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1 Investigation of the influence of metallic fuel 2 improvers on coal combustion/pyrolysis

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8 ABSTRACT

9 The influence of iron, aluminium and silicon based oxides (fuel improver) towards coal
10 combustion was investigated in a Thermogravimetric analyser (TGA) coupled with Fourier
11 transform infra-red (FTir) spectrophotometer, temperature controlled two stage bench reactor
12 (TSBR) and 100 kWth combustion test facility (CTF). The metallic oxides, 5%, 15% and 33%
13 by weight, in order to prepare overall 20 mg of sample blends were mixed with pulverised coal
14 for the TGA-FTir study. The individual un-blended samples of fuel improver and coal were also
15 analysed separately. The analysis of fuel improver samples revealed no evidence of hydrocarbon
16 release or weight change, however, substantial changes in the weight as well as release of
17 hydrocarbons (H-Cs) and CO were observed for coal. More importantly study of the combustion
18 data shows a distinct change in the peak intensities for CO and H-Cs, especially when coal
19 sample was blended with 5%, 15% and 33% (by weight) of fuel improvers. This suggests

1 enhanced cracking of the coal matrix in presence of fuel improvers. This impact of the presence
2 of fuel improver was also confirmed to increase the Gas / Oil yield in the temperature controlled
3 two stage fixed bed reactor. The increase in the combustion zone temperature, improvement in
4 NO_x reduction and loss on ignition of fly ash samples collected from 100kWth CTF, proved the
5 enhanced combustion characteristics of coal with studied metallic fuel additive. Hence these fuel
6 improvers can be utilized in the heat-power engineering related to solid hydrocarbon fuels.

7 KEYWORDS

8 Fuel improver; TGA; FTir; Bench Reactor; Combustion test facility; Coal; Combustion;
9 Hydrocarbons; CO; Gas / Oil yield; NO_x; Loss on ignition.

10 INTRODUCTION

11 The heat to power (electricity) related coal fired power plants have been challenged under the
12 environment legislations to substantially reduce the flue gas emissions and/or the fuel
13 consumption. One of the solutions for this dilemma is to enhance the fuel or mix it with
14 catalysts/ fuel improvers to grasp the aforementioned issues as proficiently as possible. The fuel
15 improvers / catalysts have been found to increase the reactivity or reduce pollution at a lower
16 cost than current post combustion emission reduction technologies^{1,2}. It has also been found that
17 with the presence of oxides of iron the ignition temperature of different ranks of coal were
18 decreased. Similarly, Fe proved to be the effective additive promoting cracking of tar from
19 biomass gasification^{2,3}. Similarly in a separate study the effect of iron based granules on biomass
20 tar decomposition have been verified. The results demonstrated a clear tar reduction capacity for
21 all the tested conditions⁴. Moreover, it has been reported that volatile aromatic hydrocarbons
22 (VAC) (mainly benzene, toluene, and xylene) and polycyclic aromatic hydrocarbons (PAH)

1 during coal combustion or biomass gasification can easily be converted to produce high gas yield
2 and or reduce NO_x emissions using iron / CeZrO₂ supported fuel catalysts, respectively^{4, 5}. The
3 iron oxide-silica fuel improver is also an excellent catalyst for benzene cracking⁶.

4 Iron oxide (Fe₂O₃) has also been utilised in producing pure hydrogen from syngas. It is also
5 known as a suitable oxygen transfer agent for converting CO present in the syngas to CO₂. The
6 investigation into conversion of iron oxide in presence of gas mixtures (10%CO; 5.7%CO +
7 4.3% H₂; 10% H₂ with balanced 90% N₂) reveals shifting from surface-controlled process to
8 diffusional control⁷. Similarly in a separate study⁸ the data showed that the reduction of hematite
9 to wusite (FeO) is favoured at high temperatures for production of CO₂ from CO (present in
10 syngas).

11 Iron oxide utilisation to reduce nitrogen oxides by carbon monoxide over an iron oxide catalyst
12 under dynamic conditions has also been studied⁹. A strong impact of concentration of oxygen on
13 the efficiency of NO reduction was found compared to concentration of carbon monoxide¹⁰. The
14 reduction of NO to N₂ by iron has been reported to be initially supported by; dissociation of NO
15 on the surface to yield chemisorbed O₂⁻ ions, nitrogen gas and electron holes in the solid;
16 followed by diffusion of Fe⁺² ions and free electrons through vacancies in the FeO lattice^{11,12}.
17 Similarly, it has been shown that a bare Fe₂O₃ cluster can oxidize CO to form CO₂ and reduce
18 NO to form N₂¹³.

19 In the present study, the investigation of the impact of iron based fuel improvers over coal
20 pyrolysis / combustion have been investigated using TGA, fixed bed reactor and a pilot scale
21 combustion test facilities. The findings of the study towards enhanced combustion were later put
22 to test on 100kWth combustion test facility to verify the reduction in unburned carbon left in fly
23 ash and increase in combustion zone temperature.

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3 1 MATERIALS AND METHODS
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5 2 The impact of fuel improver on coal combustion and the behaviour of unblended fuel
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8 3 improvers was investigated using a Stanton Redcroft TG782 thermo-gravimetric analyser (TGA)
9
10 4 connected to a Nicolet Magna 560 Fourier transform infra-red (FTir) spectrometer via a heated
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12 5 interface and heated transfer line (Figure 1A). A thermo-gravimetric analyser is in essence a
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14 6 micro-balance, with a sample crucible suspended from one side of the balance beam into an
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16 7 electrically-heated furnace on a hang-down. The TGA in this study was equipped with a
17
18 8 platinum crucible and an automated gas selector to enable the atmosphere in the furnace to be
19
20 9 changed. Two types of runs were performed on the TGA, proximate analysis and reduced
21
22 10 oxygen proximate analysis. Similar TGA conditions were used for both runs, as shown in Table
23
24 11 1, except 3% v/v oxygen in nitrogen was substituted for air during the final hold period in
25
26 12 reduced oxygen proximate analysis. In proximate analysis, the first hold period is used to drive
27
28 13 moisture from the sample. The second ramp and hold drives off volatile matter, leaving char in
29
30 14 the TGA crucible. The char is then combusted when air or other oxidant gas is introduced during
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32 15 the final hold period.
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39 **Table 1.** TGA conditions employed.
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Parameter	Hold 1	Hold 2	Hold 3
Heating rate ($^{\circ}\text{C min}^{-1}$)	10	25	Not applicable
Temperature ($^{\circ}\text{C}$)	105	950	950
Hold time (min)	10	30	
Atmosphere	Gas 1 (Nitrogen)	Gas 1 (Nitrogen)	Gas 2 (Air or 3%O ₂)
Gas flow rate ($\text{cm}^3 \text{min}^{-1}$)	60	60	60

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1 Many diatomic bonds are susceptible to bending, stretching or vibration reactions when
2 exposed to energy in the form of infra-red radiation. A given reaction of an individual bond
3 occurs when radiation of a discrete wavelength is absorbed, so when infra-red radiation of the
4 correct wavelength is passed through the sample, a reduction in transmission will be seen. Since
5 infra-red absorption only occurs in molecules where there are diatomic bonds, such as carbon
6 dioxide, species such as nitrogen and oxygen cannot be detected using infra-red spectrometry.
7 'Scanning' across the full infra-red wavelength range results in the sample spectrum, which is
8 normally plotted as transmission against wavenumber ($1/\text{wavelength}$, units cm^{-1}). Because the
9 transmission is inversely proportional to the concentration of the bond in question, we can use
10 the intensity of response at a particular wavenumber (or wavenumber range) to measure the
11 concentration of the gas of interest.

12 FTIR spectrometer operated in $400\text{-}4000\text{cm}^{-1}$ scan range and a spectrum was taken every 45s
13 during the course of the TGA run. Background scans were also taken to correct for ambient
14 moisture and CO_2 prior to each run. The TGA interface cell was held at 300°C under a constant
15 nitrogen flow to minimise the effect of changes in ambient moisture and CO_2 , whereas the
16 transfer line was maintained at 170°C . The intensity of absorbance in the wavenumber range
17 $2000\text{-}2500\text{cm}^{-1}$ corresponding to the concentration of CO and CO_2 in the sample gas was plotted
18 versus time during combustion test. Whereas, the wavenumber ranges $2170\text{-}2180\text{cm}^{-1}$ (CO only)
19 and $2800\text{-}3200\text{cm}^{-1}$ (a variety of C-H bonds released during coal pyrolysis) were plotted from the
20 spectral series data.

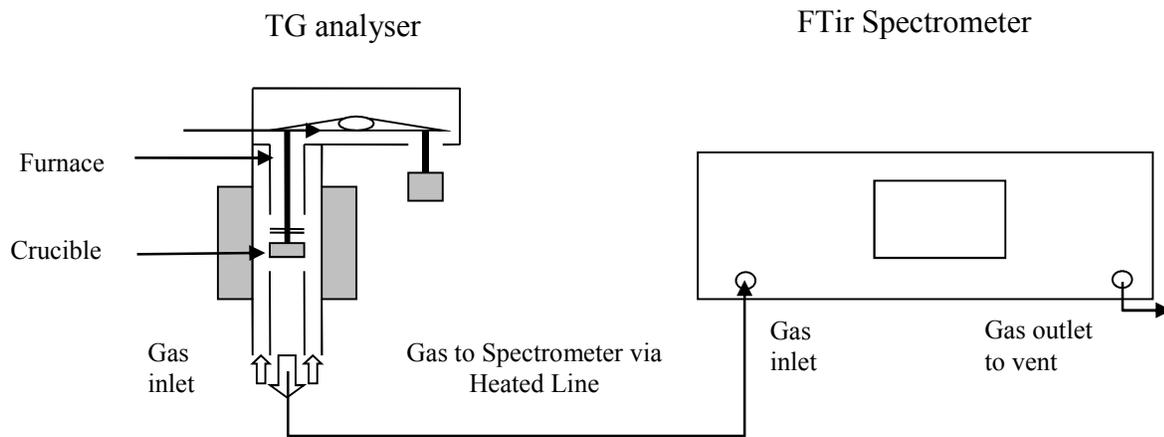
21 The investigation of the impact of fuel improver was also carried out for the coal pyrolysis /
22 reforming in the absence (silica sand) / presence of the improver in a two stage fixed bed
23 reaction system (Figure 1B). Coal sample (2-4 gram) was pyrolysed in the first reactor and the

1 derived gases were reformed in the second reactor, where the fuel improver (2-4 gram) was
 2 placed. Products after the second-stage reaction were condensed by air and dry-ice. The non-
 3 condensed gases were collected by the gas sample bag and further analysed by gas
 4 chromatograph (GC). Table 2 shows the composition of the Fuel improvers and studied coal.

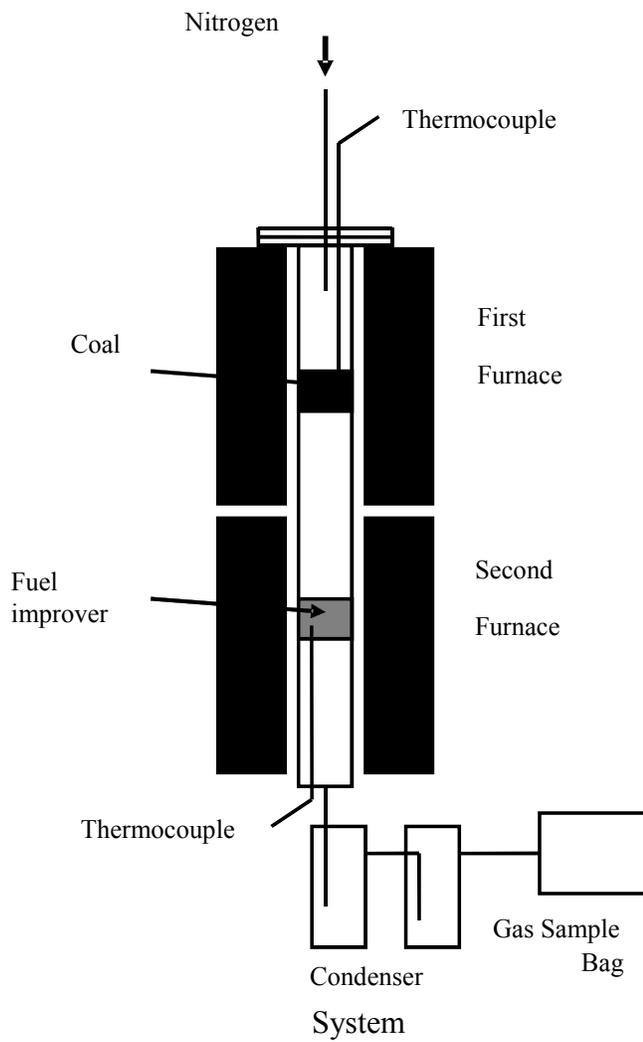
5 The combustion test facility (CTF) employed for combustion characteristics comprised of 4 m
 6 high, 400 mm internal diameter down fired furnace. The furnace (Figure 1C) was fed with blends
 7 of coal with additive to observe changes in coal combustion characteristics (emissions,
 8 temperatures and loss on ignition of produced fly ash). Fly ash solids were collected by the fly
 9 ash catch pot connected to a cyclone separator. The samples and emissions were collected and
 10 measured after attaining steady state condition for each test.

11 **Table 2.** Chemical composition of coal and XRF / XRD composition of fuel improvers

Ultimate analysis as received, (%)	Russian Coal (RC)	XRF Description	Water Cooled Fuel Improver, WCFI (%)	Air Cooled Fuel Improver, ACFI (%)
C	66.29	Na ₂ O	0.8-1.3	0.5-0.97
H	4.55	MgO	1.62-1.98	1.0-1.7
N	2.09	Al ₂ O ₃	4.71-5.1	3.1-5.5
O (diff)	8.95	SiO ₂	34.69-38.5	32.14-39.0
S	0.20	K ₂ O	0.362-0.6	0.35-0.847
H ₂ O	6.23	CaO	2.5-7.06	2.0-5.37
Ash	11.69	TiO ₂	0.09-0.25	0.1-0.28
		Fe ₂ O ₃	42.22-51.9	41.2-50.9
		P ₂ O ₅	0.208-0.9	0.1-0.721
		SO ₃	0.2-1.05	0.5-0.75
Proximate analysis as received, (%)	Russian Coal (RC)	XRD Description	Water Cooled Fuel Improver, WCFI (%)	Air Cooled Fuel Improver, ACFI (%)
Volatile Matter	32.90	Faylite, Fe ₂ (SiO ₄)	7-15	49-64
Fixed Carbon	49.20	Magnetite, Fe ₃ O ₄	Trace	15-25
Moisture	6.23	Amorphous	81-91	21-25
Ash	11.69			



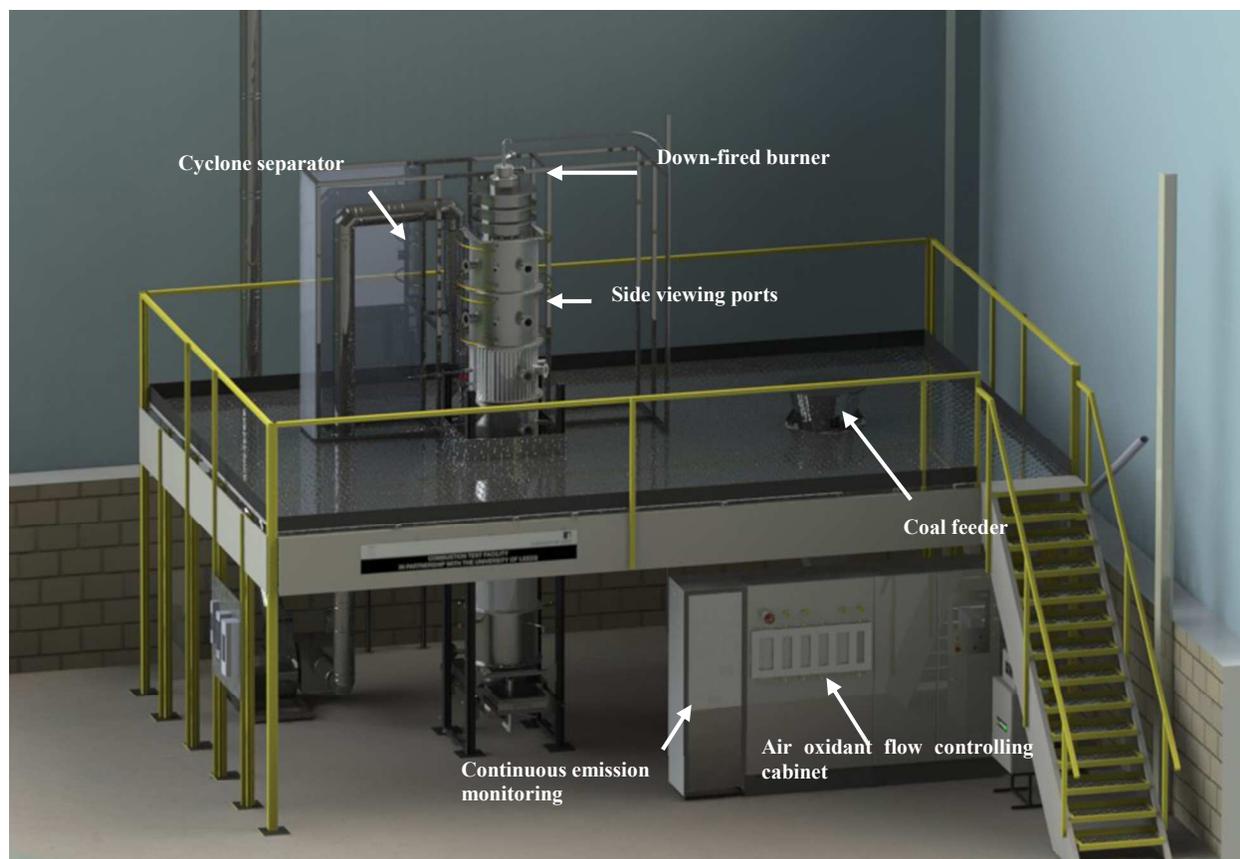
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3 **Figure 1.** (A) Schematic representation of the Stanton Redcroft TGA and Nicolet Magna 560
4 FTir Spectrometer; (B) Schematic representation of the temperature controlled two staged fixed
5 bed reactor; (C) Experimental set up of 100kW combustion test facility.

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3 1 RESULTS AND DISCUSSION
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6 2 3.1. Un-blended Fuel improvers and RC tests
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8 3 The individual un-blended samples of fuel improvers and coal were analysed separately. The
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10 4 tests were performed using N₂ until final burnout under 3% O₂ and balance N₂. Figure 2A shows
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12 5 the weight changes along with temperature profiles. However, there does appear to be a weight
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14 6 gain which is probably due to buoyancy effects with low weights. Analysis of the FTir data and
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16 7 focusing on the absorbance for 2170-2180cm⁻¹ wavenumber band for CO (Figure 2B) shows no
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18 8 indication of CO being released for all the improvers tested. On the contrary, changes in the
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20 9 weight were observed for coal. Similarly the CO release for coal is shown for comparison in
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22 10 Figure 2B as well. Analysis for hydrocarbons absorbance in the 2800-3200cm⁻¹ wavenumber
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24 11 band relating to a range of C-H bonds, incl. aliphatic and aromatic groups, similarly showed no
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26 12 evidence of hydrocarbon release (Figure 2C). Analysis of the FTIR data focusing on absorbance
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28 13 for 2000-2500cm⁻¹ wavenumber band for CO₂ and CO shows no indication of CO/CO₂ being
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30 14 released (Figure 2D). The analysis revealed no evidence of hydrocarbon, CO and CO/CO₂
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32 15 release, or weight change for the studied fuel improvers. The blank test confirmed that there
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34 16 would be no interference in the analysis of the data from the reacting coal and improver mixtures
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36 17 during reactive tests.
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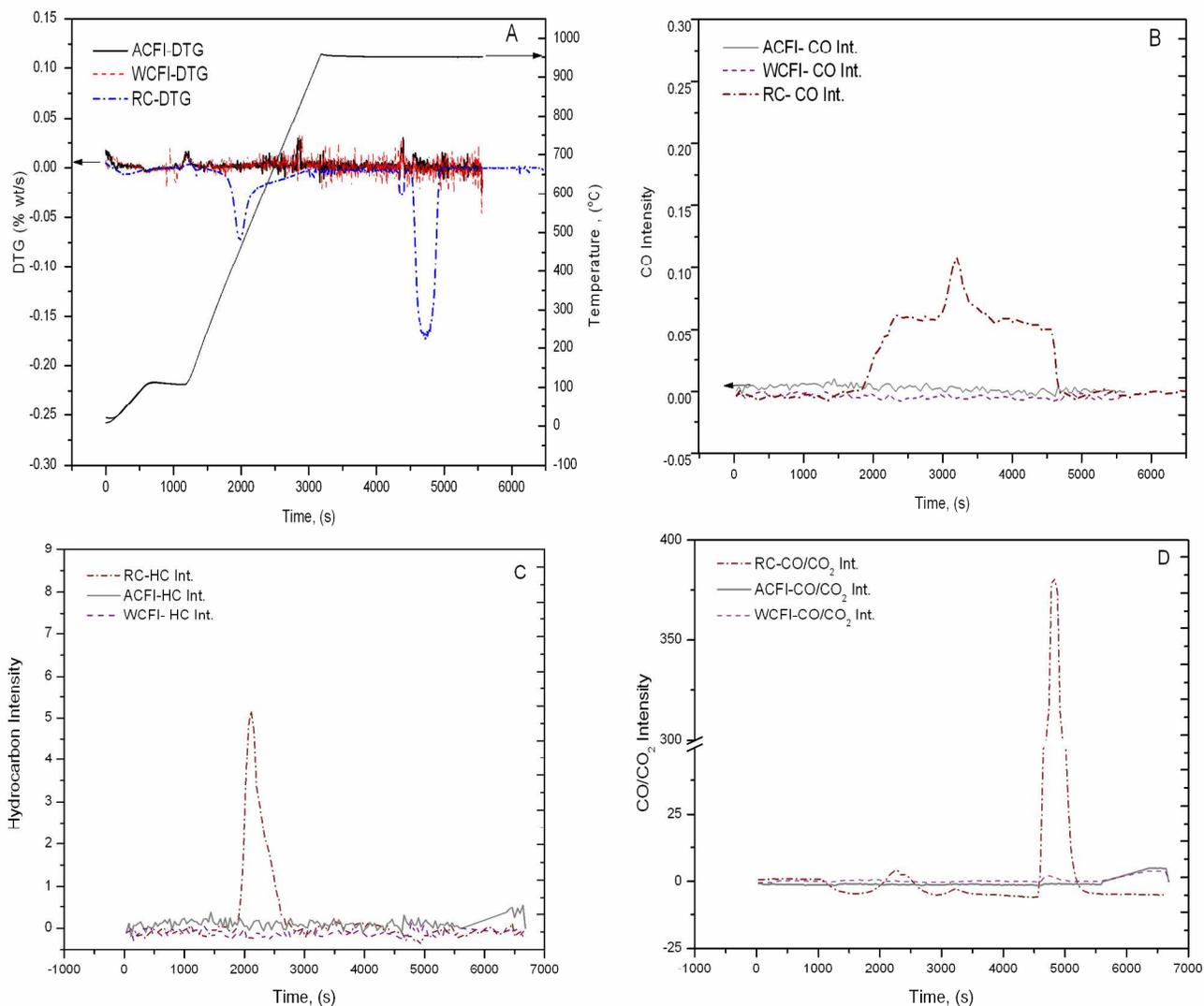


Figure 2. (A) DTG profile and CO (B)¹⁴, Hydrocarbon (C) and CO/CO₂ (D) intensities for un-blended fuel improvers and Russian coal (RC).

3.2. Effect of the Fuel improver on Coal in nitrogen/ air

The fuel improver (ACFI) blends with coal (~20mg) were prepared and time weight loss history was analysed (Figure 3A). It can be observed from the Figure 3A-B, the initial rate of change of weight is associated with water evaporation, followed by devolatilization region under pyrolysis conditions. The later part of the DTG curve is associated with char combustion in air.

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3 1 Analysis of the combustion data are presented in Table 3. The weight loss data collected
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5 2 during combustion in air at 950°C are presented as combustion rates in the table and vary from
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8 3 0.35 mg/min to 2.34 mg/min. The rate of combustion of coal char in air was measured at
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10 4 2.34mg/min, whereas the rates of coal char with fuel improver blends were 1.97 mg/min to 2.05
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12 5 mg/min. Figure 3A-B indicates that increasing the fuel improver content (ACFI) did not appear
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14 6 to affect the char combustion rates which were lower than coal alone. On the other hand,
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16 7 combustion in 3% O₂ gave lower combustion rates but incomplete burnout and therefore not
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18 8 useful for comparative purposes. Moreover, coal and coal + 5% mass fraction of both types of
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20 9 fuel improvers (ACFI and WCFI) show little difference in combustion rate between the fuel
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22 10 improvers. Table 4 shows FTIR data which has been corrected for any variation in initial coal
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24 11 weights between the samples tested for 5% addition of fuel improver. The results show that the
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26 12 standard deviation of coal between samples was 0.56 mg and is shown to be insufficient a
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28 13 difference to influence the overall trend of the graphs and results.
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1 **Table 3.** Analysis of combustion data from TG tests.
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Run	Improver		TGA Gases		Char	Char	Combustion			Char
					Combustion	Combustion	Time (min)			Combustion Rate
No.	Name	(wt %)	Gas 1	Gas 2	Wt Loss (mg)	Complete?	Onset	End	Time	(mg/min)
1	RC	0	N ₂	Air	10.06	Yes	76.74	81.04	4.30	2.34
2	ACFI	5	N ₂	Air	9.75	Yes	76.47	81.24	4.77	2.04
3	WCFI	5	N ₂	Air	10.07	Yes	76.52	81.42	4.90	2.06
4	ACFI	33	N ₂	Air	9.84	Yes	76.49	81.48	4.99	1.97
5	ACFI	15	N ₂	Air	10.16	Yes	76.51	81.43	4.92	2.07
6	WCFI	15	N ₂	Air	9.86	Yes	76.50	81.34	4.84	2.04
7	RC	0	N ₂	3% O ₂	10.06	No	78.2	103.00	24.80	0.41
8	RC	0	N ₂	3% O ₂	10.71	No	78.35	103.00	24.65	0.43
9	ACFI	5	N ₂	3% O ₂	9.99	No	77.03	103.00	25.97	0.38
10	WCFI	5	N ₂	3% O ₂	10.87	No	76.87	103.00	26.13	0.42
11	ACFI	100	N ₂	3% O ₂	No weight loss seen- just buoyancy effect as TGA furnace ramped to final temp.					
12	WCFI	100	N ₂	3% O ₂	No weight loss seen- just buoyancy effect as TGA furnace ramped to final temp.					

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Table 4. TG-FTir Results, peak height correction for initial weight difference between coal in the samples.

TGA wts	initial	initial		
	coal + adds	coal in sample	factor	
RC	20.16	20.16	1	
RC + 5% ACFI	22.26	21.15	0.953	
RC+ 5% WCFI	22.23	21.12	0.955	
CO				corrected
	base	peak	height	height
RC	0.003	0.107	0.104	0.104
RC + 5% ACFI	0.003	0.183	0.18	0.172
RC+ 5% WCFI	0.003	0.177	0.174	0.166
CO ₂ + CO				corrected
	base	peak	height	height
RC	-5.5	379	384.5	384.500
RC + 5% ACFI	4.2	338	333.8	318.220
RC+ 5% WCFI	4.2	377	372.8	355.880
Hydrocarbons				corrected
	base	peak	height	height
RC	0.01	5.14	5.13	5.130
RC + 5% ACFI	0.25	7.38	7.13	6.797
RC+ 5% WCFI	0.01	7.01	7	6.682

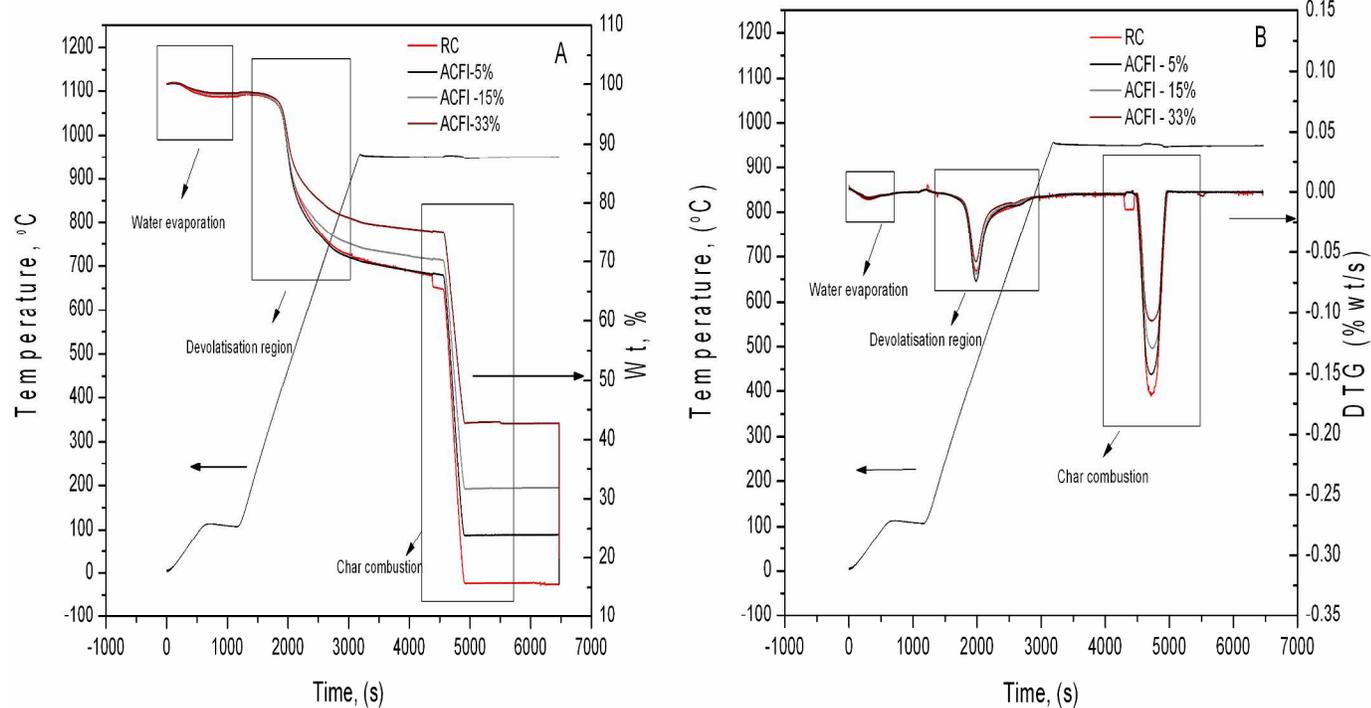
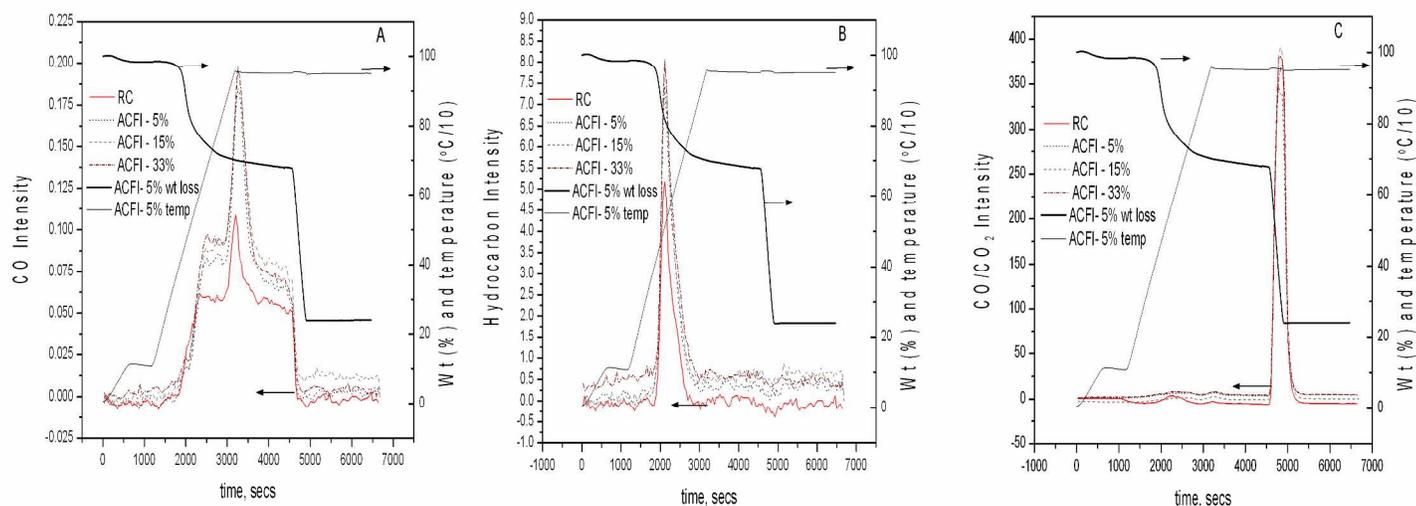


Figure 3. TGA-DTG profiles for RC and ACFI blends from 5% to 33% with RC.

The analysis of the FTIR data for CO shows the CO measured during the pyrolysis stage of the heating process between temperatures of 350°C and 950°C (Figure 4A). The onset of CO release at 350°C reaches a plateau at under 650°C. CO peaks at about 950°C followed by a reduction then complete burnout upon introduction of O₂ containing mixture. There has been an increase in the CO produced in presence of ACFI compared to coal alone. No significant difference in CO concentration was measured while comparing amongst the types and amounts of the fuel improvers. An overall range of 69% to 79% increase in the intensity of CO was observed with ACFI for 5% to 33% blending ratios (Figure 4A).

1 The hydrocarbons released during the coal pyrolysis/combustion tests were analysed in the
 2 FTIR (Figure 4B). Hydrocarbon release from the coal (under N₂) starting at 300°C, reaching a
 3 maximum at about 500°C gets completed at about 900°C. The concentration of hydrocarbons (H-
 4 Cs) with fuel improvers was higher compared to that from the coal alone. An overall range of
 5 44% to 55% increase in the intensity of H-Cs was observed with 5% to 33% blending ratios of
 6 ACFI with coal (Figure 4B). A Combined CO₂ and CO level in the gas which is eluted during
 7 the TG experiments is shown in Figure 4C. There was not significant enhancement in CO₂
 8 release by analysis of the curves. This confirms the results from the mass loss data obtained
 9 from the TG data. However, In order to understand and validate the increase of CO and
 10 hydrocarbon intensities in presence of fuel improver, further bench scale tests were performed on
 11 a two staged fixed bed reactor. This meant that samples in couple of grams (i.e. 2-4 grams) can
 12 be studied into the reactor rather than 20mg.



14 **Figure 4.** CO (A) [18], Hydrocarbon (B) and CO/CO₂ (C) intensities for un-blended fuel
 15 improvers and Russian coal (RC).

3.2.1. Pyrolysis tests in two stage fixed bed reactor

The pyrolysis tests on two stage fixed bed reactor gave higher yields of gas when compared to coal alone (Figure 5). It has also been found that the higher yield of gas resulted in lesser proportion of the oil (tar). This means that the heavier hydrocarbons originally present in the coal are broken down into lighter hydrocarbons while interacting with the fine iron based fuel additive, biased towards producing more gas than oil. In a separate study⁴, generally 10% to 20% of the total tar conversion has been reported with an increase in the gas yield within temperature ranges of 750- 850°C.

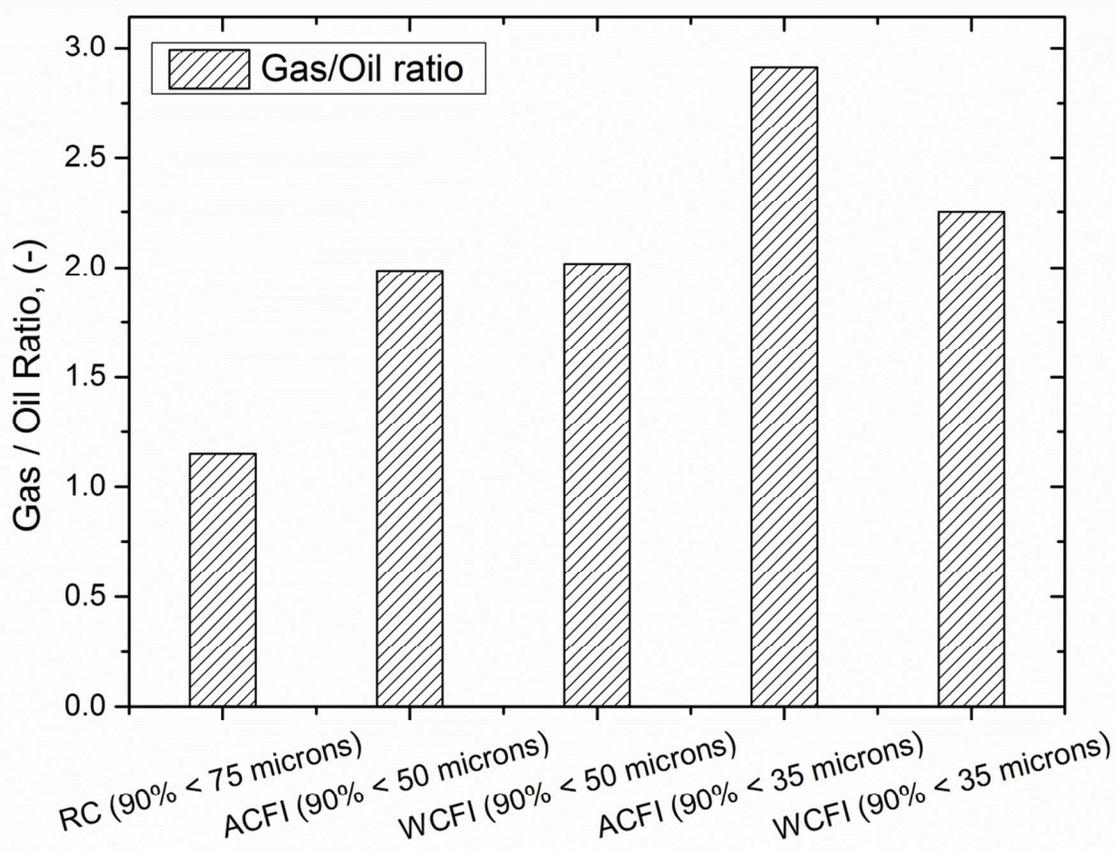
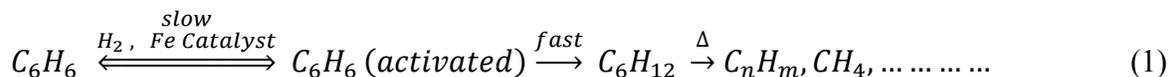


Figure 5. Gas / Oil Yield ratio with and without fuel improver.

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3 1 There has been noticeable difference observed in gas to oil (tar) yield between ACFI and
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5 2 WCFI. It has been observed that finer particle size distribution of ACFI (90% less than 35
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8 3 microns) resulted in higher gas to oil ratio i.e. 46% higher when compared to ACFI having 90%
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10 4 of the particles less than 50 microns size. Whereas WCFI < 35 microns produced 11% more of
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12 5 the gas to oil yield compared to WCFI < 50 microns. The end product oil (tar) was dark brown
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14 6 for RC; however was changed to be cleaner in the presence of fuel improvers. It has been
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16 7 reported that highest tar reducing capacity is possible for both a pure metallic iron material or an
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18 8 iron based material with higher oxygen content due to shift from one rate determining reaction to
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20 9 another. Moreover, it has also been suggested that tar (mainly naphthalene) reduction pathway
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22 10 could have governed by both catalytic decomposition over a pure metallic iron and naphthalene's
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24 11 oxidative decomposition over oxide matrix of the iron. In literature it has been reported that in
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26 12 addition to naphthalene reduction controlled by catalytic decomposition on pure metallic iron,
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28 13 the oxidative decomposition on iron oxide can also be possible for high oxygen content
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30 14 materials. This would require either loosely bonded oxygen or free dissolved in the oxide matrix
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32 15 in the material^{5, 15}. Similarly in case of volatile aromatic hydrocarbons; Benzene, though not
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34 16 counted as pure tar but being an important intermediate and product of complex tar reduction
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36 17 network, has been reported to undergo pronounced reduction over iron based catalysts (Equation
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38 18 1) ^{5,6}.



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22 Similarly for Fe-Al catalysts, the steam reforming of naphthalene increased with the increase
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24 of Fe contents due to increased surface area, pore structure. However, the chemical properties

1 such as crystalline phase and oxidative states of the active sites are much important than physical
 2 influences¹⁶.

3 **Table 5.** Gas / Oil yields and concentration of gases.

Un-corrected Yield	RC	ACFI	WCFI	ACFI	WCFI
	d(0.9) < 75 μm	d(0.9) < 50 μm	d(0.9) < 50 μm	d(0.9) < 35 μm	d(0.9) < 35 μm
Gas yield (wt.%)	14.37	21.97	18.26	19.00	20.20
Oil Yield (wt.%)	12.50	11.06	9.05	6.53	8.97
Residue Yield (wt.%)	64.50	65.83	65.33	65.33	65.11
Mass balance (wt.%)	91.37	98.86	92.63	90.86	94.28
Corrected Yield					
Gas yield (wt.%)	15.73	22.22	19.71	20.91	21.42
Oil Yield (wt.%)	13.68	11.19	9.77	7.19	9.51
Residue Yield (wt.%)	70.59	66.59	70.52	71.90	69.06
Mass balance (wt.%)	100.00	100.00	100.00	100.00	100.00
Gaseous Compositions					
CO	16.50	18.14	16.54	18.80	18.85
H ₂	58.42	56.04	56.74	55.67	56.55
CO ₂	3.54	4.88	3.87	4.38	3.99
CH ₄	19.64	19.09	20.80	19.15	20.61
C ₂ H ₄	0.0184	0.0005	0.0019	0.0018	0.002
C ₂ H ₆	0.0004	0.0001	0.0001	0.0001	0.0001
Total	100.00	100.00	100.00	100.00	100.00

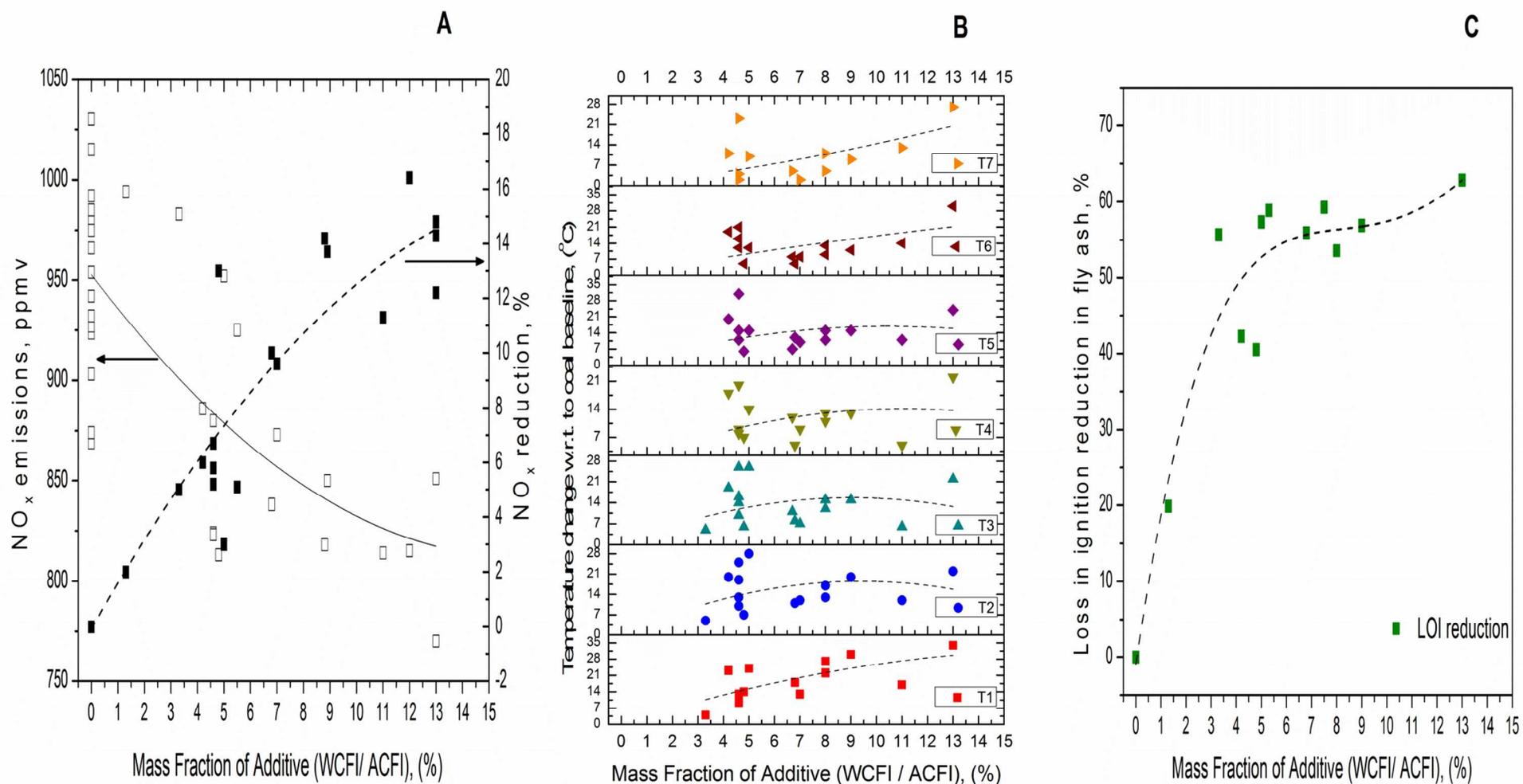
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1 The overall composition of the gases produced under pyrolysis is reported in Table 5. The gas
2 concentration for each experiment was presented as N₂ (carrier gas) free. It can be seen that CO,
3 H₂, CO₂, CH₄, C₂H₄, C₂H₆ were measured and other gases (i.e. C₃H₆, C₃H₈, C₄H₈ and C₄H₁₀)
4 were un-detectable. The overall concentration of the gases was not much changed except that
5 additional amounts were produced because of higher gas yield. In general, iron enhances the tar
6 and carbon reforming producing mainly CO and H₂. A maximum of 65% v/v syngas yield has
7 been reported for 40% w/w Fe in the mixture with olive kernels reducing tar yield by 45% w/w¹⁷.
8 In the present study ~ 15.75% w/w iron (ACFI) with coal produced an overall gas yield of about
9 20-22% v/v with about 7-11% w/w tar yield. This resulted in 33-41% increase in the gas yield
10 compared to coal baseline (Table 5). The optimum condition during the 20%w/w iron: olive
11 kernel experiments yielded 3.65 H₂/CO at 1050°C with steam gasification¹⁶ in comparison to
12 3.11 H₂/CO at 950°C for 15.75%w/w iron:coal mixture in this study (Table 5). Similarly in a
13 separate study related to pyrolytic cracking of coal tar, the initial heavy tar in the liquid product
14 decreased by 88% over iron oxide catalyst¹⁸. However, in the present study a range of 18% to
15 47% reduction in tar yield was observed compared to coal baseline (Table 5; Figure 5).

17 3.2.2. Combustion results on 100kW CTF and reaction mechanism

18 The blending ratios of the fuel improvers was tested from 5% to 33% on smaller bench scale
19 units, which when scaled up to pilot scale trials was limited up to 13%. The commercial trials
20 and optimum blending ratio findings on CTF revealed an optimum range of blending ratios of
21 these fuel improvers. NO_x reductions, improvement in combustion zone temperature and loss on
22 ignition (LOI) findings have been reported for 100kWth CTF. The process for NO_x reduction
23 observed during fuel improver addition (Figure 6) is associated with the interaction of oxides of

1 iron, aluminum, silicon particles and coal matrix, resulting in cracking the heavier hydrocarbons
2 into lighter and thus favours the split of fuel-N more into volatile-N. Moreover, it is also reported
3 in literature¹¹⁻¹³ that iron oxide of the fuel improver get reduce to produce iron particles resulting
4 in reduction of NO into N₂ i.e. Fe₂O₃ cluster oxidizes CO to form CO₂ and reduce NO to form
5 N₂. Fuel improvers hence assists in cracking the heavier hydrocarbons supported by the findings
6 of increase in gas and CO – HCs intensities (Figure 4-5); favours the split of fuel-N into more of
7 volatile-N¹⁹ (Figure 7). The reduced form of iron oxide also help in additional NO reduction
8 reactions supplementing the existing pathway towards N₂ formation. The increase in the mass
9 fraction of fuel improver confirms increasing effect on NO_x reduction. The optimum fraction
10 range of fuel improver 5-13% for coal resulted in a range of 6-20% improvement in NO_x
11 reduction (Figure 6A). The optimum mass fraction of fuel improver was based on the ease of
12 onsite material handling for later commercial trials i.e. consumption of 1500-3000 kg/hr of fuel
13 improver especially for a 260 tons/hr steam producing commercial boiler.



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Figure 6. (A) NO reduction; (B) Temperature change w.r.t coal baseline; (C) Reduction in loss on ignition

1 The organic fuels especially C with available O₂ releases energy at furnace temperature of
2 about 1000°C, the addition of fuel improver containing SiO₂ and Fe₂O₃ can also cause an
3 exothermic reaction releasing additional energy at temperature between 650-900°C. Thus the
4 exchange of energy due to series of exothermic and endothermic reactions with in the flame
5 creates small areas of high O₂ / H₂ content that create enhanced combustion dynamics, as evident
6 by increased temperature (Figure 6B) and higher reduction in loss on ignition in resultant fly ash
7 (Figure 6C). The proposed reaction mechanisms describing the plausible steps involved behind
8 the enhanced cracking/combustion are presented in Figure 7. It is trusted that during the heating
9 and softening /swelling of the coal particles, the fuel improver because of finer particle size
10 distribution enters into the coal matrix. The exchange of exothermic and endothermic reactions
11 in presence of oxygen or hydrogen rich pockets helps to produce lighter hydrocarbons via
12 cracking of heavier hydrocarbons. This would also enhance the HCN production resulting in
13 reduction of NO via NO_x reduction pathway supplemented by presence of reduced form of oxide
14 of iron. The proposed reactions towards interaction of coal particles (C_nH_m) are represented in
15 the Figure 7A. NO_x and volatile carbon chemical reaction pathways are presented in Figure 7B.
16 It has also been evident that about 15-35°C temperature increase has been observed between
17 various mass fractions of added fuel improver to that of the coal baseline temperatures (Figure
18 6B). More importantly up to about 60% improvement in LOI has been observed compared to
19 coal baseline loss on ignition values.

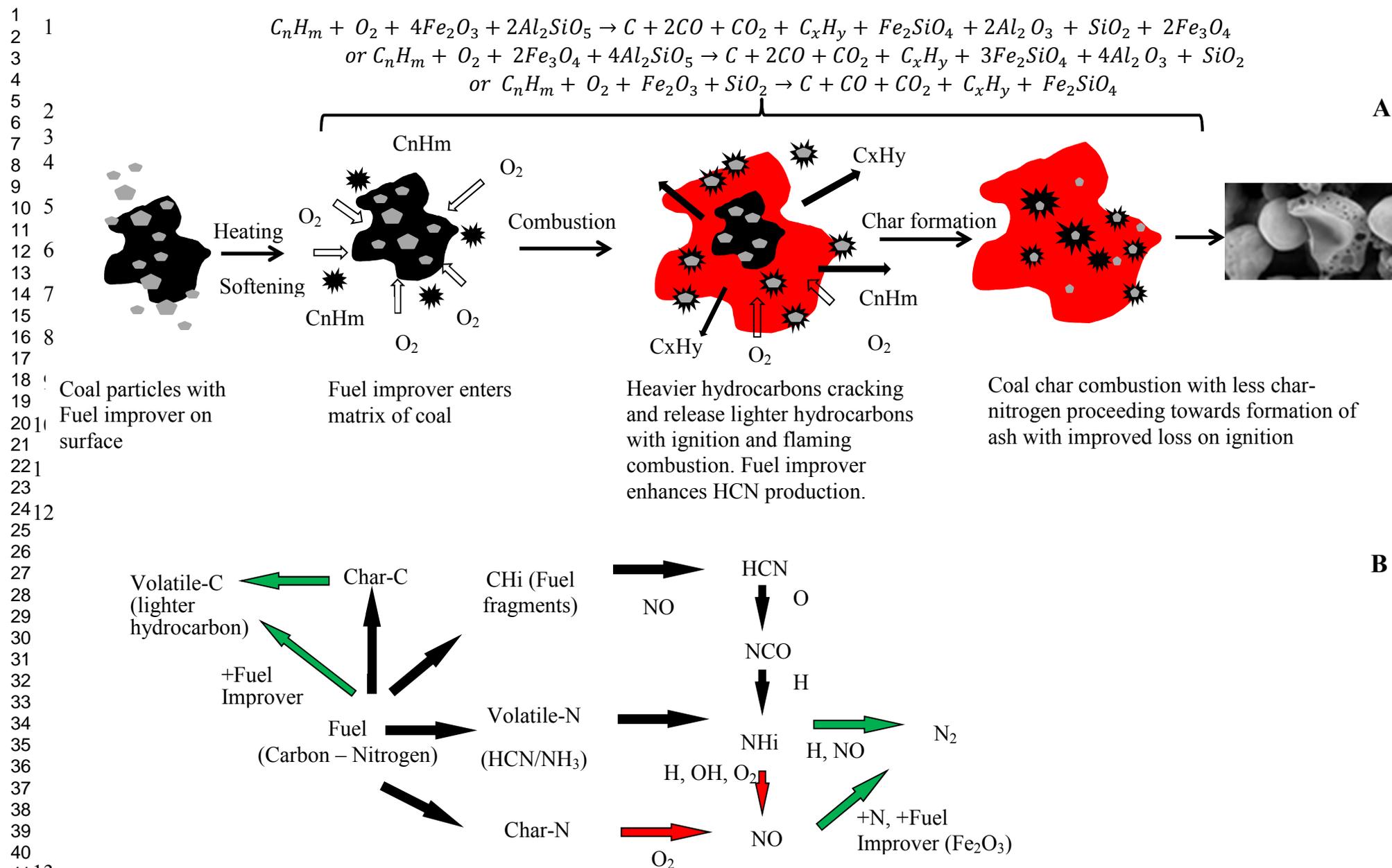


Figure 7. : (A) Proposed schematic mechanism for the interaction of the fuel improver with RC: (B) NO_x reduction chemistry¹⁹ and volatile carbon pathways in presence of improver.

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3 1 CONCLUSION
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8 3 There were differences in the evolution of CO and hydrocarbons during pyrolysis under pure
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10 4 N₂ as observed by FTIR analysis of the gases eluted during heating in the TG furnace. There
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12 5 appears to be an increase in the CO produced when the additive is present compared to that
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14 6 measured from coal alone. Iron based fuel improver having higher surface area because of finer
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16 7 particle size distribution compared to the coal, has facilitated the thermal degradation of heavier
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18 8 hydrocarbon into the lighter hydrocarbons. This suggests enhanced cracking of the coal matrix in
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20 9 the presence of fuel improvers. The increase in the peak intensities of CO, H-Cs and gas to oil
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22 10 yields have also been observed for coal in presence of fuel improvers. The H-Cs and CO
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24 11 intensities were increased by 44%-55% and 69%-79%, respectively in presence of iron based
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26 12 fuel additive. Similarly an increase of 33-41% in the gas yield and 18-47% reduction in tar yield
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28 13 was observed with ACFI. The thermal conversion of the coal heavier hydrocarbon (especially the
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30 14 tar based compounds) has resulted in increase in the gas yield. Iron based fuel improvers due to
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32 15 relatively better heat transfer properties compared to coal constituents could have resulted in
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34 16 provision of absorbed heat to break down the evolved heavier hydrocarbons of the coal matrix. It
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36 17 is also believed that heavier hydrocarbon's oxidative decomposition has also taken place over
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38 18 oxide matrix of the iron. The combustion results with sub bituminous coal provided 6-20%
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40 19 improvement in NO_x reduction with 15-35°C temperature increase and up to 60% improvement
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42 20 in LOI for 5-13% added fuel improver.
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