High Temperature Pyrolysis of SRF [2014-2016]

Background

In 2014 I was contracted to operate a gas heated 40 kg/h high temperature pyrolysis process to run on SRF from a major Uk recycling firm. At the time, SRF was regularly exported to Europe for co-firing, but my client was involved in large scale projects of 10 t/h to use pyrolysis for power. My part in the project was to carry out the testwork on the SRF, assess all the products, have everything analysed and use the information for assessing configurations: syngas to steam, syngas to engines and potential energy generation. The testwork would be used to generate detailed raw syngas analysis to provide this information to gas cleaning companies to assess CAPEX and OPEX as part of an overall techno-economic assessment.

40 kg/h pyrolysis kiln

The pyrolysis kiln was a rotary kiln, 6 internal baffles/lifters and discharge of the char into a sealed drum and the raw syngas was then characterised and analysed for multiple contaminants. The raw syngas was then flared to atmosphere. Various trials at different kiln temperatures and durations were carried out over a 5 month period.

The pyrolysis kiln comes with a feed inlet screw, rotating pyrolysis drum (geared drive with inverter control), air fan for the 3 x LPG burners, 3 kiln burner monitoring thermocouple wells, char discharge end to sealed char bin, syngas exit line, combustion gas flue line (optional heat exchanger for heat recovery, though the heat exchanger supplied was not used) and a control cabinet for the burners, fan, motor drives and flap valve feed system. A flap valve feed system was used to allow sealed feeding of material. N_2 purging was added to the seals and the kiln feed valves to reduce air ingress. The kiln main body is shown below in Figure 1.

Figure 1. Pyrolysis kiln main body with burner view ports and thermocouples

The kiln was built in 1995 and had been previously used on other sites for the testing of sewage sludge and its derivatives.

Rig operation

The rig Process flowsheet is shown in Figure 2 below.

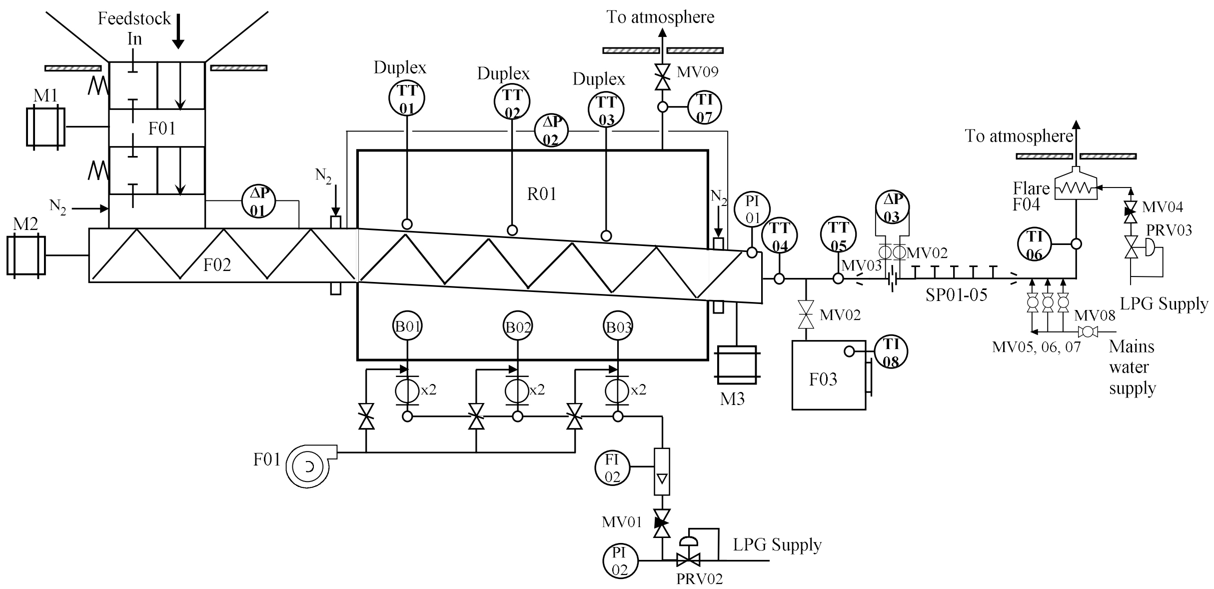

Figure 2. Process flowsheet

During operation, the feedstock is fed into the flap valve system, F01, which operates on an adjustable timer. Material drops in through the first valve onto the closed second valve. The top valve closes and then the bottom one opens dropping material onto the feed screw, F02. The space between the valves and the void above the feed screw, F02, are N_2 purged.

The variable feed screw conveys the feedstock into the rotary kiln which is heated by the 3 LPG burners, with the setpoints measured at 3 points close to the kiln tube. The combusted gases heat the tube and exit from the top of the kiln to atmosphere. Once the feedstock has been pyrolysed, taking approximately 20 minutes, the residual solids pour over a 25mm lip at the end of the kiln down into the char bin, F03, which has an isolation valve. The bin also has a pressure gauge and thermocouple.

The syngas exits the kiln and passes into a 4" insulated pipe. The pipe expands into a 6" line which has 6 x 3000lb 4" bosses for sampling equipment [SP01-6], 5 generally in use with 1 spare. Each boss was fitted with sampling equipment by ESG and Cranfield University. Cranfield recovered gas samples for tars and particulates only; ESG analysed the gases for a wide range of contaminants and gases as listed in Table .

The warm syngas was then piped to a pilot flare, operating with maximum excess air and ignited prior to atmospheric discharge. After a run was completed, the unit was turned off, allowed to cool overnight and product char and condensates recovered and weighed the next day. N_2 purging and flare operation would continue until the kiln had cooled to below 600°C and the burners ramped down to 450°C to allow the kiln tube to cool down uniformly. The char bin was isolated at the end of the run by closing the butterfly valve MV02 as char can be pyrophoric and left to cool overnight.

Table 1. Contaminants analysed for in the raw syngas

Pyrolysis Gas exiting the Kiln	Measurement Units
SO_x	mg/$_n$m^3
NO_x	mg/$_n$m^3
Tars [to BS DD CEN/TS 15439:2006] *	mg/$_n$m^3
Particulate [to BS DD CEN/TS 15439:2006] *	mg/Nm^3
H_2O	vol%
TOC	mg/$_n$m^3
HCl	mg/$_n$m^3
H_2S	mg/$_n$m^3
HF	mg/$_n$m^3
Hg	mg/$_n$m^3
Cd + Ti	ppm
As + Pb + Cr + Cu + Mn +Cu + Co + V + Sb + Ni	ppm
PCDD/F, 1-TEQ	ng/m^3

Note: * The tars and particulates were carried out by Cranfield.

ESG, now Socotec also analysed the following permanent gases as listed in Table .

Table 2. Non-condensable gases analysed for in the raw syngas

Average Dry Gas analysis	Measurement Unit [vol%, raw gas]	Average Dry Gas analysis	Measurement Unit [vol%, raw gas]
CO	as quoted	C_2H_6	as quoted
CO_2	as quoted	C_3H_6	as quoted
H_2	as quoted	C_3H_8	as quoted
CH_4	as quoted	n-C_4H_{10}	as quoted
C_2H_4	as quoted	N_2	as quoted
		O_2	as quoted

Attemperating sprays [MV05-07] were also available to moderate the syngas temperature prior to the pilot burner if necessary. These were never needed during the trials. This was one of the most comprehensive set of analyses carried out on a trial. The whole range of testing and parameters that were analysed are summarised in Table 3 overleaf. As can be seen, several organisations and analytical organisations were contracted or involved. This was to provide as much information as possible for further assessment of the chars for possible energy recovery [combustion or gasification] and their characteristics if they needed to be disposed of as a waste and that included leachate data. Another important aspect was the need to assess if the SRF chars had the potential to be self-igniting and how they might burn if this was to be another option for energy enhancement and char disposal to an inert ash.

Table 3. Analysis and testing organisations and rationale

Sample type	Sent to	Purpose
Feedstocks [SRF, wood and SRF/wood blend]	EBRI	Needed for mass balances and assess potential gas phase contaminants and speciation of the elements in the chars, tars, condensate and gases.
	MEDAC	• Elemental analysis • Detailed semi-quantitative scan for 66 elements
Charcoal	MEDAC	• Elemental analysis • Detailed semi-quantitative scan for 66 elements
	EBRI	• Ash content of the charcoal
	SAL	• Leachate testing for Waste Acceptance Criteria
	Chilworth	• US/UN DoT 4.1 Burn rate testing • US DoT 4.1 Self heating tests. Essential for storage and transport and handling compliance
Condensate	EMS	• Chemicals recovered in the condensate - phenols and US EPA 16 PAHs • BOD, COD and pH Needed for gas cleaning system data and if sent for disposal/ onsite chemical treatment prior to discharge.
Tars recovered by Cranfield	ECN, the Netherlands	• Assess tar levels in gas [mg/m^3] • Assess chemicals to be removed from gas in the gas cleaning system Data needed for the gas cleaning company.
Soot	MEDAC	• Elemental analysis • Detailed semi-quantitative scan for 66 elements Needed as soot will be scrubbed out of the gas and contaminants need to be assessed.
Ash from char and feedstocks	MEDAC	• Elemental analysis • Detailed semi-quantitative scan for 66 elements Assess properties and possible uses for ash once char is burnt.
Syngas and its contaminants	ESG	• Analysis for: • Dioxins and Furans • NOx, SOx, HF, HCl, H_2S • metals [Cd, Tl, Pb, Hg] • CO, CO_2, CH_4, H_2, H_2O, O_2, N_2

Co-ordination was very important so that Cranfield, ESG and myself were available for days at a time for testing. As can be seen in Figure 2, there was an extensive syngas sampling campaign, this is shown in Figure 3 below.

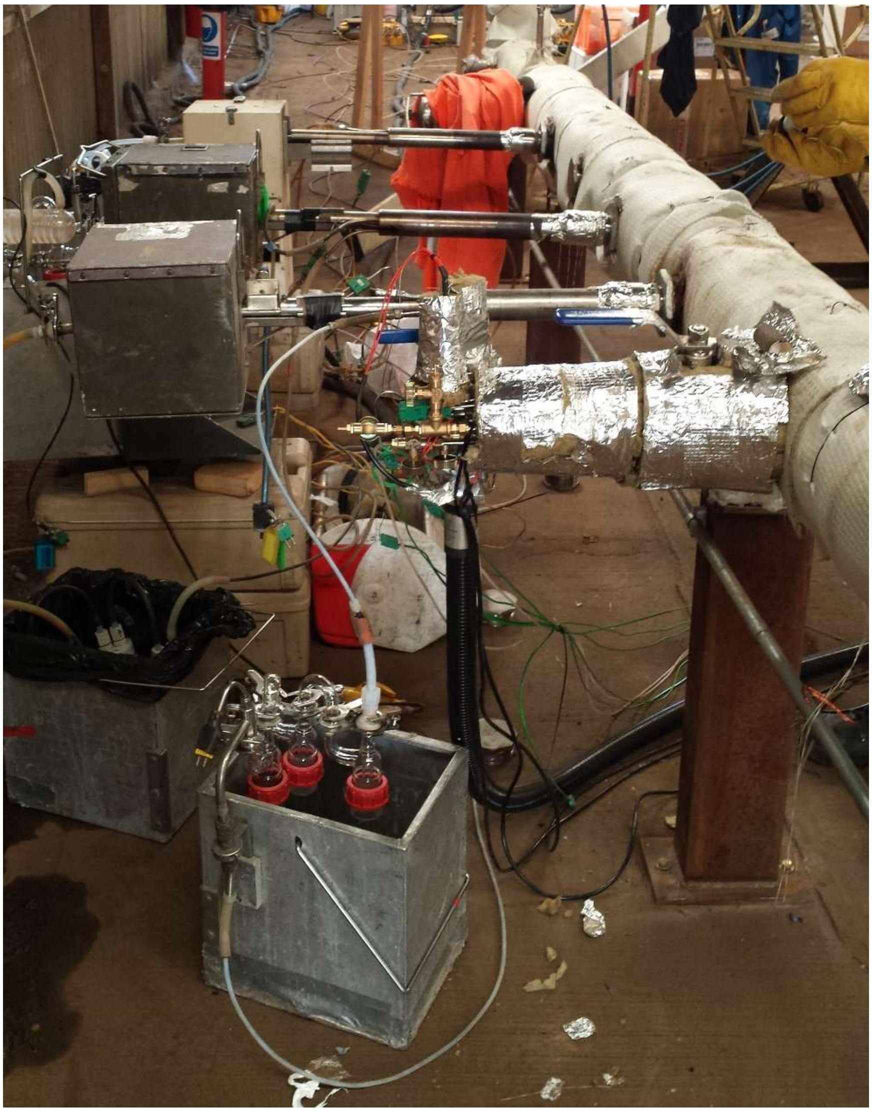

Figure 3.   Gas sampling train and hardware

The use of this gas sampling line was critical to the success of the work and required a significant manpower commitment and following health and safety procedures for the hazardous area of Zone 2/22.

SRF Feedstock

Each feedstock was randomly sampled and these samples were analysed for moisture and ash content and a wide elemental range. The water and ash results are summarised in Table 4 below. The SRF clearly is a high energy content material. Other detailed elemental analyses were carried out.

Table 4. Water and ash contents of the SRF [dry basis]

	Aston	Aston	MEDAC	
	Water content	Ash content	Ash content	
SRF	3.81	14.64		wt%
Heating values				
HHV	20.50	24.3	21.4	MJ/kg
LHV	18.60	22.4	19.5	MJ/kg
d_{dev}	0.5	1.9	0.7	-

Note: # own method (high oxidation of metals in material)

Results

Data is presented here for 2 runs: one at 718°C and one at 860°C, averaged kiln temperatures over the course of the tests, given in Table 5. One waste wood run is included for comparison.

Table 5. Overall mass balance summary for 3 runs

Feedstock	wood	SRF	SRF	Units
Kiln Temperature	753	718	860	°C
d_{dev}	13.4	42.4	56.3	-
Mass Balances				
Charcoal	14.2	26.9	28.2	%
Soot and deposits	2.6	0.2	0.6	%
Syngas	69.3	71.1	69.5	%
Volatile Metals	0.0	0.0	0.0	%
Pyrolysis tars	10.6	6.4	2.6	%
Water of pyrolysis	3.6	-5.2	-0.8	%
Closure[#]	100.3	99.4	100.1	%

The detailed methodology used to fully calculate the data is not presented here. Interestingly, the SRF showed water consumption in the gas phase.

Char analysis

A significant amount of characterisation work as indicated in Table 3 was carried out. The elemental analyses are presented here. Trace elements were also analysed for. The char was relatively high in ash, lowering the energy content of the char. The char analyses are given in Table 6.

Table 6. SRF Pyrolysis char analyses

Sample Code	Wood 753°C-	SRF 718°C	SRF 860°C	
Element				
C	40.22	38.32	48.98	wt%
H	1.31	1.81	1.58	wt%
O	51.84	37.09	30.35	wt%
N	1.28	0.51	0.58	wt%
S	0.65	0.10	0.74	wt%
Cl	0.23	1.27	2.56	wt%
Br	0.05	0.13	0.15	wt%
F	0.05	0.05	0.05	wt%
I	0.05	0.05	0.05	wt%
K	0.17	0.18	0.25	wt%
Na	0.13	0.62	0.54	wt%
Ca	1.76	5.35	6.96	wt%
Mg	0.19	0.44	0.87	wt%
P	0.07	0.06	0.19	wt%
Al	0.32	11.79	2.15	wt%
Fe	0.83	0.49	0.51	wt%
Si	0.86	1.75	3.51	wt%

The SRF char was very reactive: the char was pyrophoric and emitted CO upon exposure to air as they are high in reduced metals which can lead to O_2 adsorption. This char needs to be stored very carefully. The ash contents of the chars were also determined by Aston University. The SRF chars at 860°C had an ash content of 52.9wt%.

Raw syngas analyses

ESG carried out a very comprehensive set of analysis: at site and on samples recovered and removed from site. The data is in Table 7 overleaf. Dioxins and furans and metals were all done offline. Tar samples were taken by Cranfield and subsequently analysed by ECN, the Netherlands. To date, this is one of the most comprehensive analyses of SRF pyrolysis raw syngas.

Although the syngas from the runs would be cleaned after the pyrolysis reactor to remove tars, entrains solids and water, the composition is essential for the gas cleaning companies to allow them to design their gas cleaning unit operations. Rubber and hard plastics are the common sources for the chlorine and sulphur in the gas phase.

"Tars" in the gases also include VOCs. Cranfield measured tars for 4 runs and their data is used where relevant and then the ESG data on VOCs used (standardised on propane) and adjusted for the flow conditions. Samples of the tars are with ECN in the Netherlands for more detailed analysis and allow a better calculation of the concentration of certain phase species. The wastewater is also being analysed for oxygenates and PAHs, again to assist with determining with more accuracy the VOCs and "tars". As can be seen, CH_4, CO, CO_2 and H_2 are the dominant gases.

Table 7. Composition of raw syngas for tests

Feedstock	**wood**	**SRF**	**SRF**	
Kiln Temperature	**753**	**718**	**860**	**°C**
Methane CH_4	15.28	14.64	25.84	vol%
Carbon Monoxide CO	32.76	23.31	22.18	vol%
Carbon Dioxide CO_2	15.87	16.26	16.06	vol%
Ethylene C_2H_4	3.39	7.26	10.33	vol%
Ethane C_2H_6	1.29	3.63	1.53	vol%
Hydrogen H_2	12.85	8.03	20.38	vol%
Propylene C_3H_6	0.89	5.47	0.53	vol%
Propane C_3H_8	0.12	0.62	0.03	vol%
N-butane C_4H_{10}	0.06	0.24	0.03	vol%
n-C_8H_{18}	0.17	0.00	0.00	vol%
Naphthalene $C_{10}H_8$	2.27	0.24	0.30	vol%
Nitrogen N_2 #	1.40	1.70	0.70	vol%
Water vapour H_2O	11.27	5.11	1.08	vol%
"Tars" $C_6H_{12}O_6$	0.17339	0.13445	0.13972	vol%
Dioxins and Furans	3.5E-05	7E-05	9E-07	vol%
Hg	1E-06	6.3E-05	3.3E-06	vol%
HF	0.02011	0	0	vol%
H_2S	0.04169	0.00171	0.00207	vol%
NOx	1.26423	3.61635	0.15014	vol%
SOx	0.51393	8.01298	0.71225	vol%
HCl	0.40431	1.78627	0.03037	vol%

Note: # N_2 is purge N_2 added to the process and not thermally generated

The unexpected contaminants in the gas phase were the HF for the waste wood, possibly indicating use of preservatives or PTFE and the high levels of NOx for the SRF and SRF/wood mix. The levels of dioxins and furans were typically very low. The HF would be of concern from a materials selection perspective and would require specific treatment in the gas cleaning system, such as the use of $Ca(OH)_2$ to react.

Mass and Energy Balances

The run data was then used to construct overall mass and energy balances for scenarios of 9 t/h dry SRF input to the pyrolysis process. The basic flowsheet used is shown in Figire 4.

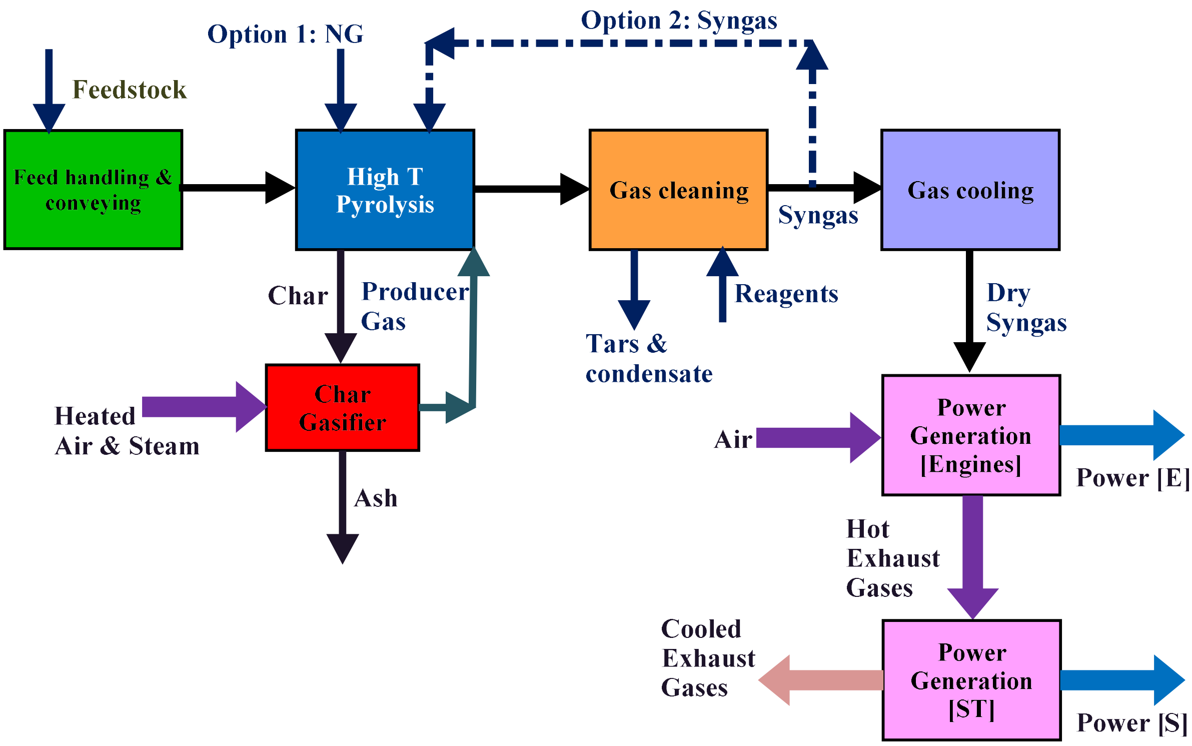

Figure 1. Process flowsheet for mass and energy balances

The assumptions are not given here, but scenarios for SRF at a pyrolysis temperature of 860°C are presented in Table 8 to power generation. Scenarios looked at gasifying the char for producer gas to heat the pyrolysis kiln, use of natural gas to heat the pyrolysis kiln; cleaning the syngas and sending all to gas engines, sending part of the cleaned syngas to heat the kiln and the rest to the gas engines; burning all the syngas and raising steam for use in a 40 bar g steam turbine. These are presented below v's standard SRF combustion and steam turbine.

Table 8. Power Generation Scenarios for SRF Pyrolysis

SRF input	9000	9000	kg/h
Use syngas for process heating of kiln	No	Yes	
Burn natural gas to heat kiln	Yes	No	
Amount needed	489	0	m^3/h
Gasify char to heat kiln	Yes	Yes	
<u>Gas Engine system [E]</u>			
Gross Engine Electrical Output	17.37	13.59	MWe
Exhaust gas heat energy	12.82	10.03	MW_{th}
Radiator water	8.27	6.47	MW_{th}

Heat Loss (non-recoverable)	2.90	2.26	MW_{th}
<u>Gas Engine system [E]</u>			
Gross Electrical Efficiency	31.0	24.3	%
Net Electrical Efficiency	29.7	22.9	%
Recoverable Heat	12.82	10.03	MW_{th}
Radiator heat	2.90	2.26	MW_{th}
<u>Steam Turbine Power Generation [S]</u>			
Gross Steam Turbine Electrical Output [S]	3.02	2.54	MWe
<u>Combined Power Outputs [E+S]</u>			
Gross Electrical Output [E+S]	20.4	16.13	MWe
Gross Electrical Efficiency [E+S]	36.4	29	%
Net Electrical Output [E+S]	19.6	15.4	MWe
Net Electrical Efficiency [E+S]	35.1	27.5	%
<u>Combustion Syngas + Steam Turbine System Only [S]</u>			
Electricity	10.41	7.89	MWe
Recoverable Heat	28.88	22.85	MW_{th}
Useable heat after heating pyrolysis kiln	28.9	17.1	MW_{th}
Electrical Efficiency	18.6	14.1	%
Recoverable Heat	49.4	29.2	%
<u>Material Combustion + Standard Steam Cycle [C+S]</u>			
Heat Input to Steam Cycle	56.0	56.0	MW_{th}
Gross Steam Turbine Electrical Output [S]	7.2	7.2	MWe
Steam Cycle Efficiency	12.9	12.9	%
NG cost	0.43	0.0	£M/y

The cleaned syngas to engines gives the highest power output for the scenarios calculated where natural gas is used to heat the kiln. There is an economic argument for doing this in some cases depending on the power prices, but the LCA would be affected. Use of your own cleaned syngas drops the gross power output by 3.8 Mwe, which is significant. There are a wide range of scenarios to consider on a case-by-case basis.