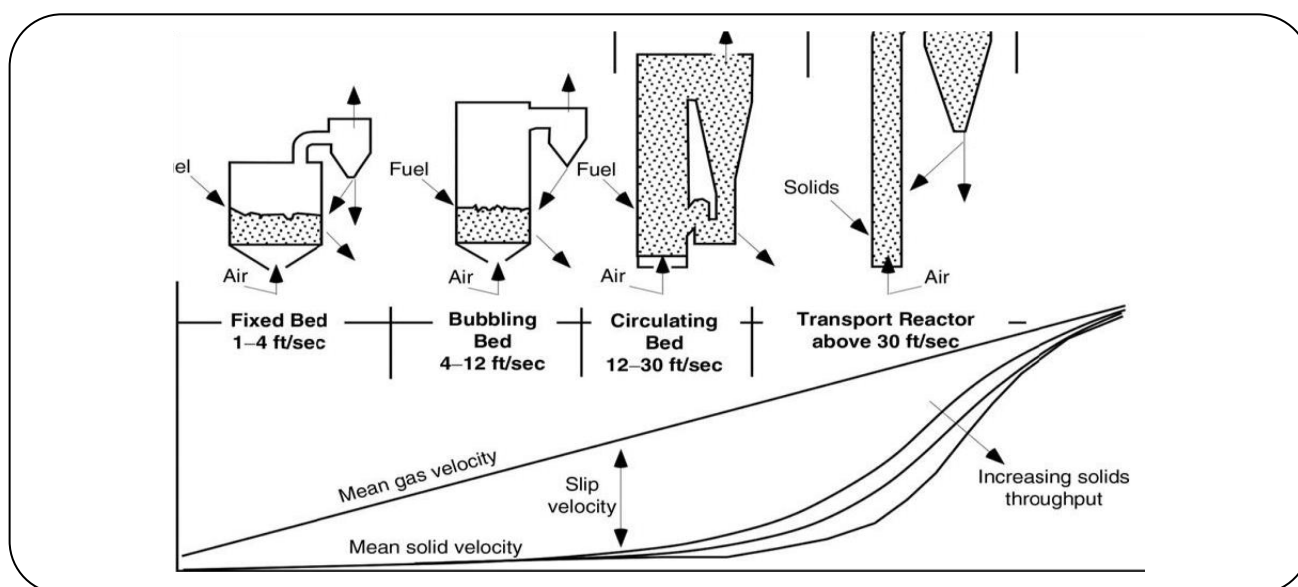


Fig. 7: Comparisons of different reactors.

The change in feedstock rate did not have any significant effect on  $H_2S$  formation., the effect of temperature and particle size on bio char yield in cylindrical batch reactor in temperature range from 950K-1250K by using coal as a feedstock [34]. It was investigated when pyrolysis temperature increased then bio char yield decreased. With increased in particle size the bio char production increased. At high temperature and smaller particle size and prominent change in heating rate which decline the bio char yield as shown in Table 6, when char pyrolyzed in presence of 5% oxygen are more swollen and more porous than chars produced in pure nitrogen and more reactive for diffusion propose. Finally, increasing soak times and heat treatment temperatures deteriorate char reactivity in all regimes. He noticed that replacing the  $N_2$  with  $CO_2$  has no

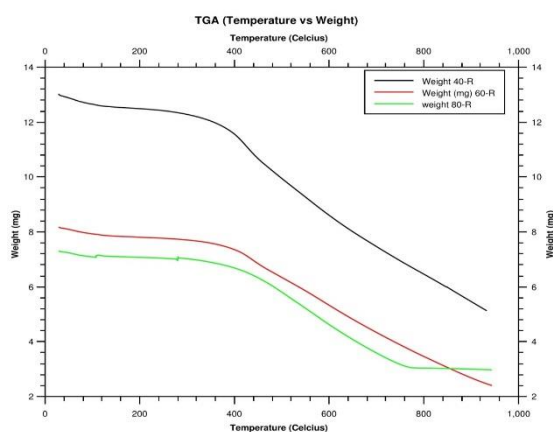
significant effect at initial stage to remove the volatile matters. When temperature increased up to 480°C then volatile releasing rate increased.

At 760°C  $CO_2$  prevent the calcite from decomposition. Volatile yield increased as the temperature increased in  $CO_2$  atmosphere and volatile yield decreased as heating rate increased. COS is controlled in  $CO_2$  condition and  $SO_2$  and  $H_2S$  formed in  $N_2$  atmosphere [40, 41]. In pyrolysis process temperature is a very important operating parameter to control the quantity of desired object. In fast pyrolysis liquid yield are generally obtained at temperature 500°C. In slow pyrolysis the liquid yield is variable reported peak liquid yield obtained about 28-41% at 377°C to 577°C [42], depend on raw material properties are shown in Fig. 9.



**Table 6: Product of pyrolysis processes [39].**

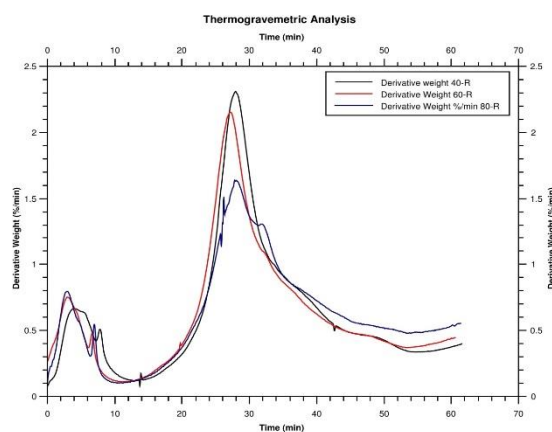
Condition	Process	Products
<350 °C	Free radical formation, water elimination, and depolymerization	Formation of carbonyl and carboxyl, the evolution of CO and CO <sub>2</sub> and mainly a charred residue
350-450 °C	The split of glycosidic connections of polysaccharide by substitution	A combination of levoglucosan, anhydrides, and oligosaccharides as a tar segment [35]
450-500 °C	Dehydration, rearrangement, and fission of sugar units	Formation of carbonyl compounds [36]
>500 °C	A combination of all the above processes	A combination of all the above products [37]
Condensation	Unsaturated products shrink and split of the char	Reactive char remain [38]



**Fig. 8: TGA of different particle size of coal [48]. (40 R large particle size, 60 R medium particle size, 80 R small particle size).**

#### Limitation of heating rate

Distinct studies have shown that heating rate effects on pyrolysis yield like char, bio oil and gas. Rate of heating supply has significant results on the product of pyrolysis. At a rate of heating supply  $0.167\text{Ks}^{-1}$  brown coal was slowly pyrolyzed and rapidly at  $2-3 \times 10^3\text{K/s}$ . In rapid pyrolysis tar yield predominant with temperature and break off at  $923\text{K}$  and  $26\text{ mol-C}/100\text{ mol-C}$  in the coal, while  $723\text{K}$  and  $15\text{mol-C}$  in the slow pyrolysis [43, 44]. The effect of heating rate and high pressure during coal pyrolysis observed, coal samples were placed in thermo gravimetric analyzer and also placed in pressurized flow reactor to scrutinize the effect of devolatilization pressure and heating rate on coal char. It was found that apparent changes occurred by varying pressure and slightly changes occur in reaction rate by changing the heating rate. It was found that result of pyrolysis temperature and heating rate on coal char rate in gasification due to surface and structure of char [45-47].



**Fig. 9: DTGA of different particle size of coal [48]. (40 R large particle size, 60 R medium particle size, 80 R small particle size).**

Thermo-gravimetric analysis determines that on what temperature the weight loss occur maximum. In above Fig. 8, particles size of  $500\mu\text{m}$ ,  $297\mu\text{m}$  and  $210\mu\text{m}$  were analyzed by researcher and the results elaborated in above Fig. 8 maximum decomposition occurred on  $500\mu\text{m}$  and time was observed for highest decomposition about 25-30min. When the derivative weight observed against temperature then maximum decomposition occurred above  $440^\circ\text{C}$  shown in Fig. 8.

Region-1 Initially the black line curve in Fig. 9 for particle size  $500\mu\text{m}$  lifted up because the primary cracking started in this region dehydration occurred in which free and binding moisture contents present in indigenous coal released at temperature  $104^\circ\text{C}$ . Region-2 the black line curve goes down which indicated the increase in weight of sample by some oxidation and other hydration reactions occurred at temperature  $108^\circ\text{C}$  to  $220^\circ\text{C}$ . Region-3 black line curve started again too lifted up and goes to temperature more than  $440^\circ\text{C}$ , in this region maximum

devolatilization occurred. Vapors matters which were 30% in feedstock decomposed in this region. Region-4 in this region black line curve again goes down because the secondary cracking occurred which minimized the desired charcoal yield and maximize the gas yield. Similarly, for derivative weight curve against time showed the maximum production of charcoal at 25-30min

#### **Limitation of particle size**

It was observed that larger particle size as shown in Table 5; higher pyrolysis yield obtained especially the solid yield. It was also investigated the sweeping gas flow rate not considerable range that's why continuous supply of seep gas not important in case of fixed bed reactor. However, in fluidized bed reactor the feed size comparatively smaller but sweep gas flow rate high that would increase the amount of liquid yield but continuous supply of seep gas also taken the volatile matters to non-condensable stream. The production of metallurgical coke from coal investigated the structure and quality of coke required for blast furnace in metallurgical operations. Initially carbonization of coal was done having different particle sizes, but the high quality coke was formed at 3mm particle size of coal. The production of bio char in fixed bed reactor from various feedstock biomasses having temperature range 300 to 750°C with 6mm particles diameter and found that maximum char yield obtained at low temperature 300°C in case of green waste. Further increase in particle size with sufficient rise in temperature the gas yield increased due to secondary cracking take place [8, 47, 49, 50].

#### **Limitation of sweep gas**

It was observed that gas flow influenced on the product distribution. Gas is used as a carrier for products to flow the product stream out of the reactor. Low gas flow rate required in slow pyrolysis which was favor to char formation and high gas flow rate provided in flash pyrolysis, high contents of vapors removed that's why liquid yield obtained in this process. At high pressure and low flow rate heat liberated during the process and known by exothermic process [51, 52]. When the gas flow rate high it will initially favorable for the oxygen removal, but after the initial supply form 15-20min then its supply cut down because the gases built inside higher pressure, no further sweeping gas flow rate required. If the non

condensable gases are recycled to the process, it leads to soars the product of coal pyrolysis. Most of the researchers recently used the (CO<sub>2</sub> + H<sub>2</sub>O) instead of inert gas like nitrogen and helium. Former process comparatively produced high product having better quality.

#### **Catalyst effect**

Table 7 shows that when Fe<sub>2</sub>O<sub>3</sub> loaded with catalyst coal sample in pyrolysis process increase pyrolysis reactivity, but ordering of char decreased by Fe<sub>2</sub>O<sub>3</sub>, Lower temperature for ignition and also residual carbon. Potassium catalyst loaded with coal mostly the carbonates of potassium are directly used, electropositive and reactivity slightly very high, gas yield higher than char because of higher quantity of organic matter. Pyrite: Used as a catalysis but sulfur can damage and polluted the environment. CaO loaded with coal Char and gas yield increased with the addition of catalyst but tar yield initially increased and then decreased. Addition of catalyst the activation energy and pre-exponential factor decreased. When KCl or ZnCl<sub>2</sub> and MnCl<sub>2</sub> loaded with coal then hydrogen yield increase with loading of ZnCl<sub>2</sub> (1-25% w/w, initially loading 10% w/w) also effect on quantity of methane production, MnCl<sub>2</sub> is most favorable for methane production because MnCl<sub>2</sub> has highest catalyst activity for aromatic formation, better result because of high surface area. KCl catalyst mechanism is different from rest of the others, effective when temp below 500°C

#### **ENVIRONMENTAL EFFECT OF PYROLYSIS**

During coal utilization the major problem is the pollutants emission to the surrounding. Some parts of the inorganic components removed to the environment when pyrolysis is being proceeds. Process of cleanness of air is at danger because of emissions of litter and other harmful gases include Sulphur oxides, carbon monoxide and nitric oxide and numerous organic aromatic poly-nuclear hydrocarbons. Elements which cause the pollutants to the air are potentially hazardous. During pyrolysis numerous researcher have researched and reported the relationship between reactivity of organic and inorganic components conversion in coal, but some of the researcher has reported the relationship between kinetics of pyrolysis of coal and inorganic materials. Tendency of vaporization of insignificant elements in coal is calculated on the basis of thermodynamic equilibrium. Segregation of these

**Table: 7 Pyrolysis conditions and pyrolysis products under different conditions.**

Reactor type	T(°C)	Sweeping gas flow rate	Residence time (s)	Catalyst type	Catalyst to coal ratio	Bio-oil			Gas (wt. %)	Char (wt. %)	Ref.
						Aqueous	Organic	Total (aqueous +organic)			
Fixed bed	400	30	10	Fe <sub>2</sub> O <sub>3</sub>	0.44	14.4	7.7	22.4	39.2	34.9	[53]
Fluidized bed	450	3.75	*	Potassium	0.4	13.1	15.8	28.9	49.4	21.7	[54]
Fixed bed	500	30	4.5	CaO	0.5	17.5	10.91	27.41	27.49	37.43	[19]
Fixed bed	500	50	0.03	KCl*, ZnCl <sub>2</sub> , MnCl <sub>2</sub>	0.1	*	*	37.29	20.45	42.27	[55]

\*Data is not available

elements is directly influenced by type of coal, ash components and redox reaction condition. Effects of temperature investigated from 300–1000°C, N<sub>2</sub> and H<sub>2</sub> atmosphere is provided, holding time 03-10 min. In pyrolysis of Datong coal (China) used clogged computer-generated drop tube reactor to examine the behavior. The trace elements and coal omit stable at 300°C. With increase the pyrolysis temperature there is also increase in the release amount of trace elements. Volatile matters discharge from coal also contains hydrogen gas, if H<sub>2</sub> atmosphere supplied it promote the investigated of all released elements. As in Table 8 Cr and Mn volatiles are in fewer amounts in pyrolytic gaseous product than Pb and Cd, both Pb and Cd show the similar behavior [56, 57]. Char is obtained after the complete transformation of elements obtained from the bottom of the reactor. Mercury (Hg) from coal removes by using the mild pyrolysis method, when treated at excessive volatility of the elements. During carbonization huge part of the minor elements formed the gaseous products which cause the pollution to the environment produced by coking of coal and coke oven gas combustion process. From the environmental protection point of view, it is an important objective before coal being process makes sure the sulfur contents should be limited. Coal consist of sulphur contain both inorganic and organic nature. Mostly inorganic sulphur present in the form of pyrite, marcasite with a small quantity of sulphates. Sulphur exists in organic compound either in the form of cyclic compounds or non-cyclic compounds [58]. Distribution behavior of organic sulphur alters from native to native coal surprisingly if the rank of coal is same. Mineral matters also present

in char or tar which is formed by conversion process of coal. Superior the percentage of organic sulfurs structures in coal, the larger the degree of organic sulfur is taking away among the reaction conditions, during pyrolysis of coal [59, 60], temperature is the most essential feature that disturbing the conversion of sulfur. High heating rate and external hydrogen is preferred. According to literature data, at different conditions during coal pyrolysis removal of sulfur changes from 15% to 40% rely on quality of coal, pyrolysis temperature, heating rate and time.

Pyrolysis done without oxygen when oxidative conditions provided mainly SO<sub>2</sub> is emitted, while mainly H<sub>2</sub>S is emitted when oxidative conditions are provided. Pyrolysis of material is done in the absence of air and inert gas mostly nitrogen is used as a carried gas, lean hydrogen or lean oxygen atmospheres in which rest of the sulfur compounds may also produce, such as COS, CH<sub>3</sub>SH, CS<sub>2</sub>, and thiophene. High volatile gaseous hydrocarbon components are also liberated; include usually CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub>

## NEW EMERGING PYROLYSIS TECHNOLOGIES

Currently the macro chemical structure of coal has been found by various analytical techniques and advanced spectroscopic apparatus. Pyrolysis of Coal Swollen with Solvent: It is essential to control the primary devolatilization reactions for increasing TVM (total volatile matters). The secondary gas phase reactions controlled, in this techniques by which effectively supplying reactive radicals from solvent to the primary pyrolysis products. Pyrolysis of Coal-Solvent Slurry: It was then intended to develop a method combining

Table: 8 Environmental effects of coal pyrolysis

Trace Elements	Environmental Impacts
Lead (Pb)	Contaminate water. Cause lead pollution. Effect food chain. Contaminate soil. Cause corrosion in pipelines.
Mercury (Hg)	Effect marine life. Contaminated food chain. Contaminate soil that Destroy crops.
Arsenic (As)	Contaminated food chain. Once entered cannot be destroyed from environment. Effect marine life.
Nickel (Ni)	There are many environmental issues associated with nickel including greenhouse gas emissions, habitat destruction, and contamination of air, water, and soil. This leads to high emissions of greenhouse gases into the atmosphere
SO <sub>2</sub>	SO <sub>x</sub> can harm trees and plants. Cause deforestation acidify waterways to the detriment of aquatic life. Corrode building materials and paints.
NO <sub>2</sub>	NO <sub>x</sub> also reacts with other pollutants in the presence of sunlight to form ozone which can damage vegetation at high concentrations. High levels of NO <sub>x</sub> can have a negative effect on vegetation, including leaf damage and reduced growth.
Chromium (Cr)	Contaminate water. Contaminate soil. Contaminate air.

the two methods introduced above to simultaneously control the primary devolatilization reactions and the secondary gas phase reactions. It tried to pyrolyze the tetralin-swollen coal in a vapor of 2-methyl-1-propanol. Pyrolysis of Solvent Solubilized Coal: The method pyrolyzing coal-solvent slurry was extended to use the coal pre-oxidized by H<sub>2</sub>O<sub>2</sub>. Swelling sites were increased by performing the pre-oxidation and carboxylic groups in a coal. Tar yield and total volatiles further increased by extended this method [61].

#### FUTURE EXTENT OF PYROLYSIS PROCESS

Pyrolysis extent investigation has been done by many researchers on the basis of products, feedstock selection and operating parameters. On the basis of various investigations parameters, different type of product obtain that is used in chemical and petrochemical industries. Organic product produced by this process depends on the amount of volatile matters present and recycling of non-condensable gases for the better results in terms of quality and expense [62-66]. If Non-condensable gases having adequate amount of inert N<sub>2</sub> along with CH<sub>4</sub>, CO<sub>2</sub>, CO, H<sub>2</sub>O, NO<sub>x</sub> and SO<sub>x</sub> extracted these compound CH<sub>4</sub>, CO, H<sub>2</sub>O from released gases and recycled to pyrolysis reactor influence on inert gas supply will be minimized. NCG further proceed towards the fertilizer, energy and hydrogen fuel production after extraction of synthesis gas remaining part of gases emitted to environment. Different fractions of

NCG released at different temperature, mostly in O<sub>2</sub>-environment exothermic reactions performed and amount of heat liberated used as a source of career energy. Clearly noticed the yields are mutually dependent and its sum will all the time equal to 100% if fully accounted.

#### CONCLUSIONS

i. It was observed from the overview of the current study that the charcoal yield is effective product in case of slow pyrolysis by maintaining the gentle heating rate and maximum product obtained by the 92% at low temperature below 400°C which can be further treated for making charcoal briquettes as a fuel [48, 67].

ii. On the contrary, the liquid product increased by increasing the appropriate heating rate further increase in temperature taking towards the gas yield and leads to the secondary cracking. Further increase in temperature resulted in decrease in charcoal yield.

iii. Heating rate also very important parameter in slow pyrolysis to obtained the charcoal yield. Maximum charcoal yield obtained at lowest ramp 1 to 10°C/min. From this present study, it was investigated that at higher heating rate the charcoal yield decreased.

iv. The charcoal yield was less influenced by particle size, but high particle size supported. Average 3.5% charcoal yield was reduced when particle size varied from 0.21mm to 0.297mm.

V. Selection of reactor also affects the product, from the literature it was observed that fixed bed reactor or ablative produce higher product and its scale up procedure is difficult to handle. Fluidized and circulating bed also gives maximum product but sweeping gas flow was too high in both reactors and particle size comparatively less than ablative and fixed bed reactor.

### Nomenclature

Ar	As received
Db	Dry basis
Afd	Ash free and dry
BKB	Brown coal briquettes
CSIR	Commonwealth scientific and industrial research organization
OCR	Occidental research corporation
40R	Large particle size of coal
60R	Medium particle size of coal
80R	Small particle size of coal
TGA	Thermo-gravimetric analysis
DTGA	Differential thermo-gravimetric analysis
TVM	Total volatile matters

### Acknowledgement

This work was supported by the National Fertilizer Corporation, Institute of Engineering and Fertilizer Research, Faisalabad. The authors also thank Professor Najaf Ali and Tanveer Iqbal to guide me about this broad range of research field.

Received: Feb. 8, 2022 ; Accepted: Jun. 13, 2022

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