Bubbling fluidized bed co-gasification of biomass and refuse derived fuel

Travis Robinson

uOttawa

A Thesis Submitted to the Faculty of Graduate and Postdoctoral Studies
in Partial Fulfillment of the Requirements for the Degree

MASTER OF APPLIED SCIENCE

Department Chemical and Biological Engineering
Faculty of Engineering
University of Ottawa

Abstract

In Canadian remote northern communities most electricity is generated by burning diesel fuel. However, because it is expensive to import fuel into remote communities the cost of electricity is very high. Waste management is also difficult in remote northern communities. The goal of this thesis was to investigate the co-gasification of refuse waste materials and biomass as a means of reducing solid waste volumes while also using locally available materials for power generation.

As part of this research, thermo-gravimetric analysis (TGA) was investigated as a potential means of characterizing refuse derived fuels (RDF). Laboratory sample preparation of RDF for TGA had not been thoroughly considered. Laboratory sample preparation is important since RDF is very heterogeneous compared to other solid fuels and since TGA typically requires a very small sample size. A TGA method was applied to a variety of materials prepared from a commercially available RDF using a variety of procedures. The repeatability of the experimental results was related to the sample preparation methods. Cryogenic ball milling was found to be an appropriate means of preparing RDF samples for TGA. Applicability of the TGA method to the determination of the renewable content of RDF was considered.

Air-blown auto-thermal gasification experiments using materials representative of waste and biomass were performed at 725°C, 800°C, and 875°C, using a 0.15 m internal diameter bubbling fluidized bed gasifier located at NRCan CametENERGY in Ottawa, Ontario. Commercially prepared RDF and PET scrap were used to represent waste materials. Commercially produced hardwood pellets were used to represent biomass. The co-gasification of hardwood pellets and commercially produced RDF indicated that each fuel make a contribution to the results which is proportional to its fraction in the feed mixture. Inclusion of the RDF in the fuel mixture led to bed agglomeration at the 875°C temperature condition. Higher temperatures were found to provide better conversion of the fuel to gas, and the limitation which inclusion of RDF places on the operating temperature of the gasifier negatively affects conversion of biomass.

Results obtained with RDF suggested that utilization of mixed waste for a thermal conversion process located in a Canadian remote northern community is probably not a viable option. It was then decided to target plastic waste in particular. Plastic could be source-separated, collected, and gasified alongside biomass. Polyethylene terephthalate (PET), which is often used for food and beverage containers, was chosen to represent plastic. Initially, attempts were made to co-gasify

mixtures of PET pellets and hardwood pellets. These attempts failed due to the formation of coke above the bed. To alleviate these problems hardwood-PET composite pellets were manufactured and these were gasified at 725°C, 800°C, and 875°C. Inclusion of PET in the pellets dramatically increased the amount of tar produced during gasification.

Résumé

Dans les communautés isolées du Nord canadien la plupart de l'électricité est produite par la combustion de carburant diesel. Cependant, parce que l'importation de ce carburant est cher, le coût de l'électricité est très élevé pour ces communautés. La gestion des déchets est également difficile dans les communautés isolées du Nord. L'objectif de cette thèse était d'étudier la co-gazéification des déchets et de la biomasse pour la production d'électricité comme un moyen de réduire les volumes de déchets communautaires tout en utilisant des matériaux disponibles localement.

Dans le cadre de cette recherche l'analyse thermo-gravimétrique (ATG) a été employée comme un moyen potentiel de caractériser les combustibles dérivés de déchets (CDD). Les techniques utilisées pour la préparation d'échantillons de ces matériaux pour l'ATG n'avaient pas été considérées rigoureusement. La préparation des échantillons est importante puisque les CDD sont très hétérogènes par rapport à d'autres combustibles solides et que l'ATG nécessite généralement un échantillon de très petite taille. L'ATG a été appliquée à une variété de matériaux préparés à partir d'un CDD commercial en utilisant une variété de procédures. La reproductibilité des résultats de l'analyse a été liée à des procédés de préparation de l'échantillon. D'après la recherche effectuée, il a été découvert que le broyage à boulets cryogénique est la méthode la plus appropriée pour la préparation des échantillons de CDD. L'applicabilité de l'ATG pour la détermination en teneur de carburant renouvelable dans le CDD a été considérée.

Les expériences de gazéification à l'air auto-thermique en utilisant des matériaux représentant des déchets et de la biomasse ont été effectuées à 725°C, 800°C et 875°C, en utilisant un gazéificateur de lit fluidisé (diamètre intérieur de 0,15 m) situé à RNCan CametÉNERGIE (Ottawa, Ontario). Le CDD commercialement préparé et le polyéthylène téréphtalate (PET) recyclé ont été utilisés pour représenter les déchets. Les granules de bois franc commerciales ont été utilisées pour représenter la biomasse. Les résultats de la co-gazéification des granules de bois et de CDD commercial a ont démontré que chaque carburant a apporté une contribution proportionnelle à sa fraction dans le mélange d'alimentation. L'inclusion des CDD dans le mélange de carburant a conduit à l'agglomération du lit à lorsque sa température était de 875°C. Des températures plus élevées ont donné une meilleure conversion du combustible pour le gaz, et la limite de la température de

fonctionnement du gazéificateur imposée par l'inclusion des CDD donne un effet négatif sur la conversion de la biomasse.

Les résultats obtenus avec les CDD ont démontré que l'utilisation des déchets mixtes pour un procédé de conversion thermique située dans une communauté éloignée du nord du Canada n'est probablement pas une option viable. Par la suite, la co-gazéification des déchets plastiques a été ciblée. Le plastique pourrait être séparé à la source, recueillie et gazéifié avec la biomasse. Le PET, qui est souvent utilisé pour les contenants alimentaires et de boissons, a été choisi pour représenter les déchets plastiques. Initialement, on a tenté de co-gazéifier des mélanges de granules de PET et les granules de bois franc. Ces tentatives ont échoué en raison de la formation de coke au-dessus du lit. Pour atténuer ces problèmes, des granules de bois franc et de PET combinés ont été fabriquées et ils ont été gazéifiées à 725°C, 800°C et 875°C. L'inclusion du PET dans les pastilles a augmenté considérablement la quantité de goudron produite lors de la gazéification.

Table of Contents

List of Figures

List of Tables

Chapter 1 Introduction

As of 2006, Canada contained 292 remote off-grid communities which were home to 194,281 people. Communities which are not connected to the North American power grid generate and distribute electricity locally on isolated micro-grids. Diesel generation is the primary means of supplying these grids. However, diesel generation is considered undesirable due to its high cost as well as pollution associated with its use. Alternatives such as solar, wind, and hydro-power have been explored. Some communities have access to watercourses which are appropriate for small scale hydroelectric generation, and some facilities do exist. However, most communities are not candidates for hydroelectric generation. Some wind and solar capacity has been installed. Wind and solar do not provide energy on demand, thus they may supplement, but not replace diesel generation. [1]

Small scale biomass gasification based electrical generation has been employed in the rural regions of underdeveloped nations [2, 3]. In the past, such systems have also been explored as a means of providing electricity in remote northern communities in Canada [4, 5]. Producer gas from a gasifier may be used to fuel internal combustion engines. Often producer gas from biomass gasification has been used to fuel diesel engines [2, 3]. This is accomplished by running the engine in what is called dual fuel or pilot ignition mode. Dual fuel mode may refer to a mode of operation where a fuel air mixture in inducted into the engine, compressed, and then ignited by injection of diesel fuel or it may refer to a mode of operation where a liquid or gaseous fuel is injected into a compressed charge of air alongside diesel fuel [6, 7]. The former of these modes is potentially interesting for application in a remote community which already uses diesel engines for power generation, since it requires only slight engine modifications, and since it is possible to maintain the engine's ability to operate on straight diesel fuel [8].

Making categorical statements about the dual fuel operation of diesel engines is difficult. There are a wide variety of diesel engine injection systems [9]. Engine operation comes with many degrees of freedom, including, but not limited to, pilot volume, injection timing, engine load, and engine speed [10]. Many studies exist but results are dependent on engine configuration so results may be contradictory [10]. What is clear is that it is possible to operate a diesel engine in dual fuel mode with as much 70-90% of the energy being derived from air-blown gasification producer gas while experiencing a relatively small power de-rating [2, 3, 5, 8, 11, 12].

Remoteness also causes difficulties with the management of household solid wastes. Most remote northern communities have fewer than 1000 residents [1]. With such small numbers of people, these communities cannot access the economy of scale which would allow for pick up and sorting of household waste. The absence of curbside pickup tends to inhibit the use of available waste management infrastructure [13]. Communities typically have a central dumping site, but individuals may end up disposing of waste closer to home either by uncontrolled incineration in burn barrels or fire pits or for non-combustible materials by unauthorized dumping in the proximity of the household [14].

The deployment of modular gasification systems to remote northern communities for the production of producer gas from biomass and municipal solid waste might help alleviate problems with power generation and waste management. Fluidized beds are of particular interest since they are known to operate with much fuel flexibility and this can greatly simplify fuel handling. The gas from such units could be burned, via dual fuel mode, in existing diesel engines, and reliability may be assured since it is possible to maintain the ability of the existing engines to run on straight diesel.

1.1 Thesis Objectives

The overall goal of this research was to investigate the co-gasification of refuse derived fuel (RDF) and biomass in a bubbling fluidized bed as a means of utilizing locally available resources to displace diesel fuel in the generation of electricity in Canada's remote northern communities. The specific objectives included:

a. Apply TGA to the characterization of refuse derived fuel
b. Study the influence of fuel composition and temperature on the raw gas composition obtained from co-gasification of biomass and waste materials
c. Study the influence of the inclusion of waste materials on the requirements for raw gas cleaning
d. Study the influence of waste materials on the operability of the bubbling fluidized bed

1.2 Thesis Outline

The thesis is divided into five chapters from which three chapters are prepared as journal publications.

1.2.1 Chapter 2

Initially, the goal of this work was to study the kinetics of the thermal decomposition of the fuel. Thermo-gravimetry is often used to determine kinetics and the aim was to obtain kinetic parameters so these could be applied to RDF. Theoretical problems with the use of relatively simple kinetic models to describe the complex thermal decomposition of bio-polymers and synthetic polymers found in RDF casted doubt on the usefulness of deriving TGA kinetics for the RDF. Since it did not seem likely that useful kinetic parameters would be derived from TGA this approach was abandoned in favour of TGA proximate analysis.

For solid fuels, proximate analysis is the determination of moisture, volatiles, fixed carbon, and ash. This normally takes place using gram scale samples and an oven connected to a supply of air and inert gas. The overall procedure may be automated using TGA, and an interesting feature of this automated proximate analysis is the ability to distinguish between biogenic and petroleum derived polymers found in RDF.

During a normal proximate analysis, the volatile content of a solid fuel would be determined by placing the dried fuel in an oven at a specified temperature under an inert atmosphere such as nitrogen. After a few minutes the fuel would be devolatilized and the volatile content would be found by the difference in sample mass before and after devolatilization. If a TGA is used, the sample may be exposed to a temperature ramp and the extent of devolatilization at a given temperature may be tracked.

Conveniently, biogenic materials decompose over a lower temperature interval than petroleum derived materials so it is possible to determine the fraction of the sample which is non-biogenic. When TGA proximate analysis of RDF was first proposed in the 1980s, the ability to distinguish between biogenic and petroleum derived materials, considered useful since it could be used to estimate the heating value of the sample [15, 16].

The utility of such an estimate is dubious given the ease and availability of bomb calorimetry. However, in the intervening years, there has been a substantial rise in concerns about global warming. These concerns have caused governments to provide incentives for the use of renewable fuels. This makes the biogenic content of RDF important since this fraction of RDF is renewable. Furthermore, the current means of determining the biogenic or renewable content of RDF are more laborious or less accessible than TGA.

The most obvious drawback to using TGA on RDF for the determination of biogenic content is the small sample sizes employed in TGA. RDF is a very heterogeneous material. Repeatability is a major issue when carrying out analyses on small samples of heterogeneous materials. Many TGA investigations of RDF have been carried out but sample preparation and repeatability have not been well addressed.

Chapter two is an investigation of sample preparation techniques for RDF. A number of techniques were employed to reduce samples of RDF to fine powders. The influence of the preparation techniques on the repeatability of TGA proximate analysis was determined by performing experiments 15 times, which allowed for the determination of reasonably accurate standard deviations for the average results.

This chapter is prepared in a journal manuscript format and is submitted to the Waste Management Journal *(Ms. Ref. No.: WM-15-1365).*

1.2.2 Chapter 3

The third chapter details co-gasification experiments performed with commercially available hardwood pellets and RDF provided by WastAway®. Mixtures containing 100, 75, 50 and 0% hardwood pellets were gasified. It had been intended to perform co-gasification experiments at 725°C, 800°C, and 875°C, but experiments with mixtures containing RDF at 875°C were abandoned due to bed agglomeration, which prevented steady state operation. The RDF caused agglomeration because it contained silica.

The presence of silica likely arises from the presence of glass in the raw MSW used to make the RDF. Its presence is in spite of the sophisticated large scale industrial process used to turn mixed waste into RDF. Any waste processing facility in a remote community would necessarily be less sophisticated due to the absence of an economy of scale. A refuse derived fuel produced in a remote community would thus be of an even lower quality than the commercially produced RDF. The tendency to cause agglomeration makes mixing of the refuse derived fuel with biomass problematic. The presence of the RDF limits the operation temperature, which limits conversion of the biomass. Furthermore, the unconverted residue from the biomass would be contaminated with RDF residue which complicates disposal.

This chapter is prepared in a journal manuscript format and will be submitted to Biomass and Bioenergy.

1.2.3 Chapter 4

Another approach for incorporating waste materials into a biomass gasification based electricity generation was devised. The third chapter compares gasification of hardwood with gasification of mixtures of hardwood and polyethylene terephthalate (PET). Rather than trying to utilize a stream of mixed waste as a fuel, a particular waste material could be source separated, collected, and utilized for electricity production. Plastic was chosen since it is not biodegradable, has low moisture and ash content, and has a high heating value. PET was chosen since it is widely used for the production of disposable containers such as plastic bottles [17]. Food grade PET was obtained from a plastics recycler. The material was scrap from the production of plastic containers. First the material was pelletized and attempts were made to gasify mixtures of these PET pellets and hardwood pellets. These attempts failed due to the formation of coke above the bed. The problem with coking was overcome by creating composite pellets composed of approximately 50 wt. % PET and 50 wt. % hardwood. Co-gasification experiments were carried out with these pellets at 725°C, 800°C, and 875°C, and the results were compared to the gasification of hardwood pellets at those same temperature conditions.

This chapter is prepared in a journal manuscript format and will be submitted to Biomass and Bioenergy.

1.2.4 Chapter 5

Chapter five presents the overall conclusions of this research and recommendations for future investigation.

References

[1] Government of Canada, "Status of Remote/Off grid Communities in Canada," Government of Canada, 2011.

[2] S. Ghosh, T. K. Das and T. Jash, "Sustainability of decentralized woodfuel-based power plant: an experience in India," *Energy,* vol. 29, pp. 155-166, 2004.

[3] S. Dasappa, D. Subbukrishna, K. Suresh, P. Paul and G. Prahu, "Operational experience on a grid connected 100 kWe biomass gasification power plant in Karnataka, India," *Energy for Sustainable Development,* vol. 15, pp. 231-239, 2011.

[4] A. Verma and G. Weisgerber, "Wood Gasification for Gas and Power," in *Thermal Conversion of solid Wastes and Biomass*, Washington DC, American Chemical Society, 1980, pp. 379-394.

[5] A. Verma and G. Weisgerber, "Wood Gasification for Heat and Power Generation," in *Thermal conversion of wastes and biomass*, Washington, DC, American Chemical Society , 1980, pp. 381-394.

[6] A. Boretti, "Advantages of the direct injection of both diesel and hydrogen in dual fuel H2ICE," *International Journal of Hydrogen Energy ,* vol. 36, pp. 9312-9317, 2011.

[7] A. Boretti, "Advantage of converting Diesel engines to run as dual fuel ethanol-Diesel," *Applied Thermal Engineering ,* vol. 47, pp. 1-9, 2012.

[8] Solar Energy Research Institute , Handbook of Biomass Downdraft Gasifier Engine Systems, Golden, Colorado: Solar Energy Research Institute, 1988.

[9] P. J. Dingle and M.-C. D. Lai, Diesel common rail and advanced fuel injection systems, Warrendale, PA: SAE, 2005.

[10] F. Konigsson, "Advancing the limits of dual fual combustion," Kunglia Tekniska Hogskolan, Stockholm, Sweden, 2012.

[11] R. M. Jorapur and A. K. Rajvanshi, "Development of a sugarcane leaf gasifier for electricity

generation," *Biomass and Bioenergy,* vol. 8, pp. 91-98, 1995.

[12] A. Ramhadas, S. Jayaraj and C. Muraleedharan, "Power generation using coir-pith and wood derived producer gas," *Fuel Processing Technology,* vol. 87, pp. 849-853, 2006.

[13] R. E. Rhodes, M. R. Beauchamp, M. Conner, G.-J. deBruijn, A. Latimer-Cheung and Kaushal, "Are mere instructions enough? Evaluation of four types of messaging on community depot recycling," *Resources, Conservation and Recycling ,* vol. 90, pp. 1-8, 2014.

[14] R. Zagozewski, I. Judd-Henrey, S. Nilson and L. Bharadwaj, "Perspectives on past and present waste disposal practices: a community based participatory research project in three Saskachewan First Nations," *Environmental Health Insights,* vol. 5, pp. 9-20, 2011.

[15] R. K. Argawal, "Compositional Analysis of Solid Waste and Refuse derived fuels by thermogravimetry," in *Compositional analysis by thermogravimetry*, Philadelphia, ASTM, 1988, pp. 259-271.

[16] R. K. Argawal, "A Rapid method for characterization and proximate analysis of refuse-derived fuels and its implications for thermal conversion," *Waste Management and Research,* vol. 6, pp. 271-280, 1988.

[17] National association for PET container resources, "Post Consumer PET container recycling activity in 2012," 2012. [Online]. Available: www.napcor.com/pdf/NAPCOR_2012RateReport.pdf. [Accessed 13 07 2015].

Chapter 2 Sample preparation for thermo-gravimetric determination and thermo-gravimetric characterization of refuse derived fuel

*T. Robinson[1], B. Bronson[2], P. Gogolek[2], P. Mehrani[1]**

[1]Department of Chemical and Biological Engineering, University of Ottawa, Ottawa, Ontario, K1N 6N5 Canada

[2]Natural Resources Canada, CanmetENERGY, 1 Haanel Drive, Ottawa, Ontario, K1A 1M1, Canada

Abstract

Thermo-gravimetric analysis (TGA) is a useful method for characterizing fuels. In the past it has been applied to the study of Refuse derived fuel (RDF) and related materials. However, the heterogeneity of RDF makes the preparation of small representative samples very difficult and this difficulty has limited the effectiveness of TGA for characterization of RDF. A TGA method was applied to a variety of materials prepared from a commercially available RDF using a variety of procedures. Applicability of the TGA method to the determination of the renewable content of RDF was considered. Cryogenic ball milling was found to be an effective means of preparing RDF samples for TGA. When combined with an effective sample preparation, TGA could be used as an alternative method for assessing the renewable content of RDF.

Keywords*:* Refuse derived fuel (RDF), Thermo-gravimetric analysis (TGA), Sample preparation, cryo-milling, Sample characterization, proximate analysis

2.1 Introduction

Refuse derived fuel (RDF) is solid fuel manufactured from mixed waste streams. The purpose of RDF is to divert material from landfills. Municipal solid waste (MSW) and solid recovered fuel (SRF) are related terms. MSW refers to solid waste materials collected by municipal waste management services, which are more or less mixed upon collection. RDF is manufactured from MSW by application of a combination of processes [1] which may include: sorting, shredding, hygienization, drying and densification. SRF refers to fuel produced from non-hazardous waste which meets a given set of fuel quality standards like CEN/TS 15357. [1, 2]

Energy may be recovered from MSW by directly combusting the material using established technologies such as a grate furnace. This practice is problematic because valuable materials escape recovery and because MSW may contain high concentrations of materials which foul and corrode process equipment [3, 4], or materials which cause pollution control problems. Processing MSW into RDF allows recovery of materials like glass and metals which may be recycled. It may also reduce the concentration of materials which cause maintenance or pollution issues [5]. Processing may also change the legal designation of the material. In some jurisdictions processing MSW into RDF allows the material to be shipped to approved facilities outside of the jurisdiction [1]. Processing also improves the consistency of RDF allowing it to be marketed to consumers of solid fuel as a commodity. However, despite processing efforts RDF is typically quite heterogeneous.

In addition to reducing the amount of material entering landfills, the production of RDF may reduce the overall production of greenhouse gases by displacing conventional fossil fuels. Of course the extent to which use of RDF reduces overall emissions of greenhouse gases depends heavily on what fraction of the fuel is composed of petroleum derived materials [6]. Argawal [7, 8] presented a TGA based proximate analysis technique for RDF and MSW. The technique was informed by the work of Elder [9] who related experience gained while using a TGA based proximate analysis technique for coal. The advantages of the TGA technique over traditional proximate analysis were the automation provided by TGA and the small sample sizes [9]. Argawal noted, that for RDF and MSW, an advantage of the TGA technique was the ability to distinguish between cellulosic materials and petroleum derived materials found in RDF and MSW [7, 8].

When a dry RDF sample is subjected to a temperature ramp under a flow of inert gas two major mass loss steps are evident. The first of these steps is attributed to cellulosic materials and generally finishes at a temperature lower than 400°C, and second of these steps is attributed to petroleum-

derived polymers and it usually begins at temperatures higher than 400°C and ends around 500°C [7, 8, 10, 11]. After the volatile material is driven out of the sample and only char and ash remain, char may then be determined by switching the gas flow to air. Since, except for polyvinyl chloride, petroleum derived polymers, yield little or no char [12, 13], the cellulosic fraction may be estimated as the sum of the first, lower temperature mass loss step, and the char yield. The plastic content may be estimated as the mass loss during the second, higher temperature, mass loss step.

Argawal [7] considered the ability of TGA to distinguish between cellulosic and petroleum derived materials in RDF and MSW as a major advantage of the technique, because this information could be used to estimate the heating value of RDF and MSW. Concern over global warming has caused governments to employ regulations to discourage the emission of greenhouse gases. Regulations make it important to distinguish between the renewable and non-renewable content of RDF since the renewable portion may be eligible for credit designed to incentivise the use of renewable energy [14]. Using the information from a TGA proximate analysis of RDF to estimate the renewable fraction of the fuel might be more useful than an estimate of heating value. ^{14}C analysis and selective dissolution are currently used for determining the renewable content of RDF.

^{14}C analysis uses the same principle as radio-carbon dating. Cosmic radiation causes the production of ^{14}C in the atmosphere. From the atmosphere it is absorbed by plants and then animals. As a result of this process biogenic materials contain roughly the same proportion of ^{14}C as the atmosphere. The uptake of ^{14}C ceases when life ends and the ^{14}C in the material decays with a half-life of 5730 years. After about 100,000 years the concentration of ^{14}C is undetectable. Since fossil materials like coal and oil are much older than 100,000 years they contain practically no ^{14}C and it is possible to distinguish between modern and fossil carbon by assuming a particular proportion of ^{14}C in modern biogenic materials. [15]

Jones et al. [16] examined the fossil content of MSW derived solid fuel samples by accelerator mass spectrometric (AMS) detection of ^{14}C. Thirty (30) gram samples were combusted in a bomb calorimeter. Carbon dioxide produced by combustion of the samples was collected in a sodium hydroxide solution and then converted to graphite for AMS analysis. ^{14}C analysis requires assumptions about the amount of ^{14}C in the biogenic materials found in RDF and MSW. The ^{14}C concentration in the modern atmosphere has varied significantly over the last six decades. A significant rise in the atmospheric concentration of ^{14}C occurred during the 1950s and 1960s due to above ground nuclear weapons testing followed by a rapid decline caused by international

restrictions on nuclear weapons testing [17]. The large variation in the atmospheric ^{14}C over the last six decades means that the proportion of ^{14}C in the biogenic fraction of RDF and MSW varies significantly.

Fellner and Rechberger [18] studied the ^{14}C content in European waste. They found that the average ^{14}C content of sorted waste was 117.3 percent modern carbon (pMC). The average ^{14}C content of unsorted waste was found to be 115.2 pMC indicating that sorting tends to select for older materials. The uncertainty, for a 95 % confidence interval, was ± 3.9 pMC for sorted waste and ± 3.5 pMC for unsorted waste and the margin of error for the calculation of biogenic content was at least 6 %.

Selective dissolution works by decomposing the biogenic fraction of RDF in a solution of sulfuric acid and hydrogen peroxide then filtering the solution to obtain the fossil fraction [19]. Dissolution requires 16 h or >18 h [20]. Gram scale samples are used for selective dissolution [19, 21]. The method is complicated by the fact that a portion of the ash forming components in the sample also dissolve in the solution. A separate sample must be used to determine the total ash content and the ash content of the un-decomposed material, filtered from the solution must also be determined [19]. The results of selective dissolution are combined with calorimetry or elemental analysis and results are reported on the basis of heating value [19] or on the basis of carbon content [15].

Small, milligram scale, samples are employed for TGA. Elder [9] considered small sample sizes to be an advantage when the sample availability is limited. RDF and MSW sample material is readily available and sample availability should never be a concern. However, the heterogeneity of RDF is a major concern. RDF and MSW are very heterogeneous materials. Samples must be ground to very fine powders to obtain results with reasonably small variances [20]. Producing fine powders from these materials is difficult due to the presence of a variety of materials with different mechanical properties. Even if repeatability is achieved, results may be subject to significant sample preparation error, because sample preparation may alter the composition of the material being analysed.

TGA has been widely employed for the analysis of RDF and MSW since the proximate analysis technique of Argawal was presented. When TGA is performed on RDF or MSW the focus is usually the determination of kinetic parameters. In some works, samples were ground to 100 mesh and mixed overnight on a rotating riffler [7]. The same author proposed a method where samples must

be ground below 50 µm [8]. Since then samples have been: cooled with liquid nitrogen and milled to fine powders [10], ground to 40-60 mesh [22], milled and sieved to between 150-250 µm [11], milled to particle sizes of under 250 µm [23], and milled to 150-250 µm [24]. Conspicuously absent from most accounts of laboratory particle size reduction procedures are the amount of material milled, the yield from the milling process, and the equipment used in the milling process.

Despite acknowledged problems with the heterogeneity of RDF and MSW, repeatability is not usually addressed and most procedures seem to be substantially un-validated. When repeatability is addressed, it is usually addressed without reference to variance or standard deviation. Average results from three [23] or five [11] replicates have been employed and in some cases the results of duplicate analysis are displayed to show that the variations between results are small [24].

Any application of TGA to the analysis of RDF or MSW requires the production of fine representative samples. To better understand the effect of sample preparation on TGA of RDF and MSW, in this work a method adapted from Argawal [7] was used to analyse materials prepared from commercially available RDF pellets. The materials were prepared using a variety of equipment and procedures. All analyses were performed 15 times to obtain robust estimates of standard deviation. It is anticipated that this information will support the useful application of TGA to the analysis of RDF.

2.2 Materials and Methods

2.2.1 Refuse Derived Fuel

Refuse derived fuel pellets were obtained from WastAway®. Refuse derived fuel pellets were obtained from a producer based in the United States. The fuel is produced from MSW by a series of shredding and sorting processes followed by hygienization under steam pressure. After hygienization, the RDF is dried and formed into pellets. The RDF was received as 16 mm diameter pellets.

2.2.2 Sample Preparation

The RDF pellets were prepared for the TGA analysis in several different ways. The comminution techniques included knife milling with sieving, rotary grinding with sieving, ultra-centrifugal milling, and cryo-milling.

Materials termed Coarse, Medium, and Fine were produced by knife milling a specimen of RDF pellets, splitting the milled material by coning and quartering and sieving the smaller sub-sample with a 1.7 mm sieve (Coarse material) and a 0.3 mm sieve (Medium material). The Fine material, which passed the 0.3 mm sieve, was collected from the bottom tray. Details of the procedure are presented in Table 2.1 and Table 2.2.

Table 2.1 Production of Coarse, Medium, and Fine materials

	Material In (g)	Material Out (g)	Material Out (%)
Knife Milling	500.0	466.0	93.2
Coning and Quartering	466.0	17.9	3.8
Sieving	17.9	17.4	97.2

Table 2.2 Recovery of sieved Coarse, Medium, and Fine fractions

	Mass (g)	Mass (g)%
Coarse	8.2	47.1
Medium	1.9	10.9
Fine	7.3	42.0
Total	17.4	100.0

Rotary grinding and sieving were used to produce a material termed 300UM, for 300 micrometers, from a single fuel pellet. The pellet was ground in a bench top rotary grinder. The ground material was sieved using a 1.7 mm and a 0.3 mm sieve. Material retained on the 1.7 mm and 0.3 mm sieves was collected and ground again in a bench top rotary grinder. The process was repeated until most of the ground material passed the 1.7 mm and 0.3 mm sieves. From 6.4 g of material entering the process, 5.5 g of ground material was recovered and the overall recovery was 85.9 %. A Retsch™ ZM-100 Ultra-centrifugal mill fitted with an 80 µm screen was used to produce materials termed 80UM, for 80 micrometers, and Retained, so called because the material was retained in the mill. These materials were produced from a single RDF pellet. From 3.2 g of material entering the process, 2.1 g of ground material was recovered and the overall recovery was 65.6 %.

A Retsch™ CryoMill was used to produce materials termed RCM1, RCM2, and RCM3, from three individual fuel pellets. The mill works by shaking the sample and a 20 mm diameter steel ball in a sealed steel jar. The outside of the jar is cooled by boiling liquid nitrogen. Samples were pre-cooled for ten minutes while being shook at 5 Hz. Then samples were subjected to five grinding cycles.

Grinding was conducted at 20 Hz for five minutes. Samples were intercooled at 5 Hz for three minutes between grinding cycles. Recoveries from this method are presented in Table 2.3.

Table 2.3 Recovery of RCM1, RCM2, and RCM3 materials from cryogenic milling

	Material In (g)	Material Out (g)	Material Out (%)
RCM1	2.74	2.60	94.89
RCM2	2.28	2.13	93.42
RCM3	2.81	2.72	96.80

Materials termed RS1, RS2, and RS3, for representative sample, were produced by representative sampling of the whole lot of RDF. The 1045 kg lot of RDF was coned and quartered down to 3.2 kg. This material was knife milled using a 6 mm screen. Coning and quartering was again employed to produce three representative samples of the ground material. These samples were cryogenically milled in the same manner as the RCM materials. Details are presented in Table 2.4, Table 2.5, and Table 2.6.

Table 2.4 Production of RS1, RS2, and RS3 materials by representative sampling method

	Mass In (kg)	Mass Out (kg)	Mass Out (%)
Coning and Quartering Pellets	1045.0	3.2	0.3
Knife Milling	3.2	3.1	96.9

Table 2.5 Production of RS1, RS2, and RS3 materials by coning and quartering of knife milled material

	Mass In (g)	Mass Out (g)	Mass Out (%)
RS1	3100	5.15	0.17
RS2	3100	4.84	0.16
RS3	3100	5.14	0.17

Table 2.6 Production of RS1, RS2, and RS3 materials recovery from cryogenic milling

	Mass In (g)	Mass Out (g)	Mass Out (%)
RS1	5.15	4.95	96.12
RS2	4.84	4.72	97.52
RS3	5.14	4.91	95.53

2.2.3 TGA Method

TGA experiments were performed on 10 mg samples. All materials were analysed fifteen times using a four stage TGA program. In the first stage the samples were held at 80°C for eight minutes under a flow of 50 SCCM of nitrogen to drive off any loosely bound moisture. During the second stage, the temperature was increased from 80°C to 800°C at a rate of 25 °C/min. At the end of the ramp, the temperature was held constant at 800°C for five minutes. After five minutes the gas flow was switched from 50 SCCM of nitrogen to 50 SCCM of a mixture of 80 vol. % nitrogen and 20 vol. % oxygen.

Extrapolated onset and endset temperatures were determined for the mass loss processes observed during the ramp stage of the TGA program to aid in determining temperature intervals for the proximate analysis. To find the onset and endset points for a mass loss process, a tangent line is drawn at the point in the TGA curve where the rate of mass loss reaches a maximum. The onset temperature is the temperature where the tangent line crosses the TGA baseline prior to the mass loss step and the endset temperature is the temperature at the point where the tangent line crosses the baseline after the mass loss step. An average TGA curve representing the results of the 45 determinations made on the RS materials was used for determination of the onset and endset temperatures. Three mass loss steps are evident in the curve (Figure 2.1). The first two mass loss curves are those associated with cellulosic and petroleum derived materials, and the third mass loss step is thought to be associated with the loss of carbon dioxide by mineral carbonates [25].

At the beginning of the TGA curve, the baseline was assumed to have a slope of zero. The baseline between the first and second mass loss steps was tangent to the mass loss curve at 376.5°C. The rate of change at this point is the closer to zero than any other point between the first and second mass loss steps. The maximum rate of mass loss for the first step occurs at 342°C. A tangent to the mass loss curve was draw from this point so that it intersected the first and second baselines. These intersections, at 291.5°C and 355°C, are the onset and endset temperatures for the first mass loss step (Figure 2.1). The third baseline was drawn tangent to the mass loss curve at 611°C where the rate of mass loss is the closest of any point between the second and third steps. The maximum rate of mass loss for the second step occurs at 471.5°C. A tangent to the mass loss curve was drawn at this point so that it intersected the second and third baselines. These intersections, at 439.5°C and 489.5°C, are the onset and endset temperatures for the second mass loss step (Figure 2.1). The slope of the fourth baseline is assumed to be zero. The maximum rate of mass loss for the third step

occurs at 670°C. A tangent to the mass loss curve was drawn at this point so that it intersected the third and fourth baselines at 643.5°C and 701.5°C which are the onset and endset temperatures for the third mass loss step.

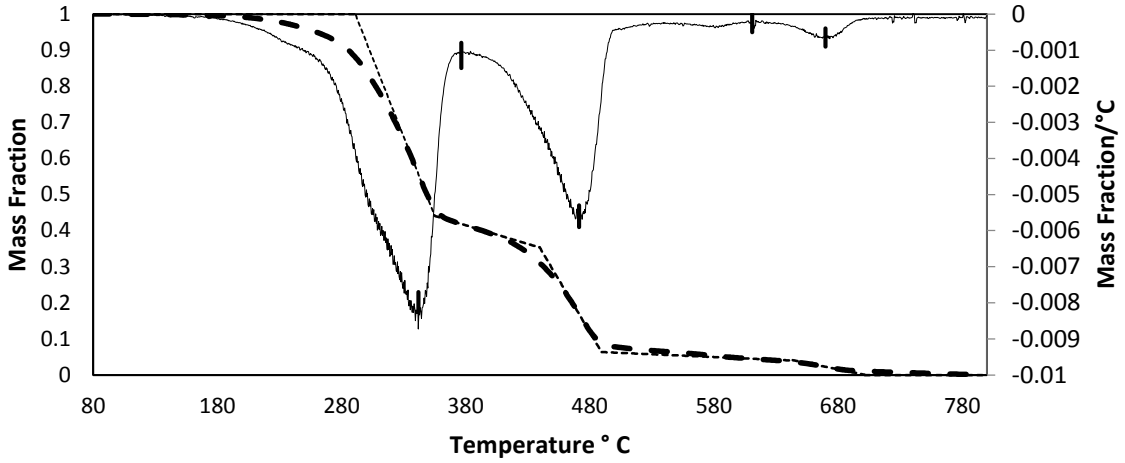


Figure 2.1 Determination of onset and endset temperatures for TGA analysis

2.2.4 Analysis

Onset and endset temperatures were used for determination of the mass loss intervals during the temperature ramp. As shown in Figure 2.2, the first mass loss step, attributed to the decomposition of cellulosic materials, has an onset temperature of 291.5°C and an endset temperature of 355°C. The boundary between secondary moisture content and the devolatilization of cellulosic material was set at 180°C. This temperature was high enough to ensure that all but the most tightly bound moisture was driven from the samples and low enough, over 100°C before the onset of the first mass loss step, to avoid overlap with the loss of cellulosic volatiles. The boundary between cellulosic volatiles and plastic decomposition was set at 397°C. This temperature is midway between 355°C, the endset temperature of the step attributed to the decomposition of cellulosic material, and 439.5°C, the onset temperature of plastic decomposition. The boundary between plastic and high temperature volatiles was set at 567°C because this temperature is midway between the endset of plastic decomposition, at 489.5°C and the onset of the high temperature mass loss at 643.5°C.

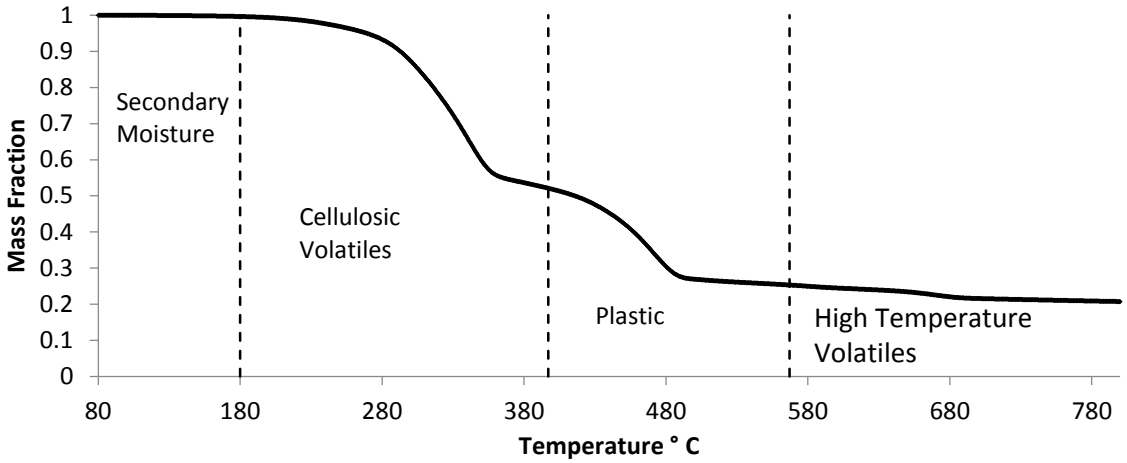


Figure 2.2 Mass loss intervals during temperature ramp

Mass losses occurring during the first isothermal stage were termed primary moisture content. Mass losses occurring in the first four minutes of the ramp were termed secondary moisture content. The sample mass four minutes into the ramp at a temperature of 180°C was considered to be the dry sample mass. The mass loss from 180°C to 397°C was termed cellulosic volatiles. The mass loss from 397°C to 567°C was termed plastic. The mass loss from 567°C until the introduction of oxygen was termed high temperature volatiles. The mass loss which occurs after the introduction of oxygen was termed char and the remaining mass was termed high temperature ash (Figure 2.3). The sum of the primary and secondary moisture contents is the total moisture content. The sum of the char and cellulosic volatiles was termed cellulosic content and the sum of the high temperature ash and high temperature volatiles was termed ash. The term cellulosic has been used for simplicity, but the mass loss to which this term refers is attributable to a number of biogenic materials including cellulose, hemicelluloses, lignin, and other natural polymers [7].

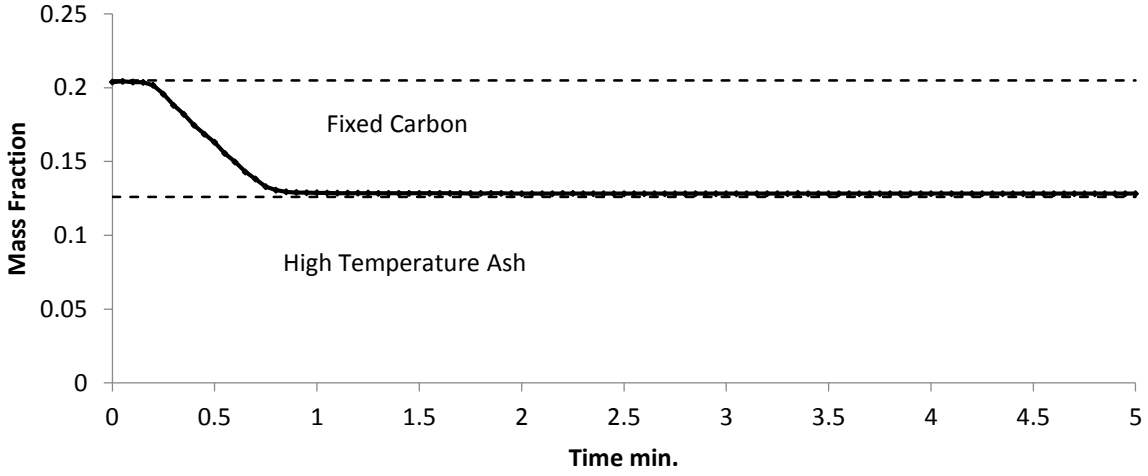


Figure 2.3 Determination of char and high temperature ash from TGA analysis

2.3 Results

Twelve materials prepared by various methods were examined by TGA with results presented in Table 2.7. Moisture content ranged between 2.1 and 4.0 dry wt. % with the Fine and RS1 material having the highest and lowest moisture content, respectively. Samples were exposed to the laboratory atmosphere for varying amounts of time before analysis. The humidity in the laboratory was not controlled so the wide variation in moisture content between materials is to be expected. Cellulosic content ranged between 48.1 and 61.5 dry wt. %. The Fine material had the highest cellulosic content while the Retained material had the lowest cellulosic content. Plastic content ranged between 14.0 and 42.5 dry wt. %. The Retained material had the highest plastic content and the 300UM material had the lowest plastic content. Ash content ranged between 12.2 and 28.4 dry wt. % and the Medium and Coarse material had the highest and the lowest ash content, respectively.

Table 2.7 Average, standard deviation (S.D.), and relative standard error (R.S.E.) for 15 TGA determinations of each of the 12 samples.

	% dry sample mass	Primary H_2O	Secondary H_2O	**Total H_2O**	Cellulosic Volatile	Fixed C	**Cellulosic**	**Plastic**	High Temp. Volatile	High Temp. Ash	**Ash**
Coarse	Average	2.89	0.32	**3.21**	42.1	9.99	**52.1**	**35.74**	4.55	7.61	**12.1**
	S.D.	1.37	0.08	**1.40**	14.0	3.20	**16.6**	**17.83**	1.07	1.96	**2.85**
	R.S.E	47.3	25.3	**43.8**	33.3	32.0	**31.9**	**49.89**	23.5	25.82	**23.4**
Medium	Average	2.46	0.33	**2.79**	39.9	8.76	**48.7**	**22.87**	4.34	24.06	**28.4**
	S.D.	0.98	0.08	**1.03**	10.9	1.98	**12.6**	**7.76**	0.57	16.76	**16.3**
	R.S.E	40.0	23.4	**36.9**	27.2	22.6	**26.0**	**33.92**	13.0	69.65	**57.6**
Fine	Average	3.61	0.37	**3.98**	51.0	10.4	**61.5**	**14.01**	4.66	19.80	**24.4**
	S.D.	1.17	0.06	**1.21**	4.53	0.82	**5.30**	**0.76**	0.31	6.17	**5.97**
	R.S.E	32.3	16.7	**30.5**	8.87	7.81	**8.61**	**5.40**	6.68	31.18	**24.4**
300UM	Average	2.48	0.27	**2.74**	51.4	10.8	**62.2**	**12.**	5.09	20.14	**25.2**
	S.D.	0.72	0.05	**0.76**	15.0	3.06	**18.0**	**4.39**	0.63	21.80	**21.7**
	R.S.E	29.2	17.8	**27.6**	29.2	28.3	**29.0**	**34.95**	12.3	108.2	**85.9**
80UM	Average	3.42	0.30	**3.72**	47.8	10.0	**57.8**	**23.47**	4.39	14.26	**18.6**
	S.D.	0.43	0.02	**0.43**	2.78	0.50	**3.11**	**2.13**	0.22	1.49	**1.46**
	R.S.E	12.4	5.76	**11.4**	5.80	4.99	**5.37**	**9.08**	5.02	10.43	**7.82**
Retained	Average	2.76	0.29	**3.04**	40.1	7.90	**48.0**	**42.46**	3.73	5.73	**9.47**
	S.D.	0.69	0.06	**0.72**	4.20	0.51	**4.31**	**4.64**	0.53	1.48	**1.72**
	R.S.E	25.11	21.49	**23.68**	10.46	6.49	**8.98**	**10.94**	14.15	25.81	**18.21**
RCM1	Average	2.39	0.35	**2.74**	49.1	7.46	**56.6**	**28.21**	4.05	11.14	**15.1**
	S.D.	0.32	0.02	**0.32**	0.35	0.07	**0.41**	**0.18**	0.06	0.61	**0.58**
	R.S.E	13.3	5.01	**11.8**	0.71	0.97	**0.73**	**0.65**	1.45	5.49	**3.82**
RCM2	Average	2.29	0.39	**2.69**	47.1	7.22	**54.3**	**27.38**	4.11	14.18	**18.2**
	S.D.	0.26	0.02	**0.27**	0.13	0.05	**0.15**	**0.15**	0.04	0.18	**0.18**
	R.S.E	11.4	4.69	**9.89**	0.27	0.66	**0.27**	**0.55**	1.01	1.24	**1.00**
RCM3	Average	2.36	0.35	**2.71**	50.1	8.64	**58.7**	**25.46**	4.56	11.25	**15.8**
	S.D.	1.00	0.10	**0.96**	0.55	0.93	**1.13**	**0.36**	0.82	1.09	**1.35**
	R.S.E	42.1	27.9	**35.3**	1.10	10.7	**1.92**	**1.40**	18.0	9.69	**8.51**
RS1	Average	1.78	0.33	**2.10**	48.0	8.29	**56.3**	**24.88**	4.74	14.01	**18.7**
	S.D.	0.31	0.11	**0.33**	0.45	0.15	**0.36**	**0.21**	0.26	0.36	**0.32**
	R.S.E	17.5	33.4	**15.5**	0.94	1.86	**0.65**	**0.85**	5.52	2.59	**1.70**
RS2	Average	1.78	0.39	**2.17**	46.8	7.65	**54.4**	**28.74**	4.58	12.20	**16.7**
	S.D.	0.23	0.05	**0.23**	0.28	0.27	**0.27**	**0.19**	0.22	0.26	**0.31**
	R.S.E	12.8	12.9	**10.6**	0.61	3.49	**0.50**	**0.67**	4.91	2.13	**1.84**
RS3	Average	1.83	0.39	**2.23**	48.1	7.92	**56.0**	**27.07**	4.46	12.40	**16.8**
	S.D.	0.35	0.06	**0.37**	0.58	0.33	**0.57**	**0.37**	0.25	0.47	**0.50**
	R.S.E	19.3	16.4	**16.5**	1.20	4.22	**1.01**	**1.36**	5.67	3.78	**2.96**

The standard deviations and relative standard errors provide measures of the repeatability of the determinations made during individual TGA experiments. Leaving aside the moisture content, the samples which were milled cryogenically had the lowest standard deviations and relative standard errors. The Coarse, Medium, and 300UM samples had much higher standard deviations and relative standard errors than the cryogenically milled samples. The 80UM and Retained materials, made using an ultra-centrifugal, and the Fine material yielded determinations with moderate standard deviations and relative standard errors (Figure 2.4 and Figure 2.5).

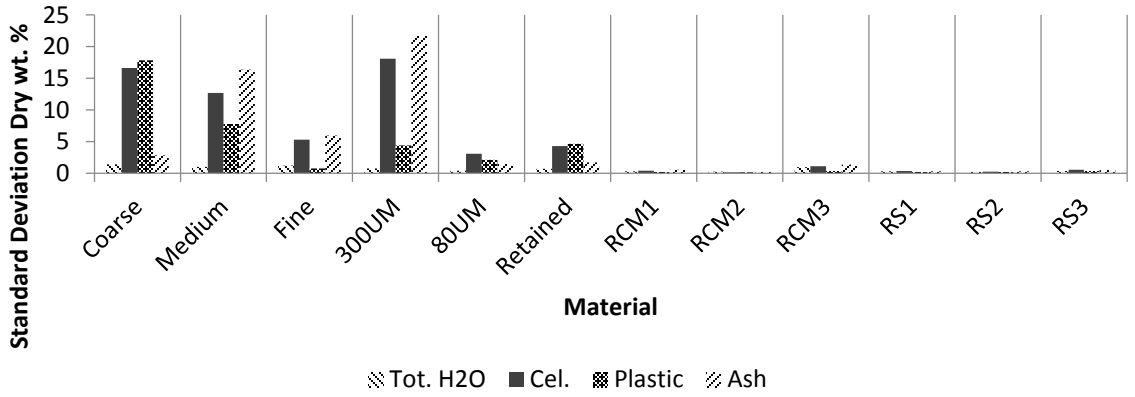


Figure 2.4 Standard deviations of averages obtained from analysis of 15 determinations of each of the 12 samples.

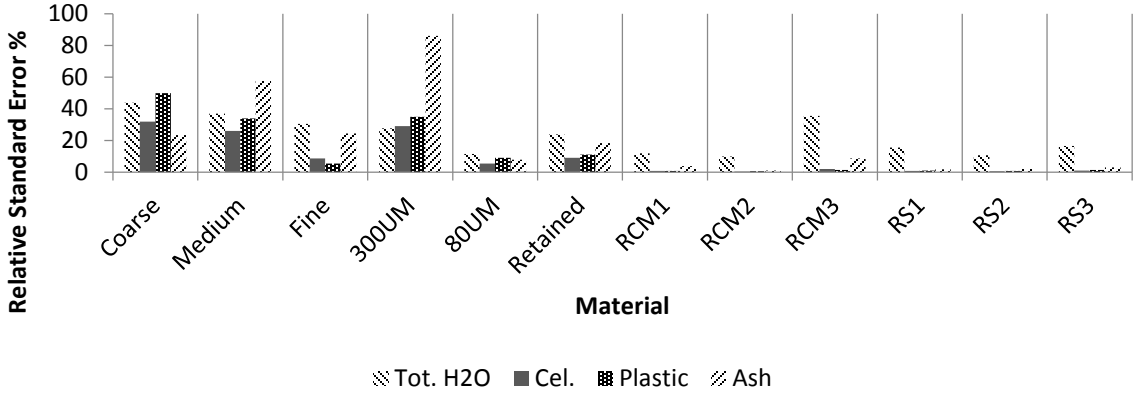


Figure 2.5 Relative Standard Errors on averages obtained from analysis of 15 determinations of each of the 12 samples

2.3.1 Influence of Sample Preparation

The results from the RS1, RS2, and RS3 materials were averaged providing an estimate of the composition of the parent material (Table 2.8). The parent material was estimated to contain 2.16 dry wt. % moisture, 55.64 dry wt. % cellulosic, 26.90 dry wt. % plastic, and 17.47 dry wt. % ash. Differences between the estimated composition of the parent material and the analysis of materials prepared by different means were used to measure the influence of the preparation procedures.

Table 2.8 Average composition of representative samples

Dry wt. %	RS1	RS2	RS3	Average	S.D.	R.S.E.
Primary H_2O	1.78	1.78	1.83	1.80	0.03	1.81
Secondary H_2O	0.33	0.39	0.39	0.37	0.04	10.31
Total H_2O	**2.10**	**2.17**	**2.23**	**2.16**	**0.06**	**2.91**
Cellulosic Volatiles	48.08	46.83	48.15	47.69	0.74	1.56
Char	8.29	7.65	7.92	7.95	0.32	3.99
Cellulosic	**56.37**	**54.48**	**56.07**	**55.64**	**1.01**	**1.82**
Plastic	**24.88**	**28.74**	**27.07**	**26.90**	**1.94**	**7.20**
High Temperature Volatiles	4.74	4.58	4.46	4.59	0.14	3.04
High Temperature Ash	14.01	12.20	12.40	12.87	0.99	7.72
Ash	**18.75**	**16.78**	**16.86**	**17.47**	**1.12**	**6.40**

As can be seen in Figure 2.6 all of the materials contain more moisture than the parent material. The Fine, 300UM, and 80UM materials contain less plastic, more cellulosic, and more ash than the parent material. The Coarse and Retained materials have less cellulosic, less ash, and more plastic than the parent material. The differences between the RCM1, and RCM2, and RCM3 materials and the parent material are very small where the differences are distributed above and below zero.

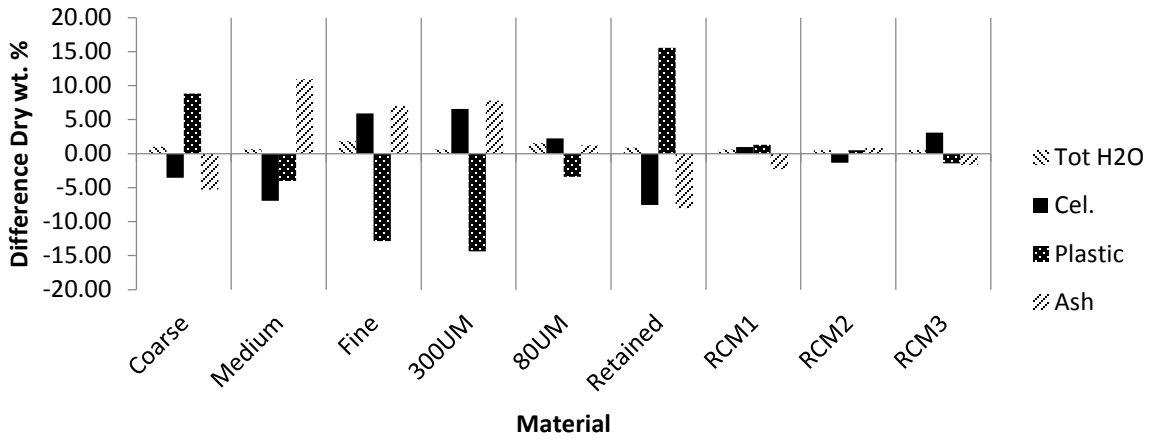


Figure 2.6 Influence of sample preparation on TGA results

The ratio of the fixed carbon determination to the cellulosic determination was not constant for the different materials (Figure 2.7). The materials which were made by cryogenic milling had a lower ratio of char to cellulosic content than the other materials. The Coarse material had the highest ratio of char to cellulosic content.

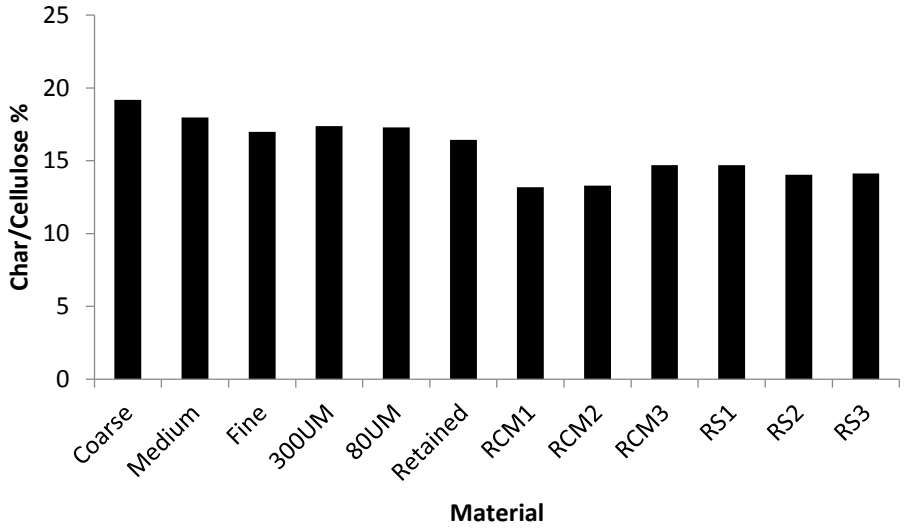


Figure 2.7 Char yield as a percentage of cellulosic content

2.3.2 Apparent Renewable content

If it is assumed that the fraction of material determined as cellulosic by TGA is an accurate representation of the biogenic fraction of the RDF and the material determined as plastic by TGA is an accurate representation of the fossil fraction of the RDF then the TGA method may be used to

approximate the renewable content of RDF. Renewable content is typically expressed on either a mass of carbon or an energy basis. Translating the TGA data into either of these bases requires assumptions about the carbon and energy contents of the biogenic and fossil fractions of RDF. These assumptions are also required by other methods such as the selective dissolution method or methods based on elementary analysis. To translate the results of the TGA analysis into a measure of renewable content, it has been assumed that the biogenic fraction has a heating value of 20 MJ/kg and the fossil fraction has a heating value of 38 MJ/kg [7]. For the mass of carbon basis it has been assumed that the biogenic material in RDF has a carbon content of 0.479 kg/kg and the fossil material has a carbon content of 0.769 kg/kg.

The ratio of biogenic heating value to fossil heating value, 0.53, is very similar to the ratio of biogenic carbon mass fraction to fossil carbon mass fraction, 0.62, so the two bases provide similar results. There is a difference of 30 % between the materials with the highest and lowest renewable content (Figure 2.8).

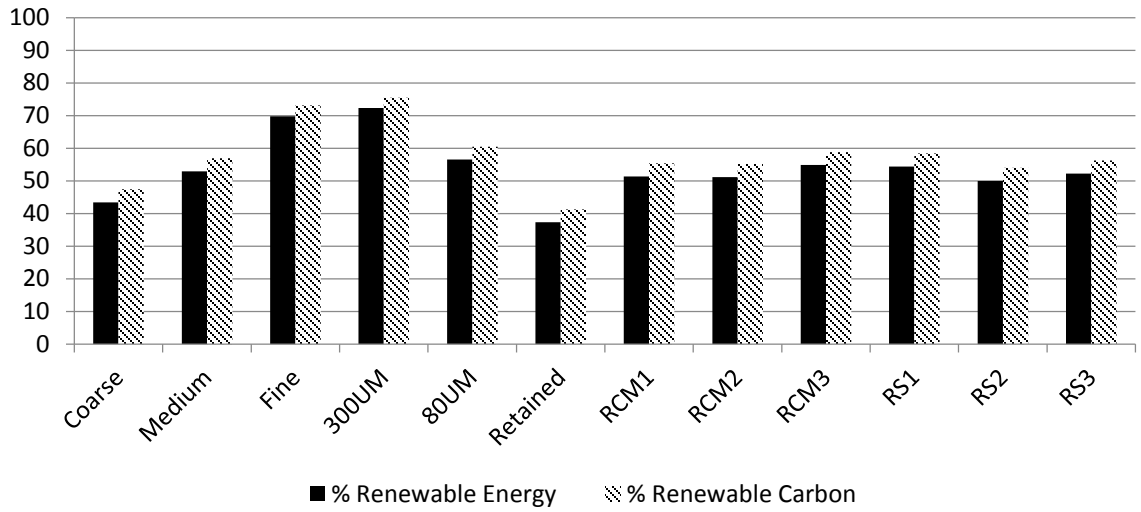


Figure 2.8 Apparent renewable content on energy and mass of carbon bases

2.4 Discussion

2.4.1 Coarse, Medium, and Fine Samples

Results from the analysis of the Coarse, Medium and Fine samples clearly illustrate the influence that grinding and sieving had on the composition of the RDF. The Coarse material had the greatest plastic content of the sieved fractions while the Fine material had the lowest plastic content (Table 2.7). The Coarse material had nearly 10 dry wt. % more plastic while the Fine material had more than 10 dry wt. % less plastic than the parent material (Figure 2.6). Apparently plastic materials are relatively resistant to size reduction and this resistance causes the ground material to become depleted of plastic as it passes through the sieves.

The Medium material had the smallest mass of the three sieved fractions. Most material was either retained on the 1.7 mm sieve or trapped on the bottom tray after passing both the 1.7 mm sieve and the 0.3 mm sieve. The Medium material was greatly enriched in ash as it had the greatest ash content of any of the materials. This was more than 10 dry wt. % greater than the estimated ash content of the parent material. The high ash content of the Medium material probably resulted from the presence of particles of inert material in the RDF which had dimensions greater than 0.3 mm. Such materials are likely to be sand and powdered glass.

2.4.2 300UM Sample

The average composition of the 300UM material closely resembles the average composition of the Fine material (Table 2.7). This is unexpected. The 300UM material was produced by grinding a specimen of RDF until nearly all the material passed both the 1.7 mm and the 0.3 mm sieves. Analysis of the 300UM material should indicate a plastic content greater than the plastic content of the Fine material but the analysis indicates a slightly lower plastic content. Analysis of this material resulted in greater standard deviations and relative standard errors than that of the Fine material. The 300UM material has the highest standard deviation in cellulosic and ash content of all the materials (Figure 2.4, Figure 2.5).

The appearance of the 300UM material is very similar to that of the Fine material. Both are composed of matted fibres. Closer examination of the 300UM material revealed the presence of a layer of non-fibrous material hidden under the matted fiber. The Fine material did not appear to contain such a layer. This stratification may explain the high standard deviations associated with analysis of the 300UM material since the results of any individual experiment would depend heavily on how the 10 mg sample was removed from the sample container.

2.4.3 80UM and Retained Samples

The composition of the 80UM material was very close to the estimated composition of the parent material (Figure 2.6). The standard deviations and relative standard errors associated with analysis of this material were quite low (Figure 2.4 and Figure 2.5). The greatest difference between the 80UM material and the parent material was the plastic content. The 80UM material had a lower plastic content than the parent material and this influenced the apparent renewable content of the 80UM material compared to the parent material (Figure 2.6 and Figure 2.8).

The Retained material had a very high plastic content compared to the parent material. Since the retained material was the material left behind in the ultra-centrifugal mill after production of the 80UM material it seems likely that the ultra-centrifugal mill tends to retain plastic materials and that influences the analysis of the ground material.

2.4.4 RCM and RS Materials

The RCM1, RCM2, and RCM3 materials had compositions which were very close to the estimated composition of the parent material. Analysis of these materials yielded very small standard deviations and relative standard errors. The greatest uncertainties, leaving aside moisture content,

were in the ash content of the samples. The average of the RCM1, RCM2, and RCM3 materials was similar to the average of the RS1, RS2, and RS3 materials which was used to estimate the composition of the parent material (Table 2.9). The greatest differences were seen in the ash and plastic contents. It appears that the composition of the pellets did not vary much from the composition of the parent material.

Table 2.9 Comparison of average composition of the RCM and RS materials

Dry wt. %	Average RCM1, RCM2, RCM3	Average RS1, RS2, RS3	Difference	% Difference
Primary H_2O	2.00	1.80	0.21	11.42
Secondary H_2O	0.38	0.37	0.01	2.55
Total H_2O	**2.38**	**2.16**	**0.21**	**9.90**
Cellulosic Volatiles	48.04	47.69	0.35	0.74
Char	7.68	7.95	-0.27	-3.45
Cellulosic	**55.72**	**55.64**	**0.08**	**0.14**
Plastic	**28.01**	**26.90**	**1.11**	**4.13**
High Temperature Volatiles	4.36	4.59	-0.23	-5.00
High Temperature Ash	11.91	12.87	-0.96	-7.44
Ash	**16.28**	**17.47**	**-1.19**	**-6.80**

Standard deviations for the averages of results on the RCM materials were not much different from those for the RS material (Figure 2.9). This is unexpected since the RS materials were produced from the same 3.1 kg sample of RDF by coning and quartering. The intention of the coning and quartering process was to minimize changes in composition which take place when a sub-sample is produced. It was expected that there would be much less variation in the composition of the RS material than in the composition of the RCM materials.

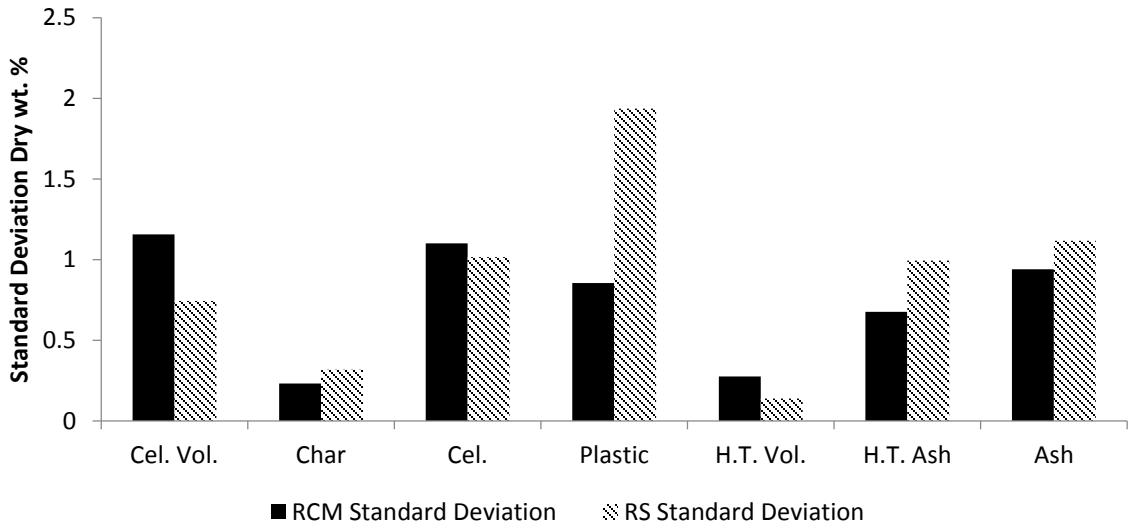


Figure 2.9 Comparison of standard deviations for average results from RCM and RS materials

2.4.5 Number of Determinations and Sample Sizes

For the TGA determinations to be of any use it must be possible to distinguish between materials which have different average composition with a reasonable measure of certainty. High standard deviations make comparison between average results quite uncertain. Uncertainty may be addressed by averaging the results of a greater number of determinations or it may be addressed by increasing the samples size.

The number of determinations required to exclude a 5 % average difference in cellulosic content from a 95 % confidence interval was calculated for each of the materials. It is well known that variances associated with determinations made on particulate samples are inversely proportional to sample mass. The idea is encapsulated in Gy's formula for the fundamental sampling error [26]. If it is assumed that the variances associated with the determination of cellulosic content result from the fundamental sampling error then it is possible to calculate the sample mass which would yield average results with a given standard deviation. A standard deviation of 3.124 % excludes a 5 % difference in average cellulosic contents for two sets of three determinations with 95 % confidence. As Seen in Table 10 the Course, Medium, and 300UM samples would all require sample masses well in excess of 100 mg for such a distinction to be possible. These sample sizes are very large for TGA. It would be difficult to place a 100 mg RDF sample in the thermo-balance. The required masses for the cryogenically milled materials are very low. Samples much lower than 1 mg would not be appropriate given the limits of the thermo-balance (Table 2.10).

It was assumed that the sample standard deviation in cellulosic content was the standard deviation in cellulosic content for RDF materials prepared in a similar manner. The Coarse, Medium, and Fine samples would require far too many determinations. The materials which were cryogenically milled would only require one determination to distinguish between a 5 % difference in the cellulosic contents.

Table 2.10 Number of determinations and sample masses to exclude 5 % difference from 95 % confidence interval on difference of means for two sets of three determinations

Material	# Determinations n	$1.96 \times \sqrt{2\sigma^2/n}$	Required Mass (mg)
Coarse	85	4.999	283.27
Medium	50	4.967	164.48
Fine	9	4.893	28.73
300UM	101	4.982	334.28
80UM	3	4.977	9.91
Retained	6	4.883	19.07
RCM1	1	1.142	0.17
RCM2	1	0.411	0.02
RCM3	1	3.122	1.30
RS1	1	1.011	0.14
RS2	1	0.762	0.08
RS3	1	1.576	0.33

The Coarse, Medium, and 300UM materials are not appropriate for TGA. The uncertainty in the results from these materials is so great that the average determinations could only be of use if a very large number of determinations were made or if the sample sizes were increased to a size that would be inappropriate for most TGA equipment. The Fine, Retained, and 80UM samples might be appropriate for TGA analysis. These materials were all produced using sieves or screens so it is likely that their compositions were altered during sample preparation, so while reasonably significant results might be obtainable they would only apply to the composition of the prepared material rather than the parent material.

2.5 Conclusions

Results from the Coarse, Medium, and Fine materials and results from the 80UM and Retained materials indicate that sieves and screens are capable of causing large changes in the composition of RDF (Figure 2.6). In particular, plastic materials appear to be held up on sieves and screens. Size

reduction procedures involving sieves or screens should be avoided. Results from sieved fractions of RDF may only be considered valid for the sieved fraction rather than for the parent material.

Very fine samples are required for repeatability. The 300UM material was not fine enough to admit reasonable analysis. Matting of fibres in the sample seemed to cause stratification which inhibited TGA analysis. The 80UM material provided much better results. Unfortunately the ultra-centrifugal mill used to produce to 80UM material relies on a screen. Plastic materials appear to be held up behind the screen which means that the composition of the 80UM material was changed by the ultra-centrifugal milling. The issue could be addressed by passing a greater quantity of material through the mill, so that the proportion of sample mass held up in the mill becomes insignificant, but the screen becomes clogged very quickly. In practice, only about two grams of material could be milled before the screen needed to be removed and cleaned. Mills equipped with cyclones have been recommended as a means of fine grinding RDF without resorting to cryogenic milling [27].

Cryogenic ball milling was found to provide repeatable results. The cryogenic temperatures achieved during the grinding process allow for extremely fine grinding of all the materials in the RDF. The process does not make use of sieves and screens and recoveries are very high, so sample preparation error is not a concern. The drawbacks of this process are that it requires expensive equipment and a supply of liquid nitrogen and that it is time consuming.

The ability of TGA to distinguish between cellulosic and petroleum derived materials is long standing and generally accepted. A TGA method could be used to provide a measure of the renewable content of RDF by dividing the combustible fraction of the fuel into cellulosic and petroleum derived materials. The apparent renewable content could then be reported on energy or a carbon basis by making assumptions about the energy or carbon content of the cellulosic and plastic fractions.

The indirectness of the TGA method compared to ^{14}C analysis might cause objections. However it has been noted that ^{14}C analysis does not provide a direct measure of renewable content or fossil content since it requires an assumption about the average ^{14}C content of biogenic material in RDF or MSW. Variation in the ^{14}C content of biogenic material means that ^{14}C analysis is subject to significant error. Additionally, the selective dissolution is very similar to TGA in that biogenic and fossil materials are distinguished by the ease with which they decompose under a given set of

experimental conditions, so there is some acceptance based on measurements which might appear less direct than the ^{14}C method.

TGA is a much more accessible analysis method than ^{14}C analysis. The equipment is cheaper to purchase and maintain and there are fewer analytical steps. TGA is somewhat faster than the selective dissolution method and it can clearly distinguish ash from biogenic material. The ^{14}C and selective dissolution methods may be carried out with gram scale samples. This simplifies sample preparation. The primary disadvantage of using TGA to determine the renewable content of fossil derived fuel is the small sample size required by TGA, which combined with the nature of RDF makes sample preparation very difficult. Cryogenic ball milling is an excellent way to overcome the difficulty associated with sample preparation. Scholler et al. [16] reached a similar conclusion when applying elemental analysis to determine the fossil content of RDF. Sample sizes for elemental analysis are somewhat larger, 100s of mg instead of 10s of mg, than sample sizes for TGA but they are still small enough to make analysis of RDF difficult [20, 28].

Though the ability of TGA to distinguish between the biogenic and fossil derived fractions of RDF is generally accepted more effort would have to be applied to the validation of the method before it could be accepted as a standardized method.

References

[1] Department for Environment Food & Rural Affairs, "Refuse derived fuel market in England Call for Evidence," United Kingdom, 2014.

[2] Life Climate Action, "Report on RDF/SRF utilization applications and technical specifications," European Commission, 2011.

[3] J. Reichelt, G. Pfrang-Stotz, B. Bergfeldt, H. Seifert and P. Knapp, "Formation of deposits on the surfaces of superheaters and economizers of MSW incinerator plants," *Waste Management,* vol. 33, pp. 43-51, 2013.

[4] D. Bankiewicz, S. Enestam, P. Yrjas and M. Hupa, "Experimental studoes of Zn and Pb induced high temperature corrosion of two commercial boiler steels," *Fuel Processing Technology,* vol. 105, pp. 89-97, 2013.

[5] Y.-H. Chang, W. Chen and N.-B. Chang, "Comparative evaluation of RDF and MSW incineration," *Journal of hazardous materials,* vol. 58, pp. 33-45, 1998.

[6] A. W. Larsen and T. Astrup, "CO2 emission factors for waste incineration: Influence from source separation of recyclable materials," *Waste Managment 31,* vol. 31, pp. 1597-1605, 2011.

[7] R. K. Argawal, "A Rapid method for characterization and proximate analysis of refuse-derived fuels and its implications for thermal conversion," *Waste Management and Research,* vol. 6, pp. 271-280, 1988.

[8] R. K. Argawal, "Compositional Analysis of Solid Waste and Refuse derived fuels by thermogravimetry," in *Compositional analysis by thermogravimetry*, Philadelphia, ASTM, 1988, pp. 259-271.

[9] J. P. Elder, "Proximate analysis by automated thermogravimetry," *Fuel,* vol. 62, pp. 580-584, 1983.

[10] V. Cozzani, L. Petarca and L. Tognotti, "Devolatilization and pyrolysis of refuse derived fuels: characterization and kinetic modelling by a thermogravimetric and calorimetric approach,"

Fuel, vol. 74, no. 6, pp. 903-912, 1995.

[11] G. Skodras, P. Grammelis, P. Basinas, P. M, E. Kakaras and G. P. Sakellaropoulos, "A thermochemical Conversion Study on the Combustion of Residue-Derived Fuels," *Water Air Soil Pollut: Focus,* vol. 9, pp. 151-157, 2009.

[12] C.-H. Wu, C.-Y. Chang, J.-L. Hor, S.-M. Shih, L.-W. Chen and F.-W. Chang, "ON THE THERMAL TREATMENT OF PLASTIC MIXTURES OF MSW: PYROLYSIS KINETICS," *Waste Management,* vol. 13, pp. 221-235, 1993.

[13] L. Sorum, M. Gronli and J. Hustad, "Pyrolysis characteristic and kinetics of municipal solid wastes," *Fuel,* vol. 80, pp. 1217-1227, 2001.

[14] G. Muir, S. Hayward, B. Tripney, G. Cook, P. Naysmith, B. Herbert, M. Garnett and M. Wilkinson, "Determining the biomass fraction of mixed waste fuels: A comparison of existing industry and 14C-based methodologies," *Waste Management,* vol. 35, pp. 293-300, 2015.

[15] W. H. Ariyaratne, M. C. Melaaen and L.-A. Tokheim, "Determinatiion of biomass fraction for partly renewable solid fuels," *Energy,* vol. 70, pp. 465-472, 2014.

[16] F. C. Jones, E. W. Blomqvist, M. Bisaillon, D. K. Lindberg and M. Hupa, "Determination of fossil carbon content in Swedish waste fuel by four different methods," *Waste Management and Research,* vol. 31, no. 10, pp. 1052-1061, 2013.

[17] Q. Hua, "Radiocarbon: A chronological tool for the recent past," *Quarternary Geochronology,* vol. 4, pp. 378-390, 2009.

[18] J. Fellner and H. Rechberger, "Abundance of 14C in biomass fractions of wastes and solid recovered fuels," *Waste Management,* vol. 29, pp. 1495-1503, 2009.

[19] W. H. Ariyaratne, O. Asgautsen, M. C. Melaanen, K. Eine and L.-A. Tokheim, "Determination of fossil fraction of Refuse Derived Fuel by the Selective Dissolution Method in Calorific value basis: Development of simplified method," *Fuel ,* vol. 98, pp. 41-47, 2012.

[20] J. Schnoller, P. Aschenbrenner, M. Hahn and J. Fellner, "Sample preparation and determination of biomass content in solid recovered fuels: A comparison of methods," *Waste Management &*

Research, vol. 32, no. 10, pp. 1024-1029, 2014.

[21] M. Severin, C. A. Velis, P. J. Longhurst and S. J. Pollard, "The biogenic content of process streams from mechanical-biolgical treatment plants producing solid recovered fuel. Do the manual sorting and selective dissolution determination methods correlate?," *Waste Management ,* vol. 30, pp. 1171-1182, 2010.

[22] K.-S. Lin, H. P. Wang, S.-H. Liu, N.-B. Chang, Y.-J. Huang and H.-C. Wang, "Pyrolysis kinetics of refuse-derived fuel," *Fuel Processing Technology,* vol. 60, pp. 103-110, 1999.

[23] M. W. Seo, S. D. Kim, S. H. Lee and J. G. Lee, "Pyrolysis characteristics of coal and RDF blends in non-isothermal and isothermal conditions," *Journal of analytical and applied pyrolysis ,* vol. 88, pp. 160-167, 2010.

[24] A. Bosmans, C. De Dobbelaere and H. Lieve, "Pyrolysis characteristics of excavated waste material processes into solid fuel," *Fuel,* vol. 122, pp. 198-205, 2014.

[25] A. Garcia, A. Marcilla and R. Font, "Thermogravimetric kinetic study of the pyrolysis of municipal solid waste," *Thermochimica Acta,* vol. 254, pp. 277-304, 1995.

[26] P. Gy, "PartIV: 50 years of sampling theory a personal history," *Chemometrics and Intelligent Laboratory Systems,* vol. 74, pp. 49-60, 2004.

[27] K. E. Lorber, R. Sarc and A. Aldrian, "Design and quality assurance for solid recovered fuel," *Waste Management & Research,* vol. 30, no. 4, pp. 370-380, 2012.

[28] J. Schnoller, P. Aschenbrenner, M. Hahn, J. Fellner and H. Rechberger, "Sample preparation and biomass determination of SRF model mixture using cryogenic milling and the adapted balance method," *Waste Management,* vol. 34, pp. 2171-2175, 2014.

Chapter 3 Air-blown bubbling fluidized bed co-gasification of woody biomass and refuse derived fuel

*T. Robinson[1], B. Bronson[2], P. Gogolek[2], P. Mehrani[1]**

[1]Department of Chemical and Biological Engineering, University of Ottawa, Ottawa, Ontario, K1N 6N5 Canada

[2]Natural Resources Canada, CanmetENERGY, 1 Haanel Drive, Ottawa, Ontario, K1A 1M1, Canada

Abstract

Air-blown auto-thermal bubbling fluidized bed gasification of Refuse derived fuel (RDF) and hardwood pellet mixtures was investigated at 725°C, 800°C, and 875°C. Gasification of mixtures containing RDF at 875°C resulted in agglomeration of bed material, which prevented steady state operation of the gasifier. Results from the analysis of produced gases, equivalence ratios, and feed rates, did not indicate significant interactions between the two different types of fuel pellets during gasification. RDF was found to yield more tar than hardwood pellets, but hardwood pellets tended to produce more problematic tar compounds. Only small variations in the lower heating value of produced gases were observed, though a greater portion of the heating value of the gases produced with RDF was provided by C_2 and C_3 hydrocarbons. Unisim^{TM} simulator was used for calculation of equilibrium compositions of the produced gases. Gases produced from RDF pellets were found to have much lower carbon dioxide and steam concentrations at equilibrium than gases produced from hardwood pellets.

Keywords: Refuse derived fuel (RDF), biomass, co-gasification, bubbling fluidized bed gasifier, bed agglomeration, waste to energy (WTE)

3.1 Introduction

There are numerous remote northern communities in Canada which are not connected to the North American power grid. As of 2006, there were 194,281 people living in 292 off-grid communities in Canada [1]. Most of the electricity which is consumed in these communities is produced by diesel fuelled generators [1]. Arriaga et al. [2] provided information about the nature of diesel generation in off-grid communities. Most diesel engines in these communities have a rated capacity between 100 kW and 3 MW, and most communities operated 3-5 engines [2]. Multiple units with the same capacity may be run in parallel or engines with varying capacities may be run one at a time to accommodate changes in load. Rated capacities of community power plants are typically 40-60 % of the total rated capacity of the generators so that there is excess capacity in case of a mechanical failure [2].

The cost of generating power from diesel fuel is quite high. Arriaga et al. [3] reported that the average cost of electricity in Canada's remote northern communities is 1.3 $/kWh. In order to reduce the consumption of expensive diesel for power generation it is desirable to find an alternative means of generating power in remote northern communities.

Asadullah [4] reviewed issues surrounding the use of biomass for power generation. It was concluded that utilization of small distributed power generation systems in remote locations might help overcome barriers to the increased use of biomass for power generation. If the technical barriers for small biomass gasification systems can be overcome, biomass potentially presents a significant cost saving compared to fossil fuels for remote communities where biomass availability is high. There may also be social and environmental benefits to displacing some diesel generated power by biomass based power generation systems.

Diesel engines may be run on a combination of combustible gas and diesel fuel. This manner of operation is referred to as dual fuel mode. In this mode the engine operates in a manner which is similar to a spark ignition engine except that the charge of compressed fuel is ignited by the injection of diesel fuel rather than a spark. Remote northern communities located below the tree line have access to large quantities of woody biomass. A gasifier could be used to convert this material to producer gas which could be used to displace diesel fuel in a community's existing power generation system. Several sources report the operation of diesel engines on produced gas [5, 6, 7, 8, 9, 10].

In addition to the high cost of electricity, remote northern communities also have difficulties with trash disposal. Dumpsites may be outdated [11] and full [12]. If some portion of a community's solid waste could be co-gasified with biomass, then, in addition to displacing diesel fuel for electricity production, a gasifier could help alleviate strain on community dumpsites.

A number of sources report the co-gasification of biomass and plastic waste materials. Bacaicoa et al. [13] investigated the gasification of wood chips and high density polyethylene in a down draft gasifier. Mastellone et al. [14] gasified mixtures of wood, plastic and coal in a fluidized bed gasifier. Moghadam et al. [15] studied the fluidized bed catalytic steam gasification of palm kernel blended with polyethylene. Brachi et al. [16] studied the fluidized bed steam-O_2-air co-gasification of olive husk-polyethylene terephthalate pellets and olive husk-tire pellets for the production of syngas for methanol production.

One motivation for gasifying mixtures of different materials is the possibility that gasification of the mixture is better than the sum of the gasification of the individual materials. During gasification the fuels may interact to produce some desirable effect such as a reduction in tar yield [14]. One fuel may allow for the other fuel to be fired in a particular type of reactor [13, 17, 18], or the utilization of an unconventional fuel in an existing facility with an existing technology [19, 20, 21]. Gas compositions may be modified to fit a particular purpose [22, 23]. A relatively difficult to gasify fuel may be used to provide heat for the gasification of a more reactive fuel [24]. Outside the reactor the relative availability of fuels may provide motivation for co-gasification. If one material is only available in small quantities, or if it is only available intermittently, then co-gasification with another material may allow the scale and reliability required for the conversion process [25].

This work focuses on air-blown fluidized bed co-gasification of woody biomass and RDF mixtures. Various fuel composition and gasification temperature are examined to determine the influence of these parameters on the application of fluidized bed gasification technology to power generation in remote northern communities.

3.2 Materials and Methods

Commercial 6 mm (1/4 inch) diameter hardwood pellets were used to represent biomass. The RDF was received as 16 mm (⅝ inch) WastAway® pellets. The RDF had been produced from MSW by a process involving shredding, screening, magnetic sorting, steam hygienization and pelletization.

3.2.1 Fuel Preparation

The hardwood pellets were used as received. The RDF pellets were too large to be used as received and thus were re-pelletized. The RDF pellets were ground using a hammer mill, equipped with a 13 mm (½ inch) screen. A California Pellet Mill, consisting of a vibratory hopper, auger, pellet die, roller, and electric motor was used to re-pelletize the milled RDF at a diameter 6 mm (1/4 inch). To produce mechanically stable pellets, water and cornstarch were added to the ground RDF prior to the re-pelletization at a ratio of 40 g / kg of RDF each. Both fuels were subjected to proximate and ultimate analysis. Table 3.1 summarizes the properties of the hardwood and RDF pellets. A thermo-gravimetric technique, which has been previously reported [26], was used to approximately determine the composition of the RDF on dry basis in terms of cellulosic material (57.5 ± 0.2 wt.%), plastics (26.2 ± 0.3 wt.%), and ash (16.3 ± 0.1 wt.%).

Table 3.1 Fuel properties of hardwood and commercial RDF pellets

		Hardwood Pellets	RDF
Proximate Analysis wt. %	**Moisture**	6.18	5.46
	Ash	0.41	14.56
	Volatiles	78.98	70.48
	Fixed Carbon	14.43	9.5
Ultimate Analysis (dry ash free) wt. %	**Carbon**	49.8	55.4
	Hydrogen	5.94	7.12
	Nitrogen	0.12	0.53
	Sulfur	0	0.18
	Oxygen	44.14	37.16
Gross Calorific Value (Dry) MJ/kg		19.71	20.01

3.2.2 Gasifier

The schematic of the gasifier is shown in Figure 3.1. The gasifier, located at NRCan CanmetENERGY (Ottawa, ON), has an internal diameter of 0.15 m (6 inch) and a height of 4.5 m (180 inch). During experiments the bed consisted of 12 kg of synthetic olivine sand with a Sauter mean diameter of 600 µm. The gasification medium was air delivered by a compressor. All experiments were conducted using an air flow rate of 0.006 kg/s (275 SLPM). During operation the pressure drop across the bed was between 2.2 and 3.2 kPa. Band heaters located around the bed were used to preheat the bed for start-up. During gasification the bed was not heated and the process ran auto-thermally.

Three thermocouples were located in the bed. The average of their temperatures was considered to be the gasification temperature. Since the air flow rate was held constant the average bed temperature was controlled by increasing or decreasing the fuel feed rate. Experiments were conducted at 725°C, 800°C, and 875°C. The highest allowable operating temperature is 950°C, thus the highest experimental temperature was 875°C to provide a safety margin in case of a feed interruption.

An afterburner was used for disposal of the bulk of the produced gases. A stream of 400°C raw gas was withdrawn through a 1 µm filter for analysis. 0.04 m^3 samples of the hot filtered gas were pulled through heated lines and stripped of tar and moisture by a column containing isopropanol. Samples were collected over approximately one hour of steady state gasifier operation. Tar-water-isopropanol solutions were collected from the column and analyzed. The moisture content of the raw gases was determined from the results of Karl-Fischer titration of these solutions. Tar compounds ranging in weight from benzene to coronene are termed GC tar, since they are amenable to the GC analysis. The GC tar content of the raw gases was determined from the results of GC-MS analysis of the tar-water-isopropanol solutions. Tar compounds heavier than coronene are not volatile enough for GC-MS. This material is termed gravimetric tar. The gravimetric tar content of the raw gases was determined by weighing the residue after evaporation of isopropanol, water, and the majority of GC tar compounds from aliquots of the tar-water-isopropanol solutions.

A second portion of the hot filtered gas was allowed to cool to approximately 120°C, so heavy tars could be removed in a knock-out vessel. Heated head diaphragm pumps were used to push the gas through heated filters while the temperature was maintained at 120°C. After filtration at 120°C the gas was dried in a condenser maintained at 1°C. A regulator was used to maintain the pressure of the dried gas stream at the 60 KPa required by the micro GC sampling system.

The dried gas stream was sampled and analysed by mirco GC at four minute intervals. Two micro GC columns, each equipped with a thermal conductivity detector (TCD) were used to measure the concentrations of H_2, O_2, N_2, CO, CH_4, CO_2, C_2H_4, C_2H_6, C_2H_2, and C_3H_6 in the dry gas stream. For gas composition results, averages of at least ten consecutive measurements are reported in this work.

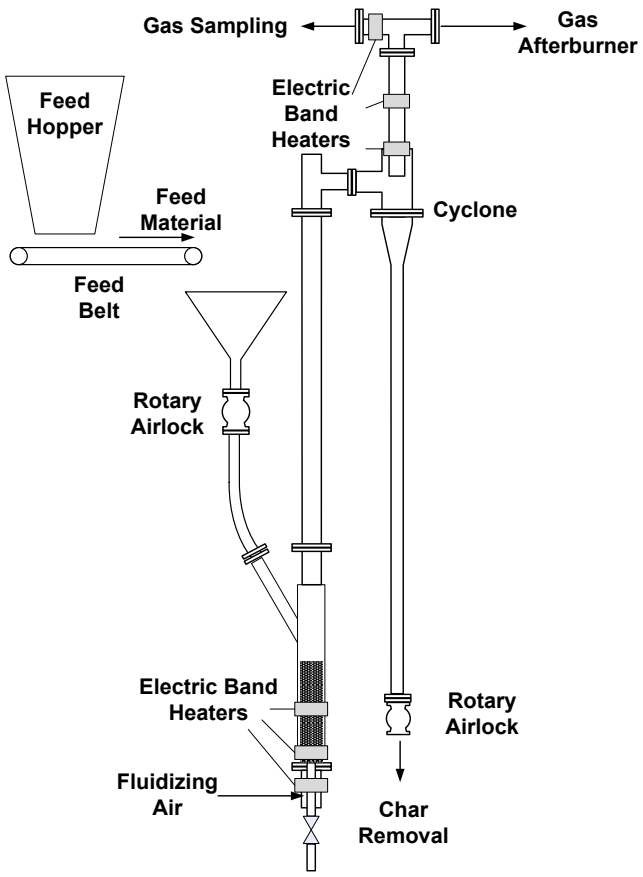


Figure 3.1 Fluidized bed gasifier

3.3 Results

Gasification of mixtures of hardwood and RDF pellets was carried out at temperatures of 725°C, 800°C and 875°C. Mixtures consisted of 100 %, 75 %, 50 %, and 0% hardwood pellets with the balance being RDF pellets. Loss of fluidization resulting from agglomeration of the bed material prevented steady state operation of the gasifier at 875°C, when RDF was included in the feed.

Mass balances for the experimental runs are found in Table 3.2. Duplicate experiments were performed for three of the 800°C conditions. Differences between the mass entering and the mass exiting the gasifier ranged between -7.39 % and 0.82 % of the total mass fed to the gasifier. The duplicate of the 75 wt. % experiment conducted at 800°C had the greatest quantity of extra mass appearing in the outlet streams. There was a problem with the gravimetric tar measurement for this run. The sample was found to be contaminated with heavy naphthenic compounds. If this result is ignored, the differences range between -1.87 and 0.82 % of the total mass fed to the gasifier.

The dry gas yield from the experiments ranges between 80.7 and 90.5 wt. % of the total mass fed to the gasifier. Increasing the proportion of hardwood pellets in the feed and increasing the reaction temperature increases the yield of dry gas. Tar accounts for between 1.12 and 3.39 wt. % of the mass fed to the gasifier. The tar yield increases as the proportion of RDF in the feed increases. The tar yield as a fraction of the mass fed to the gasifier decreases as the reaction temperature increases. If the tar yield as a fraction of the fuel is considered, the tar yield decreases with temperature for the hardwood pellets but not for the RDF pellets (Figure *3.2*).

Table 3.2 Mass Balance on percent basis

	725 °C				**800 °C**							**875 °C**	
Fraction hardwood pellets in Feed	**1.00**	**0.75**	**0.50**	**0.00**	**1.00**	**1.00**	**0.75**	**0.75**	**0.50**	**0.00**	**0.00**	**1.00**	**1.00**
Mass in (%)													
Fuel	49.3	48.3	46.5	42.4	43.7	44.5	42.8	41.3	41.0	36.3	37.8	39.1	38.8
Air	50.7	51.7	53.5	57.6	56.3	55.5	57.2	58.7	59.0	63.7	62.2	60.9	61.2
Total	100	100	100	100	100	100	100	100	100	100	100	100	100
Mass out (%)													
Gas	82.0	80.7	80.6	80.7	87.5	85.8	86.3	86.9	85.1	86.0	83.6	89.8	90.5
Tar	2.25	2.24	2.80	3.39	1.68	1.68	1.95	**8.05**	2.40	2.90	3.14	1.12	1.21
Moisture	11.5	11.2	10.2	9.1	9.2	10.3	9.3	9.3	9.4	8.4	9.0	8.7	8.5
Cyclone Solids	3.98	5.05	5.56	6.40	2.49	2.50	3.02	3.15	3.59	4.62	4.67	1.80	1.71
Total	100	99	99	100	101	100	101	107	100	102	100	101	102
Difference (In-Out)	0.35	0.82	0.82	0.41	-0.87	-0.28	-0.58	-7.39	-0.46	-1.86	-0.45	-1.41	-1.87

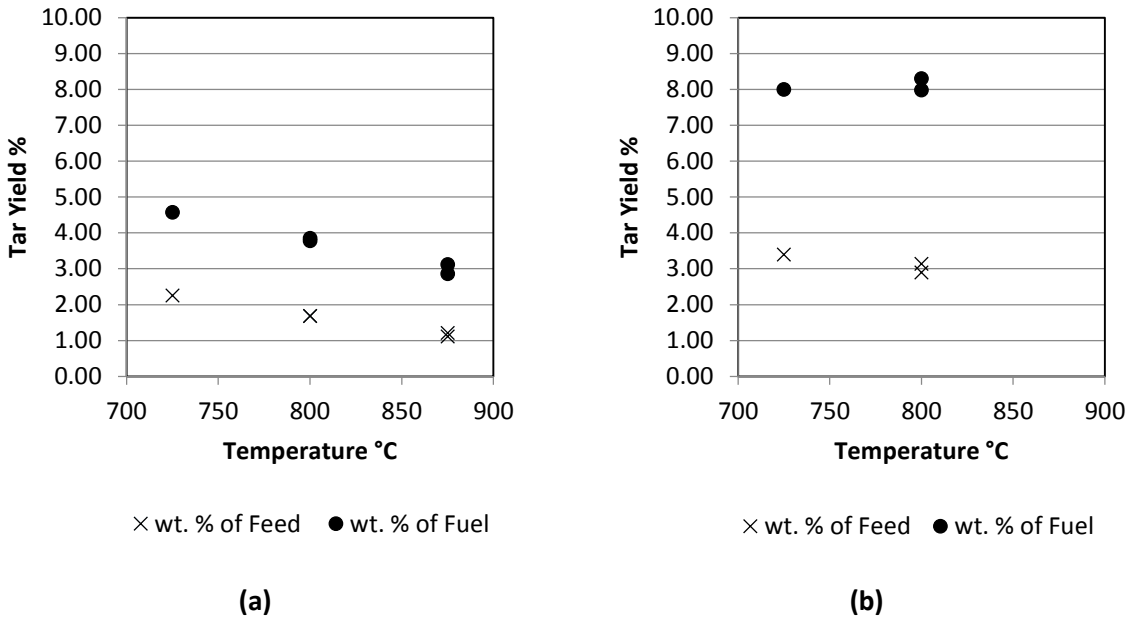


Figure 3.2 Tar yield of Hardwood (a) and RDF (b) pellets at various gasification temperatures

The most abundant components of the gases were non-combustible. The concentration of these components is plotted against the fraction of hardwood pellets in the fuel at 725°C and at 800°C in Figure 3.3. For both temperatures, the concentration of nitrogen decreased by approximately 10 mol. % as the proportion of hardwood pellets in the feed increased from 0-100 %. For a given fuel composition, the concentration of nitrogen is higher at the higher temperature condition. There was little change in the concentration of water and carbon dioxide when the fuel composition was varied. The concentrations of water and carbon dioxide tend to be slightly lower at 800°C than at 725°C.

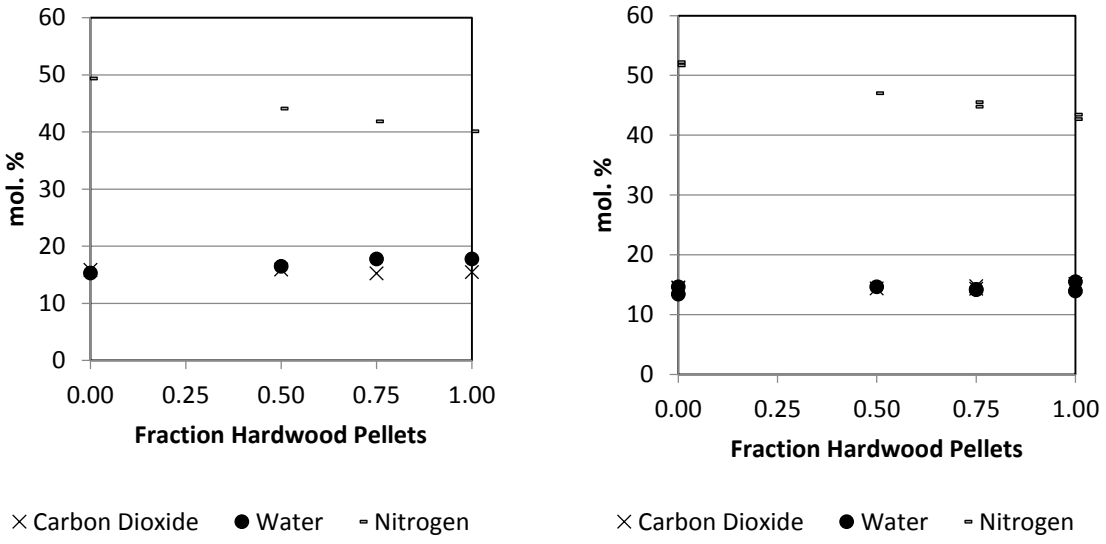


Figure 3.3 Concentrations of non-combustible species in the raw gas at 725°C (a) and 800°C (b)

The most abundant combustible components of the raw gas are carbon monoxide, hydrogen, and methane. The concentrations of these components are graphed against the fraction of hardwood pellets in the feed for the 725°C and the 800°C temperature conditions in Figure 3.4. Except for the concentration of hydrogen at 725°C the concentrations of the major combustible components of the gas increased as the fraction of hardwood pellets in the feed increased. The concentration of methane was slightly higher at 800°C than at 725°C.

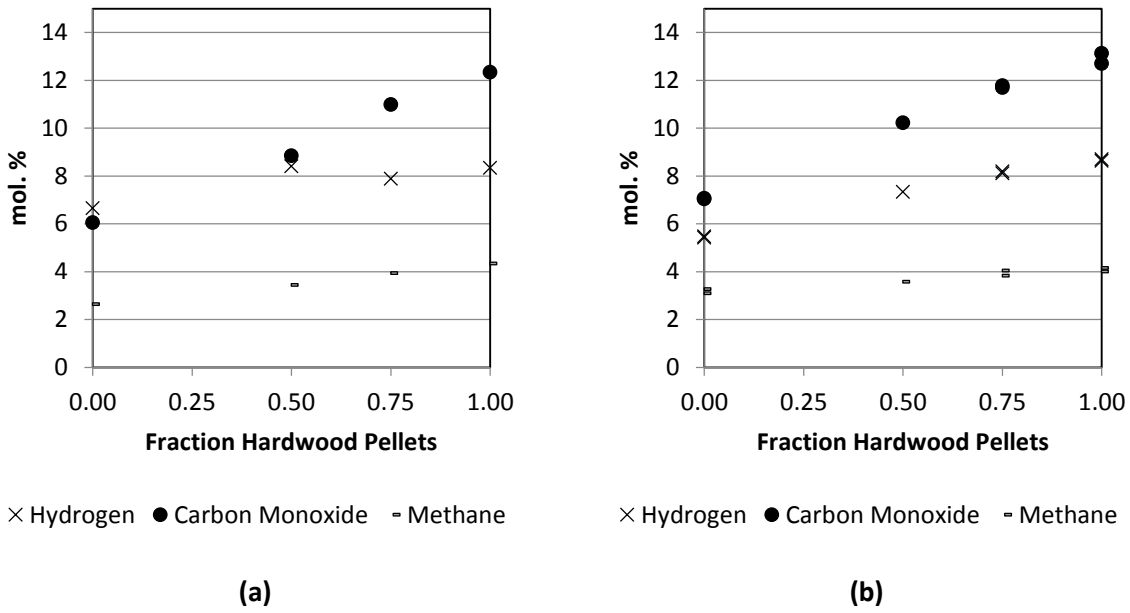


Figure 3.4 Concentrations of major combustible components of the raw gas at 725°C (a) and 800°C (b)

The concentration of the minor combustible components in the raw gas is graphed against the fraction of hardwood pellets in the fuel in Figure 3.5 for the 725°C and 800°C temperature conditions. Ethylene and propylene are the most abundant minor gas components. The concentration of both of these components decreased as the fraction of hardwood pellets increased. The concentration of ethane also decreased slightly with increases in the fraction of hardwood pellets in the feed.

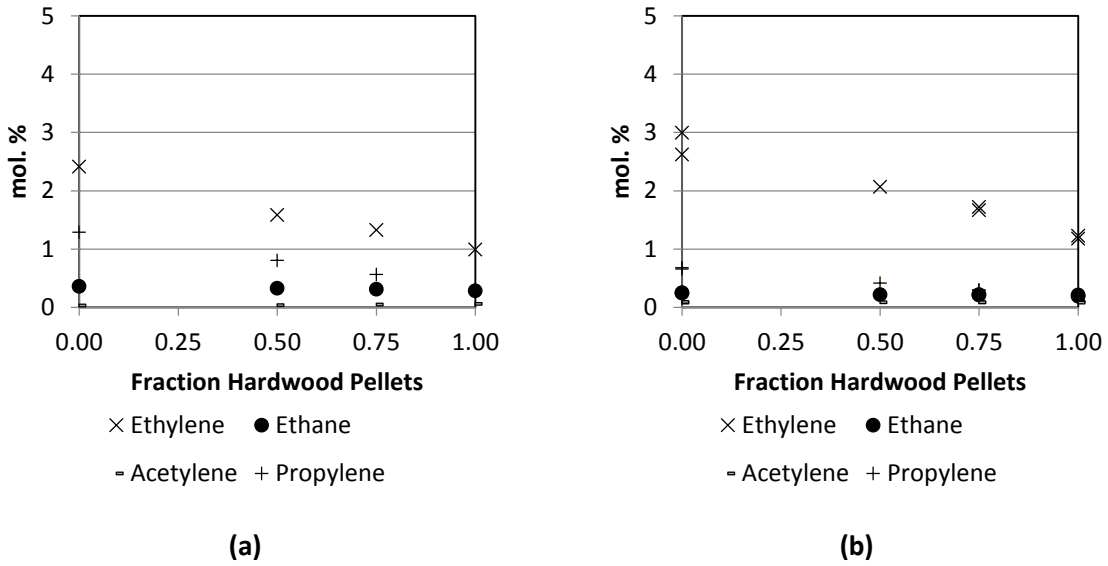


Figure 3.5 Concentrations of minor combustible components of the raw gas at 725°C (a) and 800°C (b)

The concentrations of GC and gravimetric (Grav.) tar in the raw producer gases are plotted against the fraction of hardwood pellets in the feed fuel in Figure 3.6. The concentration of the GC tar is higher than the concentration of the gravimetric tar for each condition. The concentration of GC tar declines with increases in the fraction of hardwood pellets in the feed. The highest concentrations of gravimetric tar are observed at the conditions where the fuel was composed of 75 wt. % hardwood pellets. Concentrations of GC and gravimetric tar are lower for gases produced at 800°C than for gases produced at 725°C.

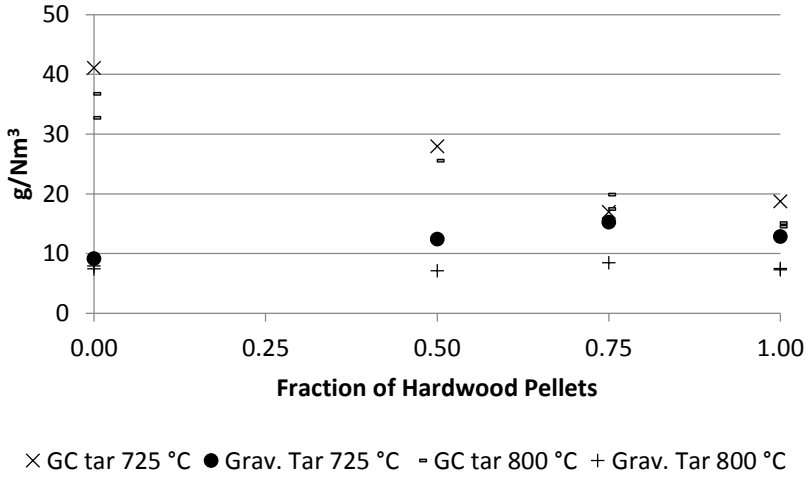


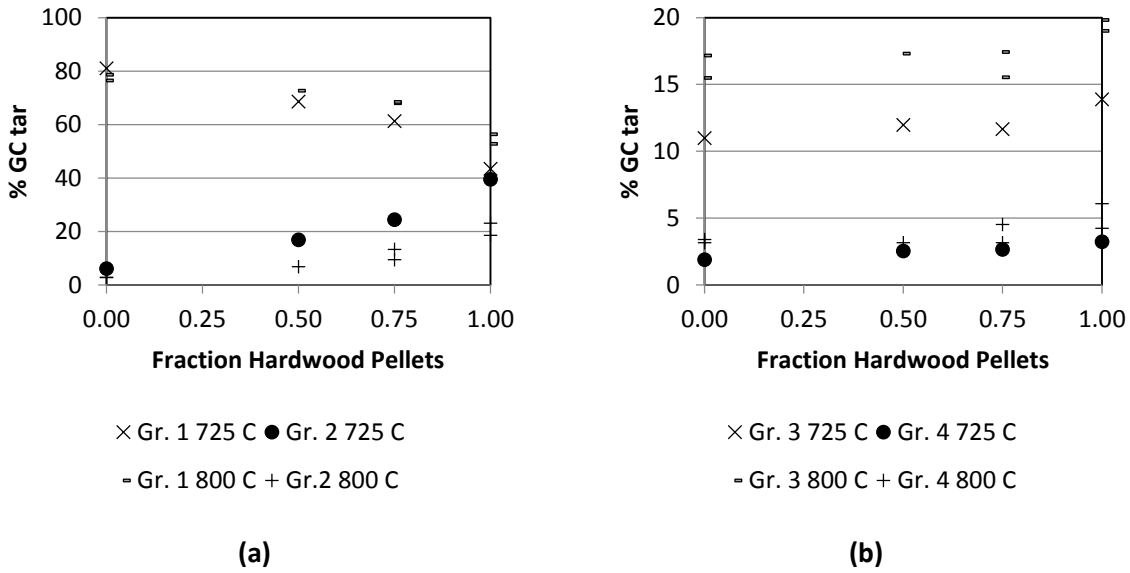
Figure 3.6 Concentration of GC and Gravimetric tar in dry produced gases

The GC tar compounds have been subdivided into four groups (Table 3.3). The first group contains single ring aromatic hydrocarbons. The second group contains phenols. The third group contains two and three ring aromatic compounds which are structurally related to naphthalene, and the fourth group contains poly-aromatics ranging from fluorene to coronene.

Table 3.3 GC tar groups

Group 1	**Group 2**	**Group 3**	**Group 4**	
benzene	phenol	indene	fluorene	benzo(k)fluoranthene
toluene	o-cresol	naphthalene	phenanthrene	benzo(e)pyrene
ethylbenzene	m and p-cresol	2-methylnaphthelene	anthracene	benzo(a)pyrene
xylene1		1-methylnaphthalene	fluoranthene	perylene
xylene2		biphenyl	pyrene	Indeno(123-cd)pyrene
styrene		acenaphthylene	benz(a)anthracene	Dibenz(a,h)anthracene
o-xylene		acenaphthene	chrysene	Benzo(ghi)perylene
			benzo(b)fluoranthene	coronene

The proportion of group 1 compounds decreased and the proportion of group 2 compounds increased when the fraction of hardwood pellets in the feed is increased (Figure 3.7). When the temperature was increased from 725°C to 800°C the proportion of group 1 compounds increased while the proportion of group 2 compounds decreased. Gasifying pure hardwood pellets results in a greater proportion of group three compounds than gasifying pure RDF, but a trend for the mixtures is not discernible (Figure 3.7). The proportion of group 3 compounds increased with temperature. The proportion of group 4 compounds increased with increases in the fraction of hardwood pellets in the fuel and with increases in temperature.



(a) **(b)**

Figure 3.7 Composition of GC tar Groups 1 and 2 (a) and Groups 3 and 4 (b)

The ratio of air fed to the gasifier to the stoichiometric air required for complete combustion of the fuel fed to the gasifier is termed equivalence ratio (ER). This ratio is a measure of the extent to which the fuel has been combusted. At 800°C the equivalence ratio ranged from 0.24-0.30 while at 725°C it ranged from 0.19-0.24 (Figure 3.8). For a given temperature condition, equivalence ratios decreased with increasing hardwood pellets in the feed. The rate at which the equivalence ratio declined as the fraction of hardwood pellets in the feed was increased is similar for both temperature conditions.

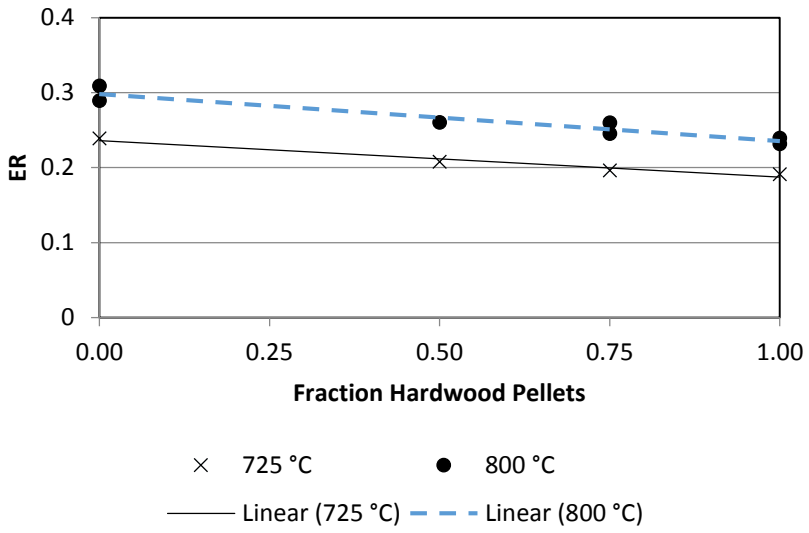
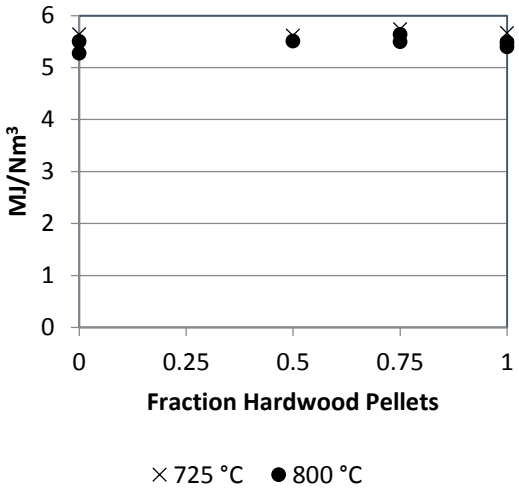


Figure 3.8 Equivalence ratios for mixtures of hardwood pellets and RDF

The dry clean gases produced from mixtures of hardwood pellets and RDF had lower heating values (LHV) in the narrow range of 5.3-5.7 MJ/Nm^3 (Figure 3.9). Experiments conducted at 75 wt. % hardwood pellets had the highest heating values. Heating values declined slightly as the temperature was increased from 725°C to 800°C. Experiments conducted with pure RDF yielded higher efficiencies than experiments conducted with pure hardwood (Figure 3.10). The results for mixtures do not suggest a clear trend. The efficiencies at 725°C are lower than the efficiencies at 800°C. The gasifier thermal efficiency on a lower heating value basis ranges between 0.43-0.61 (Figure 3.11). Switching from hardwood pellets to RDF has roughly the same influence on the gasifier thermal output as raising the temperature from 725°C to 800°C (Figure 3.11).



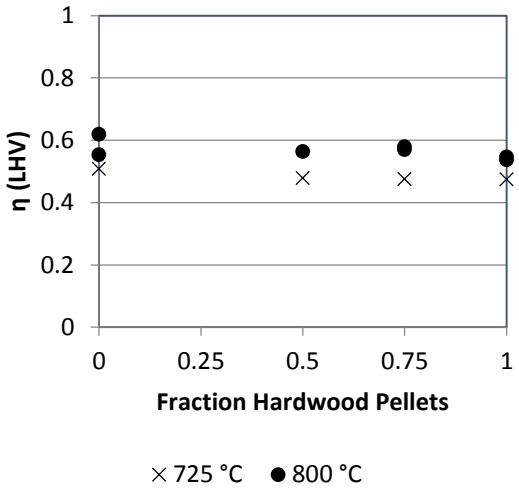


Figure 3.9 Dry produced gas lower heating value

Figure 3.10 Gasifier thermal efficiency

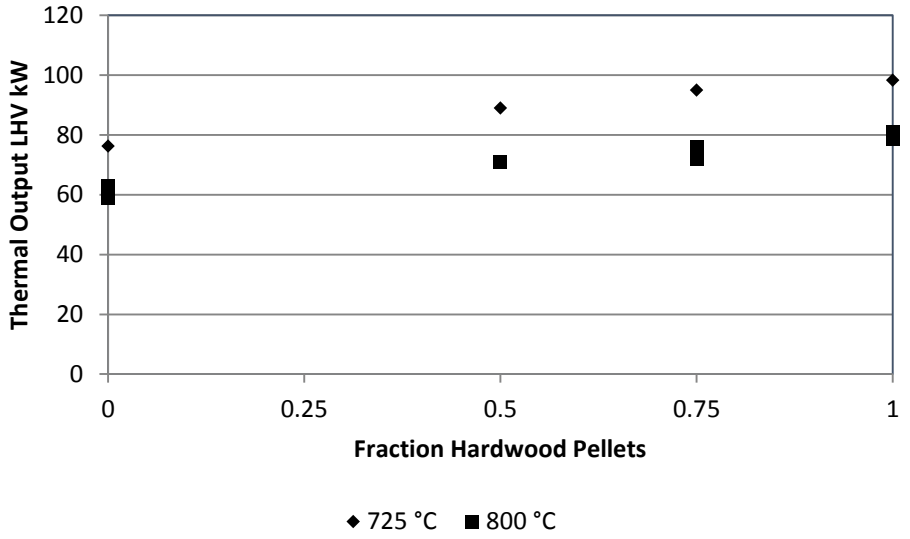
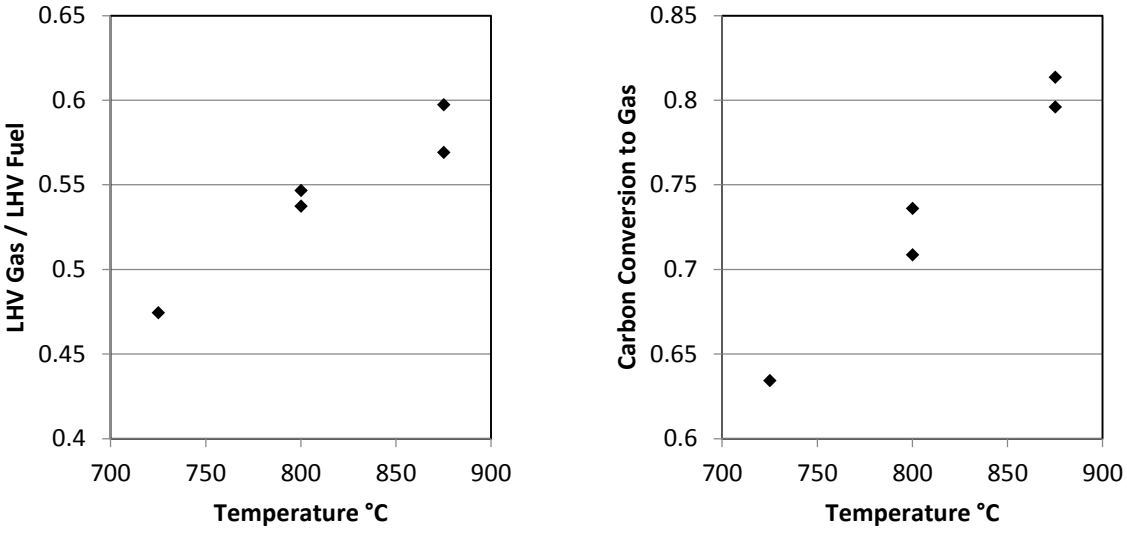


Figure 3.11 Gasifier thermal output in gas lower heating value

There were no problems gasifying the hardwood pellets at the 875°C temperature condition. Since data was collected at three temperature conditions it is possible to discern clearly how the gasification temperature increases the thermal efficiency along with carbon conversion of the gasification of the hardwood pellets (Figure 3.12).



(a) **(b)**

Figure 3.12 Effect of operating temperature on efficiency (a) and carbon conversion (b) for the hardwood pellets

3.4 Discussion

3.4.1 Consequences of co-gasifying hardwood pellets with RDF

Results indicate that temperature did not have a great influence on the heating value of the gas (Figure 3.9). However, temperature did have a significant effect on the carbon conversion and thermal efficiency. This is shown for the hardwood pellets in Figure 3.12.

For a constant air flow, less fuel is fed to the gasifier when the process is conducted at higher temperatures. This is because the equivalence ratio controls the gasifier temperature. When less fuel is fed to the gasifier the equivalence ratio is higher and the extent of combustion is greater, so the temperature is higher. The efficiency, in terms of the conversion of fuel heating value to gas heating value, rises with temperature, because a greater proportion of the fuel is converted to gas. The combustible fraction of the unconverted fuel is mostly carbon and the carbon conversion rises along with the efficiency. Since for any given fuel the equivalence ratio and gasification temperature are related, it is unclear if the higher temperature or the high equivalence ratio is most important for influencing the thermal efficiency and carbon conversion.

Steady state gasification of the RDF pellets at the highest temperature condition of 875°C was not possible due to the agglomeration of the bed material. Such agglomeration is caused by the

presence of silica and alkali metals which tend to form low melting silicates [27]. When the temperature is high enough, ash will begin to adhere to the surface of the bed material. Eventually the enlarged bed particles will begin to stick together. For mixtures of RDF and Hardwood Pellets fired at 875°C the agglomeration caused the loss of fluidization after about 60 minutes of operation.

Without application of some means to control agglomeration at temperatures above 800°C, co-gasifying the hardwood pellets with the RDF pellets lowers the maximum operating temperature for the mixtures. The efficiency of the gasification process increases with increasing temperature, so mixing the RDF pellets with the hardwood pellets limits the efficiency of the conversion of the hardwood pellets.

Char and ash from thermal conversion of virgin biomass are not considered hazardous waste and they may be used for liming or other forms of soil amendment [28, 29]. The solid residue from RDF gasification is classified as hazardous solid waste [30]. Co-gasifying RDF with hardwood pellets causes the char and ash from the hardwood pellets to be mixed with the char and ash from the RDF pellets. Once mixed the char and ash from biomass gasification become hazardous solid waste.

3.4.2 Independent Processes

Many of the results appear to be linearly related to the fraction of hardwood pellets in the feed. This is the case for the nitrogen, hydrogen, carbon dioxide, ethylene, and propylene concentrations in the raw gas. This is also the case for the feed rates and, consequently, the equivalence ratio. This suggests that the gasification of the different fuel pellets is independent of the surrounding fuel pellets.

The concentration of carbon monoxide at 725°C does not seem to be linearly related to the fraction of hardwood pellet in the feed. There are no duplicates for this set. It may be that there is slight interaction which affects the carbon monoxide concentration in the produced gas, or there may be some error in the measurements.

Results indicating independent decomposition of blended fuels during gasification have been noted elsewhere. Co-gasification of coal and wood has been found to yield gas compositions which vary linearly with the fraction of wood in the fuel blend [22]. Hydrogen and carbon monoxide concentrations in gases produced from mixtures of sewage sludge and bituminous coal and mixtures of lignite and bituminous coal have been found to be similar to linear combinations of the concentrations measured when individual components were gasified [31]. Substantial interactions

have also been found to occur between blended fuels during gasification. Interactions attributed to the catalytic effect of biomass ash components have been noted during the gasification of coal and biomass blends [32, 33]. Interactions attributed to the catalytic effect of inorganic materials have also been noted for blends of lignite and sewer sludge [31].

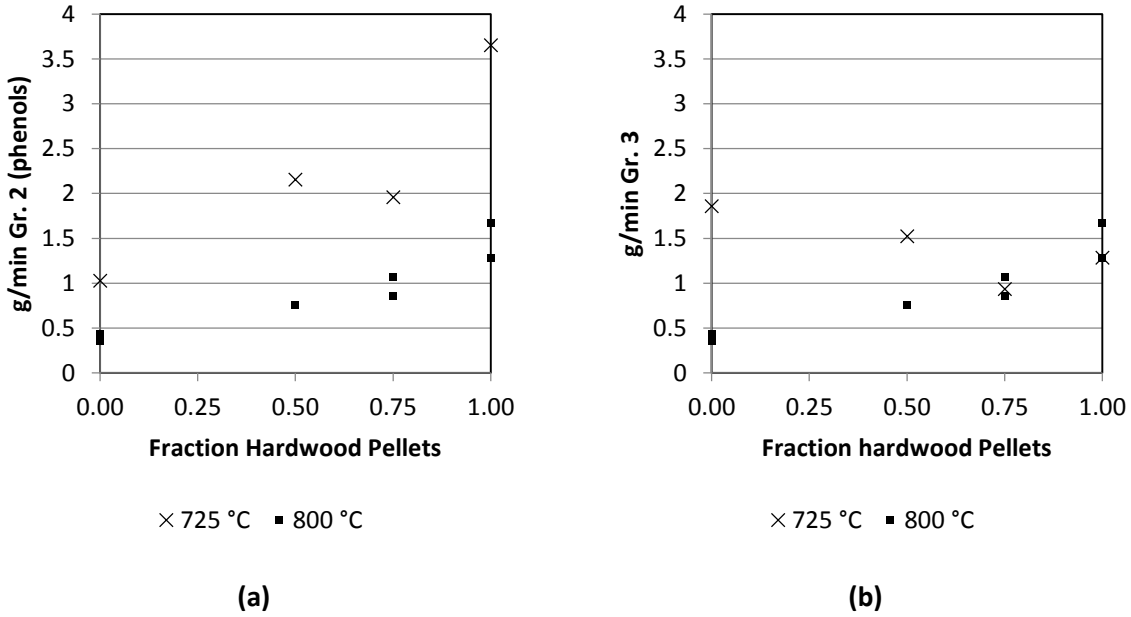
The RDF pellets used in this work contained large quantities of ash which might be capable of influencing the gasification of the hardwood pellets. No significant interactions between the two fuels are apparent in the results. Rather it appears that most of the results are explainable as a linear combination of the results from gasification experiments on the individual fuels. The fact that the ash from the RDF pellets does not seem to affect the gasification of the hardwood pellets indicates that most of the processes affecting the gasification process take place within the pellets. This could be confirmed by performing experiments on pellets produced with different ratios of sawdust and RDF or by performing gasification experiments on sawdust pelletized with different ratios of RDF ash.

3.4.3 Tar

The produced gases were heavily laden with tar. Figure 3.6 shows the variation in the concentration of tar in the produced gases. Gases produced at higher temperatures and with lower fractions of RDF in the feed contained less tar. Figure 3.7 shows the variation in the composition of the GC tars. Tar produced with greater fractions of RDF in the fuel has a much higher proportion of light tar compounds than tar produced with greater fractions of hardwood pellets in the feed. The compounds of Groups 2 and 3 make up a more significant part of the tar produced from hardwood pellets.

The light tar compounds which account for most of the weight of the GC tar from RDF gasification are not expected to have a major impact on combustion engine operation because they are too light to condense and foul engine components. Thus, concentrations of these compounds may be ignored when considering tar tolerances for combustion engines. The phenols of group 2 and heavier aromatics of group 3 are problematic for engine operation since they tend to condense. Figure 3.13 shows the mass flows of the problematic tar compounds in the raw gas. At 800°C the amount of group 2 and group 3 tar compounds increases with the amount of hardwood pellets in the feed. At 725°C, the amount of phenol appears to increase with the amount of hardwood pellets in the feed, though the mass flow of phenol declines slightly from the 50 % hardwood pellet condition to the 75 % pellet condition. At 725°C the amount of group 3 compounds declines with

increasing fraction of hardwood pellets. The data points for the 75 % hardwood pellets gasified at 725°C both seem lower than would be expected. Unfortunately this experimental condition was not duplicated so it is not possible to discern whether the measurements are in error.



(a) **(b)**

Figure 3.13 Mass flow of Gr.2 (phenols) tar (a) and Gr. 3 tar (b) compounds in the raw gas

Gases produced from RDF pellets contained more tar than gases produced from hardwood pellets but the tar from RDF gasification had a much higher proportion of volatile components than tar from hardwood gasification. Gasification of hardwood pellets tends to produce larger quantities of the most problematic tar compounds. All of the gases produced contained much more tar than an internal combustion engine can tolerate. Milne et al. [34] compiled a large set of producer gas specifications for a variety of applications. For internal combustion engines the concentration of tar must not exceed 100 mg/Nm^3, and some specifications are as low as 10 mg/Nm^3 [34].

Tar removal influences the composition of the cleaned gas. Physical separation will leave the gaseous components of the gas intact while removing the condensable organic compounds. Catalytic clean-up causes the composition of the gas to advance towards a thermodynamic equilibrium, which is dependent on elemental composition and temperature. The process of fluidized bed gasification is dominated by kinetics and the products of gasification are not in thermodynamic equilibrium. Real produced gases have lower hydrogen and carbon monoxide concentrations and higher carbon dioxide concentrations than equilibrium models predict [35]. Catalysis promotes equilibration of produced gases. Alkaline earth metal oxides like limestone and

dolomite have been widely employed for the catalytic destruction of biomass producer gas tars [36]. Heavy tars are most susceptible to destruction by alkaline earth metal oxides. Use of these materials requires more or less continuous catalyst make-up as these materials are susceptible to elutriation [37, 38] and carbon deposition [38]. Nickel based steam reforming catalysts have also been widely employed for the clean-up of biomass producer gas [39, 40, 41]. These catalysts are substantially more effective than alkaline earth metal oxides. They are capable of complete destruction of all heavy and light condensable organics as well as reforming of lighter gaseous alkanes and olefins and even methane reforming, and near equilibrium gas compositions are achievable [39, 40]. Nickel based catalysts suffer from accumulation of coke [42, 43] and require periodic regeneration [44]. Nickel catalysts are also susceptible to sulfur poisoning [45, 46, 47].

Ronkkonen et al. [48] studied a variety of precious metals supported on zirconia. Rhodium was found to have an activity similar to that of Nickel while the activity of palladium, iridium and platinum were found to be less than that of nickel. Rhodium catalysts have been found to resist sulfur poisoning [49]. Resistance to sulfur poisoning is particularly useful for application in a remote community since it is costly to obtain replacement materials.

Separation of tar is not an appropriate option for a fluidized bed gasifier located in a remote community although separation has been employed for downdraft gasifiers located in such communities [10]. Gases produced in fluidized bed gasifiers contain much more tar than gases produced in downdraft gasifiers [34], and separation would be inappropriate, because the filter material would have to be continuously turned over and large quantities of tar would require disposal. Thus, some form of high temperature catalytic reforming is necessary to avoid these problems. Alkaline earth metal catalysts would probably not be appropriate for an application in a remote community, because the catalyst would have to be continuously replaced. Catalytic destruction over a precious metal catalyst or a nickel catalyst if coking and sulfur poisoning were addressed, is probably the best option for a fluidized bed gasifier operating in a remote community. Use of such a catalyst would tend to cause the gas to approach a thermodynamic equilibrium, and it is the equilibrated compositions should be used when considering applications of the gases.

3.4.4 Equilibrium Compositions

Unisim™ was used to approximate the equilibrium composition of the gases produced from mixtures of hardwood and RDF pellets with tar accounted for as naphthalene. The raw gas compositions were compared to calculated equilibrium compositions in Figure 3.14 and Figure 3.15.

The most apparent differences between the actual gas composition and the predicted equilibrium gas compositions are the near exclusion of combustible components other than hydrogen and carbon monoxide and the reduced concentrations of non-combustible species. Reforming of tar and other non-equilibrium species causes an increase in the number of moles of gas. This along with the consumption of steam and carbon dioxide in the reforming of the larger molecules causes a reduction in the concentrations of non-combustible species in the predicted equilibrium gas compositions.

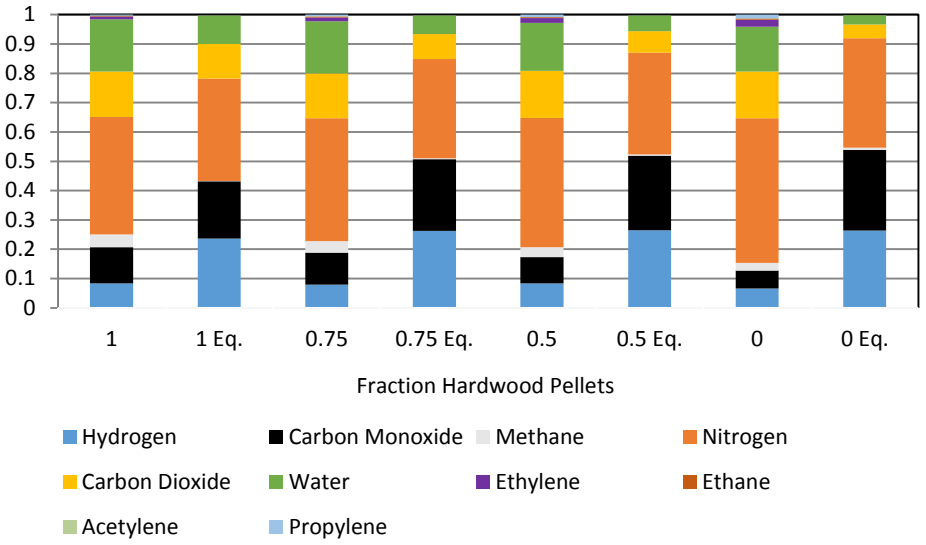


Figure 3.14 Comparison of raw gas compositions to calculated equilibrium (Eq.) composition at 750° C

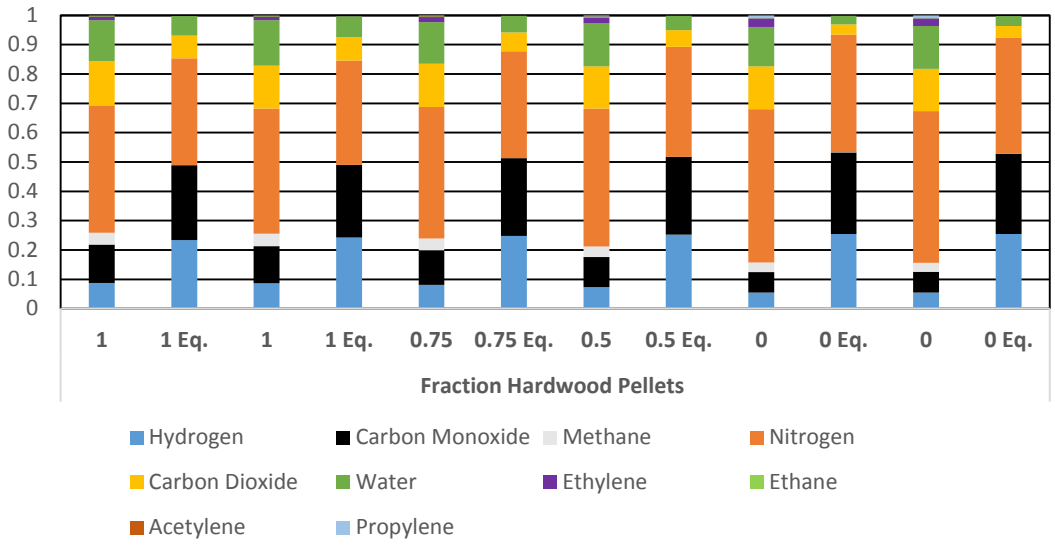


Figure 3.15 Comparison of raw gas compositions to calculated equilibrium (Eq.) composition at 800° C

3.4.5 Engine Operation

The producer gas properties which affect engine operation are the heating value, flame speed, ignition delay and knock tendency [50]. These properties depend on producer gas composition. Since producer gas composition varies with changes in the feed composition it is reasonable to expect that the heating value, flame speed, ignition delay and knock tendency vary with the feed composition as well.

The raw gases will require catalytic treatment to destroy tars before they can be used in a dual fuel engine. This means that the composition of the gases will change to more closely resemble the composition which would be in thermodynamic equilibrium at the catalytic reformer operating temperature. Unisim™ was used to determine the equilibrium compositions of the gases produced from mixtures of hardwood pellets and RDF assuming reformer temperatures of 725°C, 800°C, and 875°C. The resulting compositions are shown in Figure 3.16 and Figure 3.17. The most significant variation in the dry gas composition predicted for equilibrated gases is the decline in carbon dioxide with decreasing weight fraction of hardwood pellets in the fuel. There is also a slight increase in carbon monoxide concentrations at higher reformer temperatures. Generally the compositions of the dry gases are very similar regardless of fuel composition or reformer temperature.

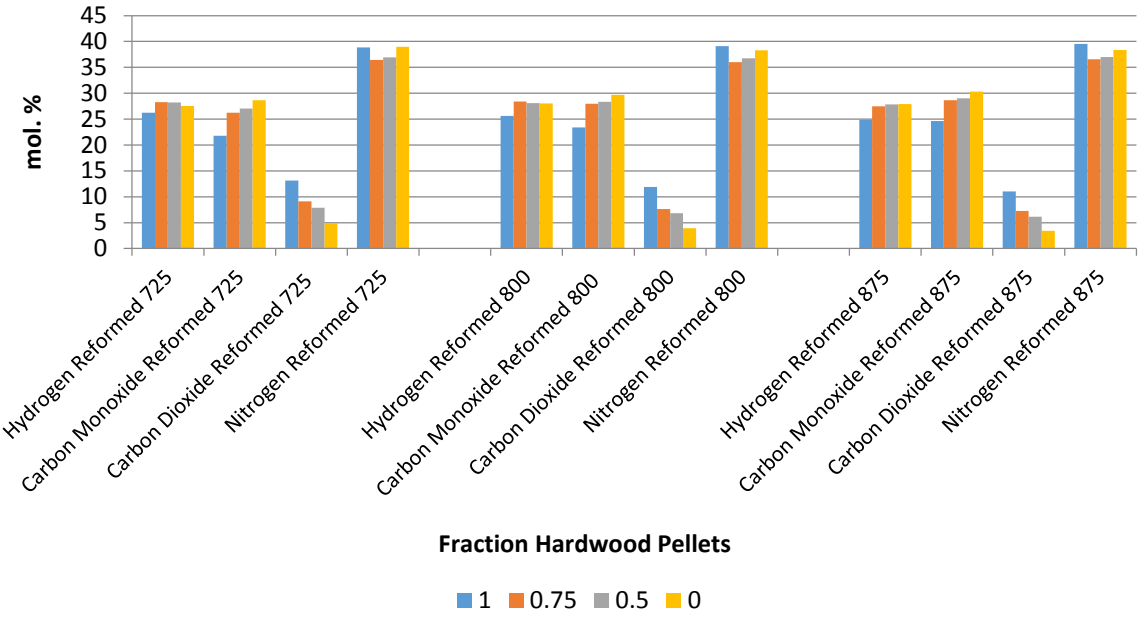


Figure 3.16 Equilibrated gas compositions of gases produced at 725°C and reformed at 725°C, 800°C, and 875°C

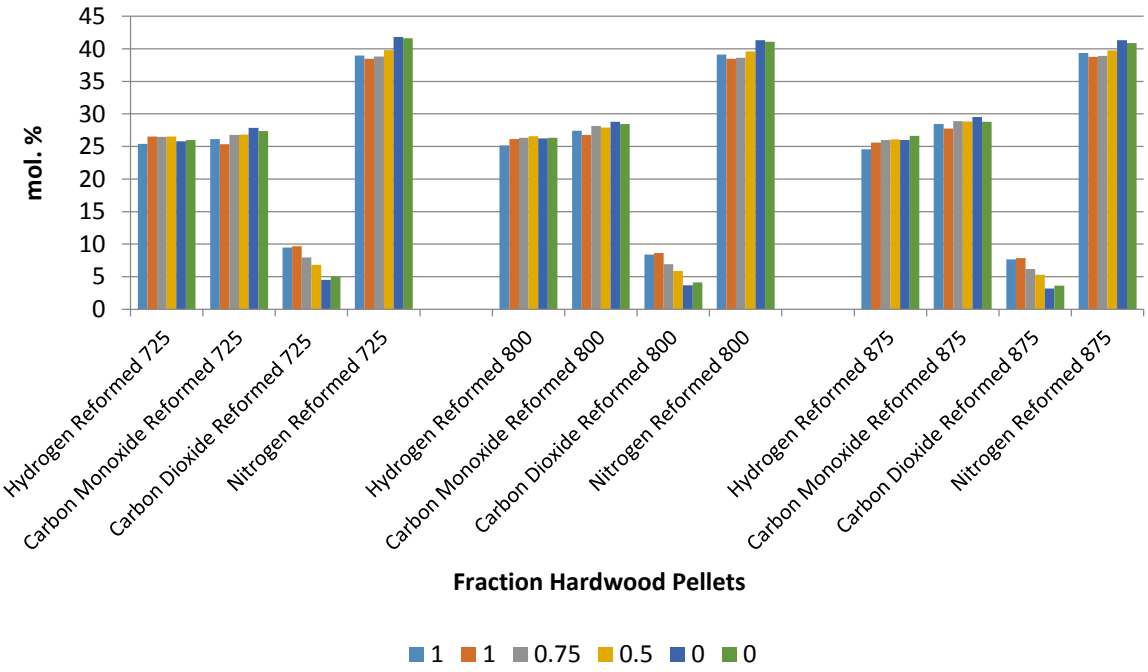


Figure 3.17 Equilibrated gas compositions of gases produced at 800°C and reformed at 725°C, 800°C, and 875°C

Of the gas properties which are likely to influence engine operation, heating value is the easiest to calculate from gas composition. The produced gases had very low heating values compared to conventional fuels and engine power de-ratings should be expected. Tinault et al. [51] predicted that an engine run on a low calorific value producer gas will suffer a 33 % power de-rating at full load compared to operation on a conventional liquid fuel. It might seem surprising that such a small power de-rating is predicted given the very low heating values of produced gases. The prediction results from comparison of the volumetric energy densities of stoichiometric fuel-air mixtures, termed the Engine Fuel Quality (EFQ), rather than comparison of the energy densities of the fuels.

Ramadhas et al. [9] investigated dual fuel operation of a 5.5 kW diesel engine operating in dual fuel using biomass derived gases with heating values similar to those found in Figure 3.9. It was found that operation on wood gas allowed for diesel replacement of up to 70 %, with engine power de-ratings of 40-50 %. This is a somewhat higher de-rating than a simple EFQ analysis would suggest.

Equilibrium compositions calculated for the gases produced from mixtures of hardwood pellets and RDF at 725°C, 800°C, and 875°C were used to calculate the EFQs of the various produced gases after high temperature catalytic reforming. The resulting EFQs are compared to the EFQ of diesel in Figure 3.18 and Figure 3.19. For calculation of the EFQ of diesel equivalent an H/C ratio of 1.8 and a lower heating value of 43 MJ/kg were assumed. All of the EFQs were close to 70 % of the EFQ of diesel. This suggests that at an equivalence ratio of 1 the predicted gas composition would have an energy density roughly 70 % that of the energy density of a diesel fuel-air mixture, so a power de-rating of approximately 30 % would be expected if a diesel engine was run on 100 % producer gas.

EFQs for the equilibrium composition are slightly higher than for a typical producer gas. This is because the combustible fraction of the equilibrium compositions is almost entirely hydrogen and carbon monoxide. These gases have very low stoichiometric requirements and thus yield high EFQs. Also, the conversion of tar, alkane and alkenes tends to reduce the nitrogen and carbon dioxide contents of the equilibrated producer gases. EFQs are slightly higher for gases produced from fuels containing higher proportions of RDF and for gases equilibrated at higher temperatures. This is because these gases tend to have higher carbon monoxide contents than gases produced with higher proportions of hardwood pellets and gases equilibrated at lower temperatures.

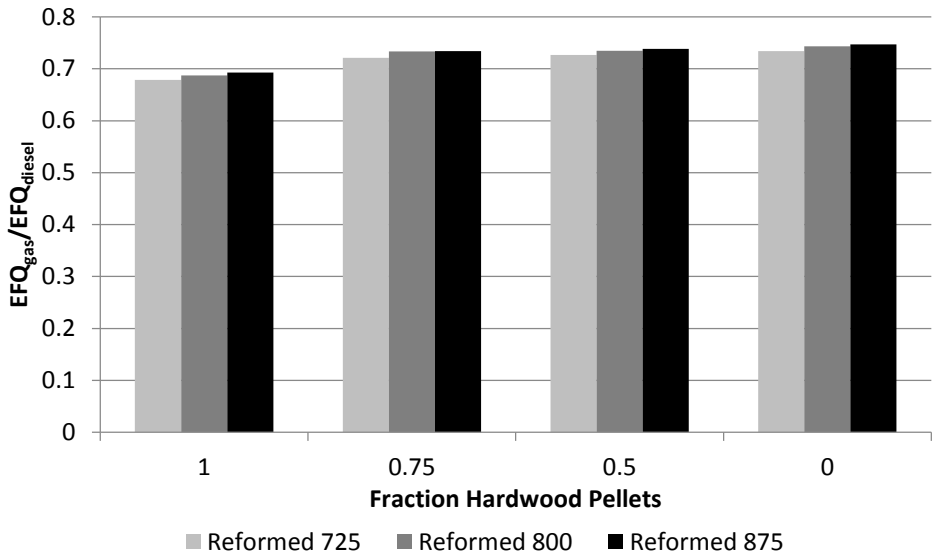


Figure 3.18 EFQ ratios for gases produced at 725°C and reformed at various temperatures

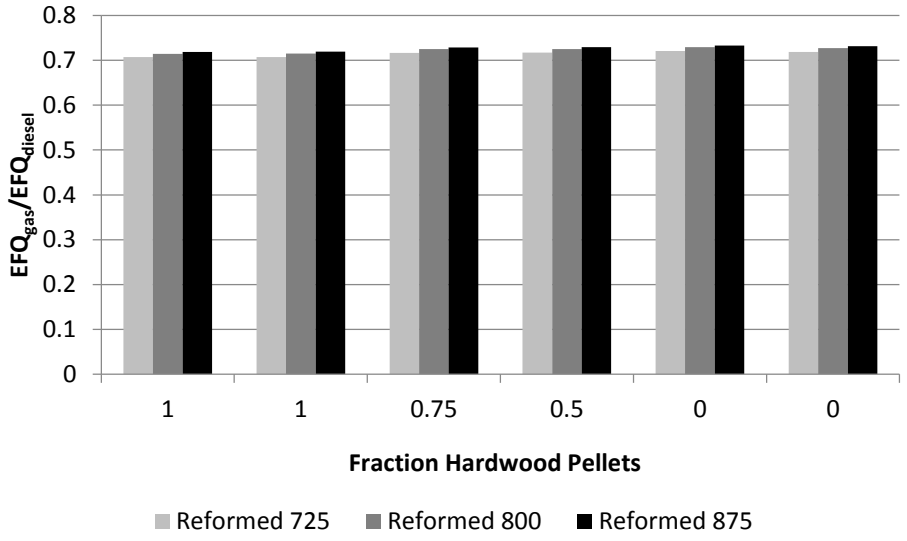


Figure 3.19 EFQ ratios gases produced at 800°C and reformed at various temperatures

EFQs may be used to compare the energy density of a producer gas-air mixture, but they do not provide any information about the combustion properties of the producer gas. Laminar flame speed and ignition delay are often used to characterize the combustion behavior of fuel air mixtures.

Along with the idea of EFQs, Tinault et al. [51] presented a two zone combustion model to predict changes in engine timing required for the use of alternative fuels. The model requires a reference flame speed. For a spark ignition engine, fuels with lower flame speeds require an advance in the

spark timing to compensate for the longer combustion duration. Serrano et al. [52] performed combustion experiments on a gas considered to be representative of biomass producer gas. The gas had a composition of 21 vol. %H_2, 24 vol. % CO, and 55 vol. % N_2. Under lean and stoichiometric conditions the gas had flame speeds ranging from 40-50 cm/s. These flame speeds are comparable to those of methane and isooctane. The blending of different fuels in the gasifier feed causes changes in the composition of the produced gas, and these changes affect the equilibrium composition of the gas. The equilibrium composition of the produced gas is the composition which will be approached during catalytic treatment of the gas. If these gases are to be used in diesel engines it would be helpful to know how their compositions affect the flame speed. This information could be used to anticipate how changes in gas composition resulting from addition of RDF would influence internal combustion operation.

It was not possible to find an empirical correlation relating producer gas flame speed to producer gas composition. This was also the case for ignition delay and methane number. The relationships between these properties and the composition of the gas are complex. Computer modelling is often used for investigation of these properties. Hernandez et al. [53] measured the laminar flame speed of producer gases with different compositions. Wise et al. [54] investigated the methane numbers of a wide variety of producer gas mixtures. Krejci et al. [55] studied the laminar flame speeds and ignition delays of various gas mixtures. In all these cases complex models were employed to explain how combustion properties vary with fuel composition. Such modelling could be employed in future studies to predict variations in the combustion properties of cleaned produced gases.

3.5 Conclusions

Air-blown fluidized bed co-gasification of mixtures of hardwood pellets and RDF at 725°C, 800°C, and 875°C has been investigated to promote the application of fluidized bed gasification technology to power generation in Canada's remote northern communities. No significant fuel interactions were noted and most results appeared to change proportionally with changes in the fraction of hardwood pellets in the feed. Differences in the heating values of the produced gases were slight. After high temperature catalytic clean-up, all of the produced gases should have EFQs of approximately 0.7 suggesting that engine operation on the produced gases should suffer an approximately 30 % power de-rating. The RDF pellets used for this work were not appropriate for mixing with woody biomass. They lowered the maximum operating temperature of the gasifier which lowers the carbon conversion. The reduction in carbon conversion reduces the thermal

efficiency of the process while the unconverted char from the hardwood pellets is contaminated with the solid residue from the RDF gasification. If biomass and RDF are to be co-gasified in remote community applications then feedstock sorting or treating strategies will have to be employed to ensure minimal levels of agglomeration causing materials in the RDF fraction. Further work needs to be done to support the application of fluidized bed gasification to power generation in remote communities. The catalytic cleaning of the raw gases needs to be investigated, so a suitable catalyst and reformer configuration may be chosen, and kinetic modelling or combustion experiments need to be performed to understand how the changes in gas composition affect clean produced gas properties relevant to engine operation.

References

[1] Government of Canada, "Status of Remote/Off grid Communities in Canada," Government of Canada, 2011.

[2] M. Arriaga, C. A. Canizares and M. Kazerani, "Northern Lights," *IEEE Power and Energy Magazine,* pp. 50-59, 17 June 2014.

[3] M. Arriaga, C. A. Canizares and M. Kazerani, "Renewable Energy Alternative for Remote Communities in Northern Ontario, Canada," *Transactions on sustainable energy,* 2012.

[4] M. Asadullah, "Barriers of commercial power generation using biomass gasification gas: A review," *Renewable and Sustainable Energy Reviws,* vol. 29, pp. 201-215, 2014.

[5] A. Verma and G. Weisgerber, "Wood Gasification for Gas and Power," in *Thermal Conversion of solid Wastes and Biomass*, Washington DC, American Chemical Society, 1980, pp. 379-394.

[6] N. Tippayawong, C. Chaichana, A. Promwungkwa and P. Rekkriangkrai, "Investigation of a Small Biomass Gasifier-engine Sytem Operation and Its Application to Water Pumping in Rural Thailand," *Energy Sources Part A,* vol. 35, pp. 476-486, 2013.

[7] B. Williams, D. McIlveen-Wright and S. Rezvani, "Gasification of Waste Medium Density Fibreboard as a Route to Power Generation," *Dev. Chem. Eng. Mineral Process.,* vol. 11, pp. 55-66, 2003.

[8] R. Uma, T. Kandpal and V. Kishore, "Emission characteristics of an electricity generation system in diesel alone and dual fuel modes," *Biomass and Bioenergy,* vol. 27, pp. 195-203, 2004.

[9] A. Ramhadas, S. Jayaraj and C. Muraleedharan, "Power generation using coir-pith and wood derived producer gas," *Fuel Processing Technology,* vol. 87, pp. 849-853, 2006.

[10] S. Ghosh, T. K. Das and T. Jash, "Sustainability of decentralized woodfuel-based power plant: an experience in India," *Energy,* vol. 29, pp. 155-166, 2004.

[11] R. Zagozewski, I. Judd-Henrey, S. Nilson and L. Bharadwaj, "Perspectives on past and present

waste disposal practices: a community based participatory research project in three Saskachewan First Nations," *Environmental Health Insights,* vol. 5, pp. 9-20, 2011.

[12] J. Smith, "Ottawa sends $2M in bottled water to First Nation," *The Star,* 14 February 2014.

[13] P. Bacaicoa-Garcia, J. Mastral, J. Ceamanos, C. Berrueco and S. Serrano, "Gasification of biomass/high density polyethylene mixtures in a downdraft gasifier," *Bioresource Technology,* vol. 99, pp. 5485-5491, 2008.

[14] M. L. Matellone, L. Zaccariello and U. Arena, "Co-gasification of coal, plastic waste and wood in a bubbling fluidized bed reactor," *Fuel,* vol. 89, pp. 2991-3000, 2010.

[15] R. A. Mogadam, S. Yusup, Y. Uemura, B. L. F. Chin, H. L. Lam and A. Al Shoaibi, "Syngas production from palm kernal shell and polyethylene waste blend in fluidized bed catalytic steam co-gasification process," *Energy ,* vol. 75, pp. 40-44, 2014.

[16] P. Brachi, R. Chirone, F. Miccio, M. Miccio, A. Picarelli and G. Ruoppolo, "Fluidized bed co-gasification of biomass and polymeric wastes for a flexible end-use syngas: Focus on bio-methanol," *Fuel,* vol. 128, pp. 88-98, 2014.

[17] Y. Pan, E. Velo, X. Roca, J. Manya and L. Puigjaner, "Fluidized-bed co-gasifocation of residual biomass/poor coal blends for fuel gas production," *Fuel,* vol. 79, pp. 1317-1326, 2000.

[18] T. McLendon, A. Lui, R. Pineault, S. Beer and S. Richardson, "High-pressure co-gasification of coal and biomass in a fluidized bed," *Biomass and Bioenergy,* vol. 26, pp. 377-388, 2004.

[19] P. E. Campbell, R. H. Evans, J. T. McMullan and B. C. Williams, "The potential for adding plastic waste fuel at a coal gasification power plant," *Waste Manage Res,* vol. 19, pp. 526-532, 2001.

[20] P. Straka and O. Bicakova, "Hydrogen rich gas as a product of two-stage co-gasification of lignite/waste plastic mixtures," *International Journal of Hydrogen Energy,* vol. 39, pp. 10987-10995, 2014.

[21] P. Straka and Z. Bucko, "Co-gasification of a lignite/waste-tyre mixture in a moving bed," *Fuel Processing Technology,* vol. 90, pp. 1202-1206, 2009.

[22] I. Aiger, C. Pfiefer and H. Hofbauer, "Co-gasification of coal and wood in a dual fluidized bed reactor," *Fuel,* vol. 90, pp. 2404-2412, 2011.

[23] H.-J. Song, J. Lee, A. Gaur, J.-J. Park and J.-W. Park, "Production of gaseous fuel from refuse plastic fuel via co-pyrolysis using low-quality coal and catalytic steam gasification," *J Mater Cycles Waste Manag ,* vol. 12, pp. 295-301, 2010.

[24] L.-Q. Wang and Z. S. Chen, "Gas generation by co-gasification of biomass and coal in an autothermal fluidized bed gasifier," *Applied Thermal Engneering,* vol. 59, pp. 278-282, 2013.

[25] S. Kern, C. Pfeifer and H. Hofbauer, "Synergetic utilization of Renewable Fuels," *APCBEE Procedia,* vol. 1, pp. 136-140, 2012.

[26] T. Robinson, B. Bronson, P. Gogolek and P. Mehrani, "Sample preparation for thermo-gravimetric determination and thermo-gravimetric characterization of refuse derived fuel," *Submitted to Waste Management,* vol. tba, p. tba, 2015.

[27] M. Bartels, W. Lin, J. Nijenhuis, F. Kapteijin and J. Ruud van Ommen, "Agglomeration in fluidized beds at high temperatures: Mechanisms, detection and prevention," *Progress in energy and Combustion Science,* vol. 34, pp. 633-666, 2008.

[28] Albeta Environment, July 2002. [Online]. Available: environment.gov.ab.ca/info/library/6680.pdf. [Accessed 10 July 2015].

[29] V. Hansen, D. Muller-Stover, J. Ahrenfeldt, J. K. Holm, U. B. Henriksen and H. Hauggaard-Nielsen, "Gasification biochar as a valuable by-product for carbon sequestration and soil amendment," *Biomass and Bioenergy,* vol. 72, pp. 300-308, 2015.

[30] EPA, "United States Environmental Protection Agency," [Online]. Available: www.epa.gov/osw/hazard/wastetypes/wasteid/pdfs/rcra2614b-ref.pdf. [Accessed 10 July 2015].

[31] G. Garcia, J. Arauzo, A. Gonzalo, J. Sanchez and J. Abrego, "Influence of feedstock composition in fluidized bed co-gasification of mixtures of lignite, bitumous coal and sewage sludge," *Chemical Engineering Journal,* vol. 222, pp. 345-352, 2013.

[32] N. Howaniac and A. Smolinski, "Effect of fuel blend composition on the efficiency of hydrogen-rich gas production in co-gasification of coal and biomass," *Fuel,* vol. 128, pp. 442-450, 2014.

[33] W. L. Saw and P. S. Pang, "Co-gasification of blended lignite and wood pellets in a 100kW dual fluidised bed steam gasifier: The influence of lignite ratio on producer gas compositionand tar content," *Fuel ,* vol. 112, pp. 117-124, 2013.

[34] T. Milne, R. Evans and N. Abatzoglou, "Biomass Gasifier "Tars" Their Nature, Formation, and Conversion," National Renewable Energy Laboratory, Golden, Colorado, 1998.

[35] A. Barea-Gomez and B. Leckner, "Estimation of gas composition and char conversion in a fluidized bed biomass gasifier," *Fuel,* vol. 107, pp. 419-431, 2013.

[36] S. Anis and Z. Zainal, "Tar reduction methods in biomass producer gas via mechanical, catalytic and thermal methods: A review," *Renewable and Sustainable Energy Reviews,* vol. 15, pp. 2355-2377, 2011.

[37] W. Torres, S. S. Pansare and J. G. J. Goodwin, "Hot Gas Removal of Tars Ammonia and Hydrogen Sulfide from Biomass Gasification Gas," *Catalysis Reviews ,* vol. 49, pp. 407-456, 2007.

[38] V. Vassilatos, G. Taralas, K. Sjostrom and E. Bjornbom, "Catalytic Cracking of Tar in Biomass Pyrolysis Gas in the Presence of Calcined Dolomite," *The Canadian Journal of Chemical Engineering ,* vol. 70, pp. 1008-1013, 1992.

[39] P. A. Simell and J. -s. Bredenberg, "Catalytic purification of tarry fuel gas," *Fuel ,* vol. 69, pp. 1219-1225, 1990.

[40] P. Simell, E. Kurkela, P. Stahlberg and J. Hepola, "Catalytic hot gas cleaning of gasification gas," *Catalysis Today,* vol. 27, pp. 55-62, 1996.

[41] N. Kaisalo, J. Kihlman, I. Hannula and P. Simell, "Reforming solutions for biomass-derived gasification gas - Experimental results and concept assessment," *fuel ,* vol. 147, pp. 208-220, 2015.

[42] D. Sutton, B. Kelleher and J. R. Ross, "Review of literature on catalysts for biomass gasification,"

Fuel Processing Technology, vol. 73, pp. 155-173, 2001.

[43] D. Bangala, N. Abatzoglou and E. Chornet, "Steam Reforming of Naphthalene on Ni-Cr/Al2O3 Catalysts Doped with MgO, TiO2, and La2O3," *AIChE,* vol. 44, no. 4, pp. 927-936, 1998.

[44] X. Yang, S. Xu, Z. Chen and J. Liu, "Improved nickel-olivine catalysts with high coking resistance and regeneration ability for the steam reforming of benzene," *Reac Kinet Mech Cat ,* vol. 108, pp. 459-472, 2013.

[45] J. Hepola and P. Simell, "Sulphur poisoning of nickel-based hot gas cleaning catalysts in the synthetic gasification gas I. Effect of different process parameters," *Applied Catalysis B: Environmental ,* vol. 14, pp. 287-303, 1997.

[46] J. Koningen and K. Sjostrom, "Sulfur-Deactivated Steam Reforming of Gasified Biomass," *Ind. Eng. Chem. Res. ,* vol. 37, pp. 341-346, 1998.

[47] K. Sato and K. Fujimoto, "Development of new nickel based catalyst for tar reforming with superior resistence to sulfur poisoning and coking in biomass gasification," *Catalysis Communication ,* vol. 8, pp. 1697-1701, 2007.

[48] H. Ronkknonen, P. Simell, M. Reinikainen, O. Krause and M. V. Niemela, "Catalytic clean-up of gasification gas with precious metal catalysts - A novel catalytic reformer development," *Fuel,* vol. 89, pp. 3272-3277, 2010.

[49] H. Ronkkonen, P. Simell, M. Reinikainen, M. Niemela and O. Krause, "Precious metal catalysts in the clean-up of biomass gasification gas Part 1: Monometallic catalysts and their impact on gasification gas composition," *Fuel Processing Technology,* vol. 92, pp. 1457-1465, 2011.

[50] J. D. Martinez, K. Mahkamov, R. V. Andrade and E. E. S. Lora, "Syngas production in downdraft biomass gasifiers and its application using internal combustion engines," *Renewable Energy ,* vol. 38, pp. 1-9, 2012.

[51] F. V. Tinaut, A. Melgar, A. Horrillo and A. de la Rosa, "Method for predicting the performance of an internal combustion engine fuelled by producer gas and other low heating value gases," *Fuel Processing Technology,* vol. 87, pp. 135-142, 2006.

[52] C. Serrano, J. Hernandez, C. Mandilas, C. Sheppard and R. Woolley, "Laminar burning velocity behavior of biomass gasification-derived producer gas," *International Journal of Hydrogen Energy,* vol. 33, pp. 851-862, 2008.

[53] J. J. Hernandez, M. Lapuerta and C. Serrano, "Estimation of the laminar flame speed of producer gas from biomass gasification," *Energy & Fuels,* vol. 19, pp. 2172-2178, 2005.

[54] D. M. Wise, D. B. Olsen and K. Myoungjin, "Characterization of methane number for producer gas blends," in *Proceedings of the ASME 2013 Internal Combustion Engine Division Fall Technical Conference*, Dearborn, Michigan, 2013.

[55] M. C. Krekci, O. Mathieu, A. J. Vissotski, S. Ravi, T. G. Sikes, E. L. Petersen, A. Kermones, W. Metcalfe and H. J. Curran, "Laminar Flame Speed and Ignition Delay Time Data for the kinetic modeling of Hydrogen and Syngas Fuel Blends," *Journal of Engineering for Gas Turbines and Power,* vol. 135, pp. 021503-1-021503-7, 2013.

Chapter 4 Comparison of the air-blown bubbling fluidized bed gasification of hardwood and hardwood-PET pellets

*T. Robinson[1], B. Bronson[2], P. Gogolek[2], P. Mehrani[1]**

[1]Department of Chemical and Biological Engineering, University of Ottawa, Ottawa, Ontario, K1N 6N5 Canada

[2]Natural Resources Canada, CanmetENERGY, 1 Haanel Drive, Ottawa, Ontario, K1A 1M1, Canada

Abstract

Air-blown bubbling fluidized bed gasification of hardwood pellets and hardwood-PET (polyethylene terephthalate) pellets was conducted at 725°C, 800°C, and 875°C. Gasification of mixtures of hardwood and PET pellets was attempted; however, rapid formation of coke above the fluidized bed prevented steady state operation of the gasifier. Coking was prevented when hardwood and PET were formed into composite hardwood-PET pellets. The performance of hardwood pellets was better than hardwood-PET pellets. Tar concentrations were lower, heating values, thermal outputs, and efficiencies tended to be higher for hardwood pellets than hardwood-PET pellets. The addition of secondary air above the fluidized bed was explored as a means of reducing the tar content of the produced gases. The influence of the produced gas tar concentrations on down-stream tar removal units was considered.

Keywords: Biomass co-gasification, bed agglomeration, Bubbling fluidized bed gasifier, Waste to energy (WTE), Polyethylene terephthalate (PET) gasification

4.1 Introduction

4.1.1 Remote Communities

The provision of electrical power to small off-grid remote northern communities in Canada is problematic. These communities are too remote to be cost-effectively connected to the North American power grid, so power is mostly supplied using diesel engines [1]. The remoteness of these communities makes diesel fuel expensive, and, consequently, electricity is very expensive with the average un-subsidized price of diesel generated electricity being 1.3 $/kWh [2].

The high cost of electricity in remote northern communities makes exploration of alternative fuels attractive. The high cost of transporting diesel might make the use of locally available biomass viable since the cost of transportation may be avoided. Dual fuel operation using combustible gases produced from wood has been found to be a promising means of generating power in remote communities [3, 4]. Remote northern communities might also be able to extract energy from refuse.

Co-gasification of biomass and refuse is attractive since remote communities have limited waste management capabilities. The authors have previously studied the bubbling fluidized bed co-gasification of biomass and a commercially available refuse derived fuel (RDF) [5]. It was found that the commercially available RDF tended to cause agglomeration of the bed material at temperatures above 800°C. This limited operation of the gasifier to a temperature range which was not optimal for conversion of biomass. Agglomeration is caused by the presence of silica and alkali metals, which are present in the RDF since it is manufactured from mixed waste. These materials are present despite the intervention of a sophisticated, large scale, commercial process, which seeks to deliver a high quality fuel. Remote northern communities do not have access to the economy of scale required for the implementation of such a process so any mixed waste derived fuel manufactured in a remote northern community would certainly be of a lower quality than commercially produced RDF.

A more appropriate option for a remote community might be to target certain waste items or materials for separation within households. Non-biodegradable plastic waste such as water bottles and plastic food containers could be diverted from the community landfill. Co-gasification of biomass and plastic in a remote community might be feasible if clean plastic materials were source-separated and subjected to minimal processing. In order to understand the gasification

performance of biomass and a sorted plastic stream gasification of wood pellets and polyethylene terephthalate (PET) was investigated in this work.

4.1.2 Co-gasification of biomass and plastic

Several studies on the co-gasification of biomass and plastic exist. Pinto et al. [6] steam co-gasified polyethylene and wood waste in a laboratory scale reactor. Baricoa et al. [7] studied the addition of high density polyethylene to wood chips in a downdraft gasifier coupled to an internal combustion engine. Ruoppolo et al. [8] compared the air-blown steam gasification of wood pellets, pellets composed of 20 wt. % polyethylene and 80 wt. % wood and olive husks. Moghadam et al. [9] studied the steam co-gasification of palm kernel shell and polyethylene in a fluidized bed reactor. Brachi et al. [10] investigated the steam-oxygen enriched air fluidized bed gasification of pellets made from olive husk, olive husk and polyethylene terephthalate (PET), and olive husk and waste tire. Narobe et al. [11] conducted dual fuel fluidized bed experiments using polyethylene and wood. Lopez et al. [12] investigated the co-firing of polyethylene and pine residue in a conical spouted bed steam gasifier.

Differing motivations exist for the gasification of biomass and plastic materials. Displacing fossil fuel with a carbon neutral energy source is the clearest motivation for the gasification of biomass. Globally, there is much concern about the release of greenhouse gases from the use of fossil fuels, and much research has been conducted on the extraction of energy from biomass as a means of reducing these emissions. On the other hand, reducing the amount of material sent to landfill is the clearest motivation for the gasification of plastic materials [13, 14, 15, 16]. However, energy derived from plastic materials is not carbon neutral. If the goal of gasifying biomass is to reduce emissions of fossil carbon to the atmosphere, then co-gasification with plastic is counter-productive, since the fossil carbon in the plastic could be interred in a landfill, where, due to its non-biodegradability, it would be sequestered. If the goal of gasifying plastic is to reduce the volume of material sent to landfill then mixing biomass with the plastic may be counter-productive since biomass tends to yield more ash and more char than most plastics [9]. Additionally, high quality biomass such as virgin wood is not classified as waste material for the purposes of regulation [17, 18]. When virgin wood is mixed with waste the mixture becomes waste and this classification complicates utilization of the material since the disposal of waste is heavily regulated.

This aside, benefits have been realized from the co-gasification of biomass and plastic. During steam gasification, increasing the fraction of plastic in a biomass-plastic feed has been found to increase

the conversion of the fuel to gas [9], since addition of plastic reduces the production of char and ash. Also, co-gasification of biomass and plastics has been conducted to overcome difficulties with the seasonal availability of biomass [8, 10], overcome difficulties encountered when plastic is fired alone [6, 8], modify the composition of the produced gas [8], and allow plastic to be fired in a downdraft gasifier [7]. Though a large body of work exists on the gasification of plastics and the co-gasification of biomass and plastics, most of that work focuses on polyethylene. Only a few references could be found to the gasification of PET.

Matsunami et al. [19] investigated the use of PET in a simulated solar gasification process. Gil et al. [20] investigated the CO_2 gasification of char produced from PET. Kannan et al. [21] simulated the co-gasification of polyethylene and polyethylene terephthalate. The use of PET in plastic bottles and the problems associated with disposal of those bottles is a motivation for the study of PET gasification [19]. The paucity of literature concerning the gasification of PET may be related to recycling of plastic bottles. The use of PET bottles for packaging of drinking water, soda, and other beverages has caused issues with disposal, but these problems are being overcome by significant demand for used PET bottles [22]. Problems providing drinking water to remote communities have been overcome, in the short term, by importing bottled water, which causes an accumulation of bottles in community landfills [23]. Normally it would not make sense to consider thermal conversion of plastic when there is demand for the unconverted material. However, remote communities are too far from recycling markets to make recycling of plastic bottles economical.

The use of local biomass resources to produce electrical power via fluidized bed gasification and dual fuel engine operation has been found to be a promising alternative for remote northern communities [4]. Thus, the air blown fluidized bed co-gasification of hardwood and PET was investigated in this work to determine the feasibility of incorporating polymeric waste such as PET into biomass based power generation systems based on dual fuel operation of diesel engines.

4.2 Materials and Methods

Commercial hardwood pellets were used to represent biomass while polyethylene terephthalate was used to represent plastic. The PET was obtained from a recycled plastics supplier. It was scrap material from the production of food containers. Experiments were conducted using hardwood pellets, PET pellets, and hardwood-PET composite pellets. All pellets had diameters of 6 mm (1/4 inch). Hardwood pellets were used as received while the PET and the hardwood-PET pellets were manufactured using a California Pellet Mill. The PET pellets were produced by feeding the PET to

the pellet mill without any binders or pre-treatment. Hardwood-PET composite pellets were made by mixing hardwood and PET pellet at a ratio of 50:50 by mass. Then the mixture was ground using a knife-mill equipped with a 6 mm screen. Batches of 10 kg of the ground mixture were placed in a cement mixer which was used to mix 500 g of cornstarch (binder) and 500 g of water into the hardwood and PET. The material which resulted from this process was then pelletized in the pellet mill. Table 4.1 contains the results of proximate and elemental analysis on the two different types of pellets.

Table 4.1 Fuel proximate, elemental and calorific analysis

	Hardwood Pellet	**Hardwood-PET Pellet**	**Analysis Method**
Moisture (wt. %)	6.18	5.12	ASTM D7582
Volatiles (wt. %)	78.98	84.76	ISO 562
Fixed Carbon (wt. %)	14.43	9.88	ASTM D7582
Ash (wt. %)	0.41	0.24	ASTM D7582
Carbon (wt. %)	46.5	52.5	ASTM D5291
Hydrogen (wt. %)	5.54	4.95	ASTM D5291
Oxygen (wt. %)	41.4	37.2	by difference
Gross calorific value (MJ/kg)	18.41	19.96	ISO 1928

Pellets were gasified in a 0.15 m internal diameter and 4.5 m tall bubbling fluidized bed located at NRCan CanmetENERGY (Ottawa, ON). See Figure 3.1 in Chapter 3 for a schematic diagram of the fluidization system. 12 kg of synthetic olivine sand with a Sauter mean diameter of 600 μm was used as the bed material. For all experiments the bed was fluidized with 0.0038 kg/s (175 SLPM) of air metered by a mass flow controller. Experiments were conducted at nominal average bed temperatures of 725°C, 800°C, and 875°C. The feed flow rate was used to control the bed temperature. Bed temperatures were measured by three thermocouples located at 0.15 m intervals in the bed and the feed flow rate was controlled by modulating the speed of a conveyor belt which was used to drain a vibrating fuel hopper.

Heated pumps were used to continuously draw 0.01 m^3/min of raw gas from the gasifier. This stream was conditioned by removal of particles, tar, and moisture. Two micro-GC columns, each equipped with a thermal conductivity detector, were used for analysis of nitrogen, carbon dioxide, carbon monoxide, hydrogen, acetylene, propylene, ethane and ethylene. Samples from the

conditioned stream were drawn and analysed every four minutes. Averages of at least ten consecutive gas samples were used when performing analysis.

Tar measurements were made by stripping gas samples in a three stage column filled with isopropanol. The solutions from this column were subjected to Karl-Fischer analysis, gas chromatography, and evaporation, to determine moisture content, GC tar, and gravimetric tar, respectively.

4.3 Results and Discussion

4.3.1 Coking

Attempts were made to gasify mixtures of PET pellets and hardwood pellets with mass ratios of 90:10 and 50:50; however, it was not possible to achieve steady state operation. After 45-90 min of operation, it was not possible to control the bed temperature by manipulating the fuel feed rate. When the gasifier was opened for examination after these experiments in was found to be plugged with coke in the region where the feed arm enters the bed and it could be seen that the coke had been preventing the gasifier feed from entering the bed. To overcome this operational difficulty, PET and hardwood were transformed into composite pellets containing approximately 50:50 PET to hardwood by mass. This case did not result in any coking and thus the pellets were successfully gasified at 725°C, 800°C, and 875°C.

4.3.2 Raw gas composition

Compositions of the raw produced gases from hardwood and hardwood-PET pellets are presented in Table 4.2. Gases produced from hardwood pellets had greater concentrations of hydrogen and water than gases produced from hardwood-PET pellets. Gases produced from hardwood-PET pellets tend to have higher concentrations of carbon dioxide, carbon monoxide, and C2, C3-hydrocarbons than gases produced from hardwood pellets.

Table 4.2 Raw gas composition

	Hardwood Pellets			Hardwood-PET pellets				
	Temperature °C							
vol. %	**725**	**800**	**875**	**725**	**800**	**800**	**875**	**875**
Nitrogen	41.97	45.75	52.97	46.15	47.11	48.50	53.11	53.90
Water	18.52	14.24	12.86	15.14	15.99	12.98	13.35	11.86
Carbon Dioxide	15.08	14.87	14.92	17.12	16.27	17.37	17.02	16.65
Carbon Monoxide	11.37	11.82	9.41	12.69	10.84	11.33	8.90	9.66
Methane	3.79	3.68	3.12	2.99	2.83	2.96	2.63	2.73
Hydrogen	7.88	8.09	5.92	4.34	5.21	5.45	3.86	4.14
Ethylene	0.84	1.21	0.86	1.05	1.40	1.10	0.93	0.91
Propylene	0.27	0.08	0.03	0.21	0.10	0.05	0.03	0.01
Ethane	0.24	0.18	0.08	0.20	0.14	0.15	0.08	0.06
Acetylene	0.05	0.08	0.05	0.13	0.11	0.12	0.11	0.11

4.3.3 Tar Content

For convenience measured tar concentration data has been divided into 5 groups as shown in Table 4.3. Group 1 contains light non-oxygenated tar compounds, Group 2 contains phenolic compounds, Group 3 contains naphthalene and similar compounds, and Group 4 contains polycyclic aromatic hydrocarbons from fluorene to coronene. Group 5 is an estimate of the amount of gravimetric tar in the raw gases. Gravimetric tar is composed of compounds which are too heavy for gas chromatography. Group 1 tar compounds do not cause concern because they are too light to form solid deposits. Group 4 compounds make up only a very small fraction of the tar. These compounds are heavy enough to form deposits, but their concentration is low, so they are not as important as the group 2 and group 3 tar compounds. Groups 2, 3, and 5 are most likely to be problematic because they make up a substantial portion of the tar and, in the case of phenols because they are corrosive.

Table 4.3 Components of the different four groups of tar

Group 1	Group 2	Group 3	Group 4	Group 5
benzene	phenol	indene	fluorene	gravimetric
toluene	o-cresol	naphthalene	phenanthrene	
ethylbenzene	m and p-cresol	2-methylnaphthelene	anthracene	
xylene1		1-methylnaphthalene	fluoranthene	
xylene2		biphenyl	pyrene	
styrene		acenaphthylene	benz(a)anthracene	
o-xylene		acenaphthene	chrysene	
			benzo(b)fluoranthene	
			benzo(k)fluoranthene	
			benzo(e)pyrene	
			benzo(a)pyrene	
			perylene	
			Indeno(123-cd)pyrene	
			Dibenz(a,h)anthracene	
			Benzo(ghi)perylene	
			coronene	

Gases produced from hardwood-PET pellets contained far greater concentrations of group 1 compounds than gases produced from hardwood pellets (Figure 4.1). In all cases, the concentration of group 1 compounds in the gases produced from hardwood-PET pellets was higher than the total tar concentration of all the gases produced from hardwood pellets. At 725°C the gases produced from hardwood-PET pellets contained much more gravimetric tar than the gases produced from hardwood pellets. Gases produced from hardwood pellets contained more group 2 compounds than hardwood-PET pellets.

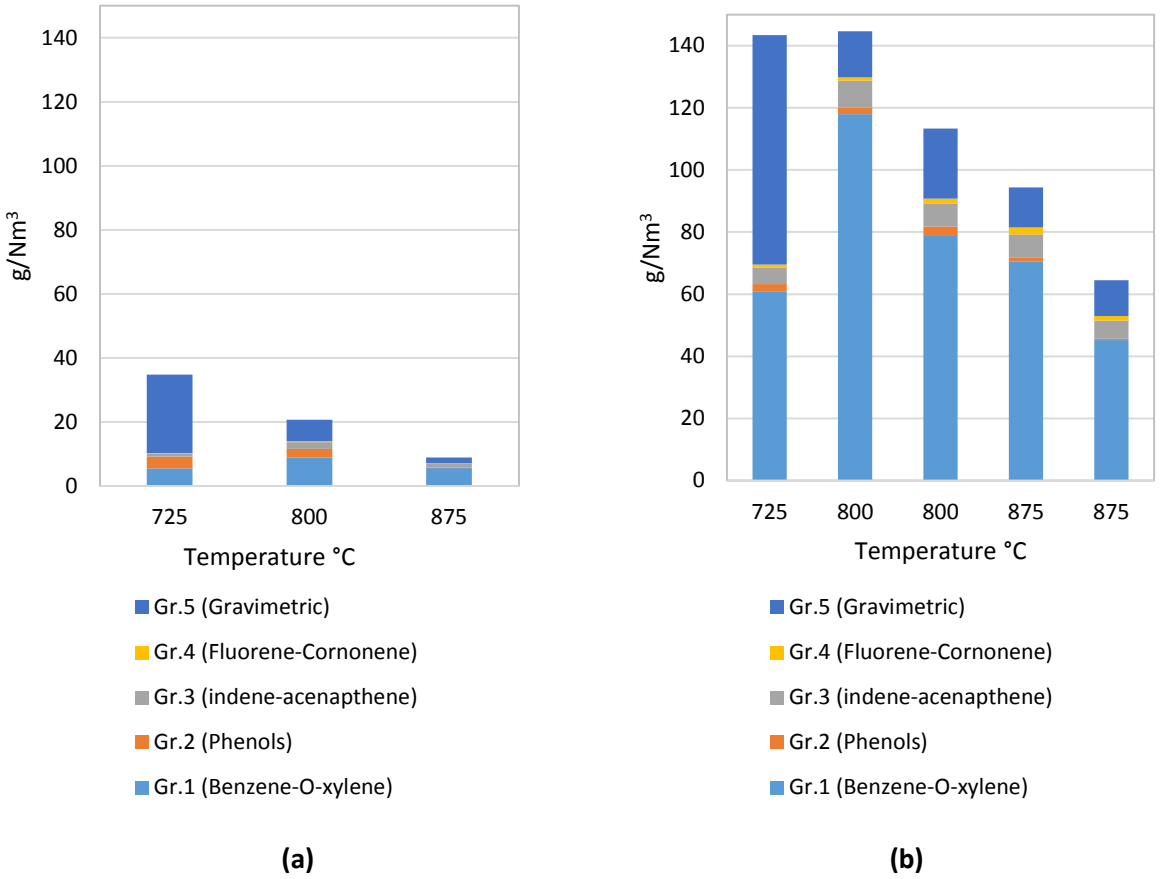
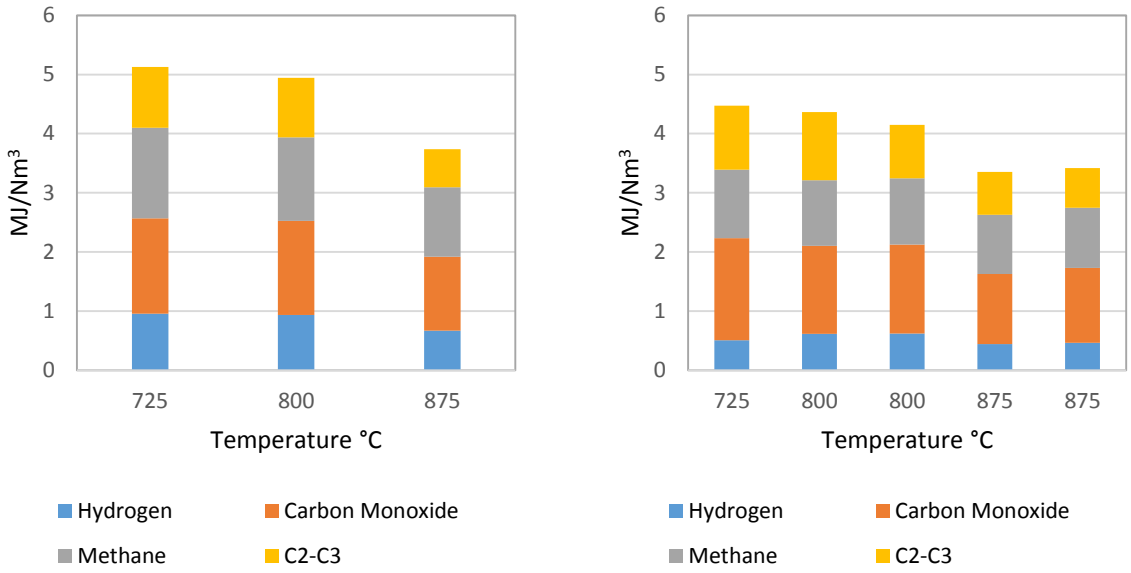


Figure 4.1 Concentration of tar in produced gas from hardwood pellets (a) and hardwood-PET pellets (b)

4.3.4 Heating value and thermal output

The produced gases had heating values ranging from 3.4 to 5.1 MJ/Nm^3 (Figure 4.2). At each temperature condition gases produced from hardwood pellets had greater heating values than gases produced from hardwood-PET pellets. For both types of fuel the produced gas heating values declined as the gasification temperature was increased and the declines occurring between 800°C and 875°C were greater than the declines occurring between 725°C and 800°C. Carbon monoxide and methane made the greatest contributions to the heating values of the gases produced from both types of pellets. For the hardwood pellets the contributions made by C_2, and C_3-hydrocarbons were similar to the contributions made by hydrogen. For the hardwood-PET pellets, the contributions made by C_2, and C_3-hydrocarbons, were greater than the contributions made by hydrogen.



(a) **(b)**

Figure 4.2 Lower heating value of gas produced from hardwood pellets (a) and hardwood-PET pellets (b)

The gasifier thermal output in terms of gas lower heating value ranged between 15 and 26 kW (Figure 4.3). For both types of pellets the thermal output of the gasifier decreased as the temperature increased and the decrease in thermal output between 800°C and 875°C was greater than the decrease 725°C and 800°C. At each temperature condition the thermal output of the gasifier was lower when hardwood-PET pellets were used. The difference in thermal output declined as the gasification temperature increased.

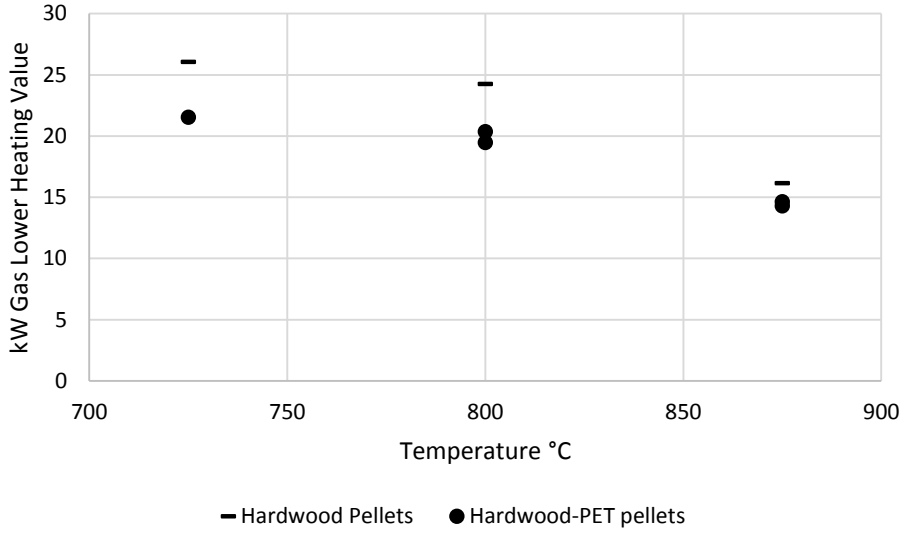


Figure 4.3 Gasifier thermal output in terms of gas lower heating value

4.3.5 Efficiency

Since the intended application of the produced gases for is engine operation lower heating values were used for the calculation of efficiency. Gasification proceeded at an efficiency of 0.37 to 0.62 (Figure 4.4). Gasification of hardwood pellets was more efficient than gasification of hardwood-PET pellets. There was a substantial change in efficiency, from 0.50 to 0.61, for the hardwood pellets when the gasification temperature was increased from 725°C to 800°C, while when the temperature was increased from 800°C to 875°C the efficiency only changed from 0.61 to 0.62. For the hardwood-PET pellets changes in efficiency were small compared to differences observed for duplicate conditions. The efficiency for these pellets appeared to rise from approximately 0.37 to 0.4 as the temperature was increased from 725°C to 875°C.

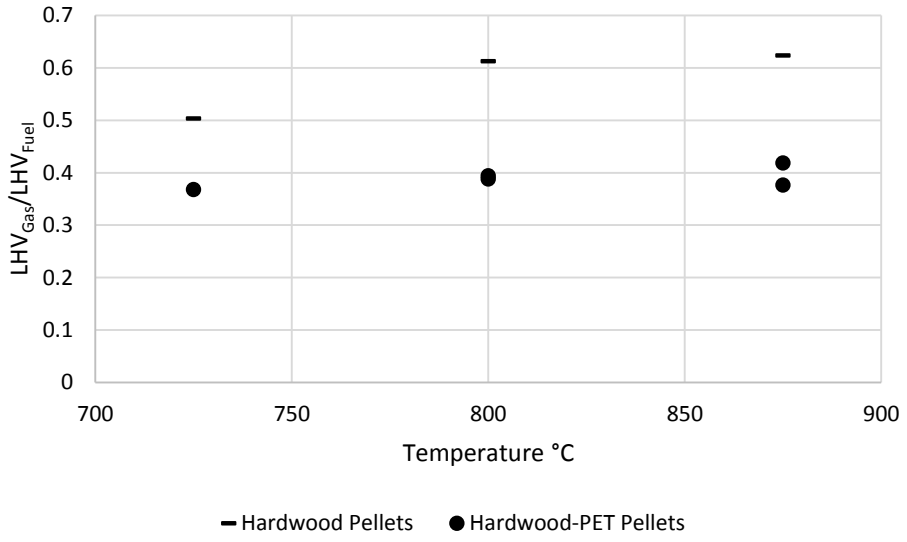


Figure 4.4 Gasifier efficiency in terms of lower heating value

4.3.6 Secondary Air Addition

The addition of secondary air above the fluidized bed was investigated as a means of reducing tar concentration in the produced gas. Two experiments were conducted, one using hardwood pellets and one using hardwood-PET pellets. The bed temperature was maintained at 800°C for both experiments. Pan et al. [24] and Narvaez et al. [25], have both obtained favourable results when the equivalence ratio was held constant but some portion of the gas is injected above the bed. For an over bed fed gasifier with a high volatile content fuel, such as wood and especially a non-char yielding plastic such as PET, it is possible that high tar loadings are related to devolatilization occurring above the bed. Introducing air above the bed may assist in tar reduction by providing oxygen to convert volatiles and by significantly raising the gas temperature where tars are produced.

Figure 4.5 and Figure 4.6 contain comparisons of the raw produced gas compositions from gasification of the hardwood and hardwood-PET pellets at a bed temperature of 800°C with and without addition of 0.0022 kg/s (100 SLPM) of secondary air above the bed. Addition of secondary air resulted in a reduction in the concentration of all combustible gas components, except acetylene, for both types of pellets. The concentration of carbon dioxide also declines with addition of secondary air. There is a substantial increase in the concentration of nitrogen when secondary air is added above the bed.

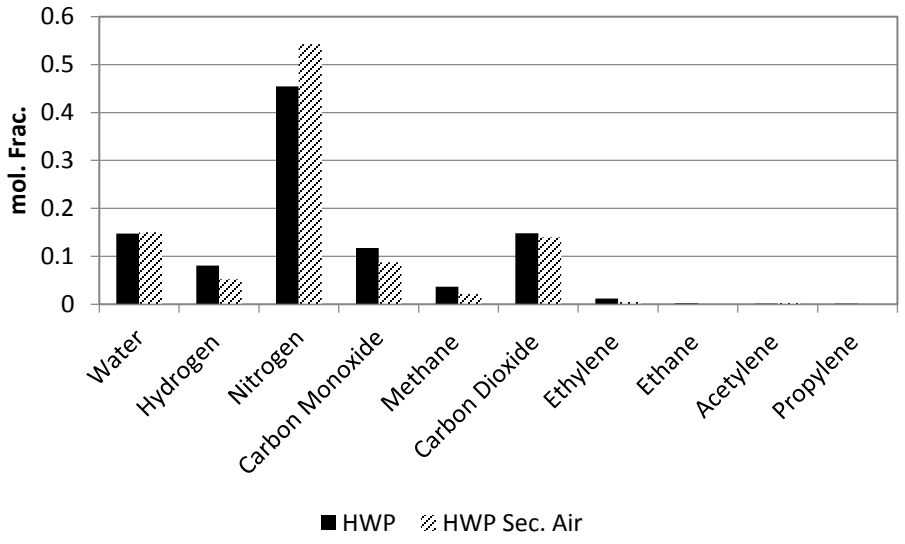


Figure 4.5 Comparison raw produced gas compositions from gasification of hardwood pellets at 800˚C with and without addition of secondary air

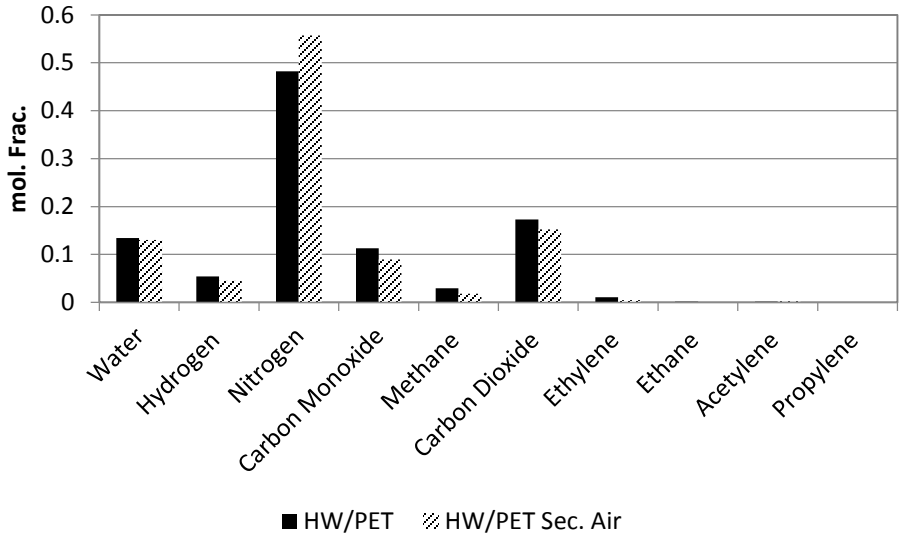


Figure 4.6 Comparison raw produced gas compositions from gasification of hardwood-PET pellets at 800°C with and without addition of secondary air

The concentrations of the four groups of GC tar compounds and gravimetric tar for the two types of pellets with and without secondary air are pictured in Figure 4.7 and Figure 4.8. For both types of pellets the concentrations of almost all the types of tar decreases with addition of secondary air

above the bed. The one exception was the concentration of group 4 tar compounds in the dry produced gas from the hardwood pellets, which actually increased with addition of secondary air. Group 2 tars are almost completely eliminated with the addition of secondary air.

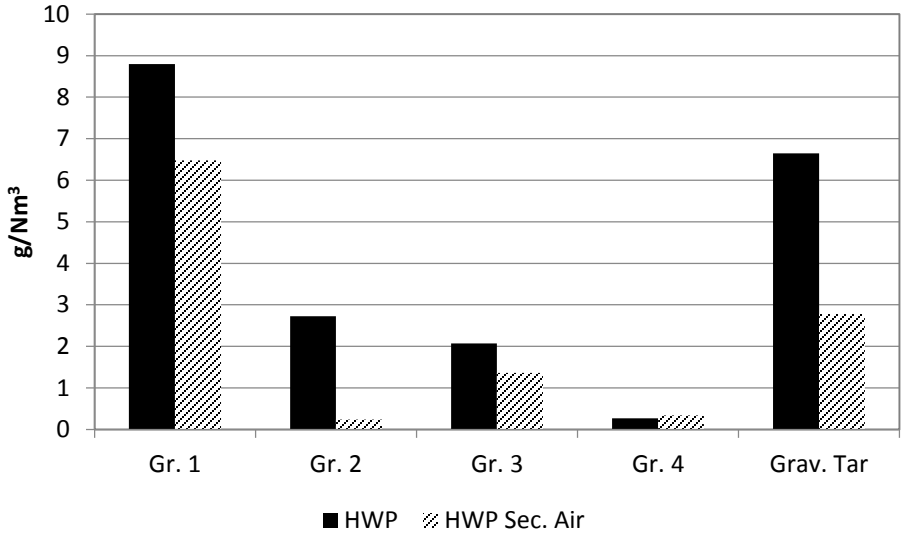


Figure 4.7 Comparison tar concentrations from gasification of hardwood pellets at 800˚C with and without addition of secondary air

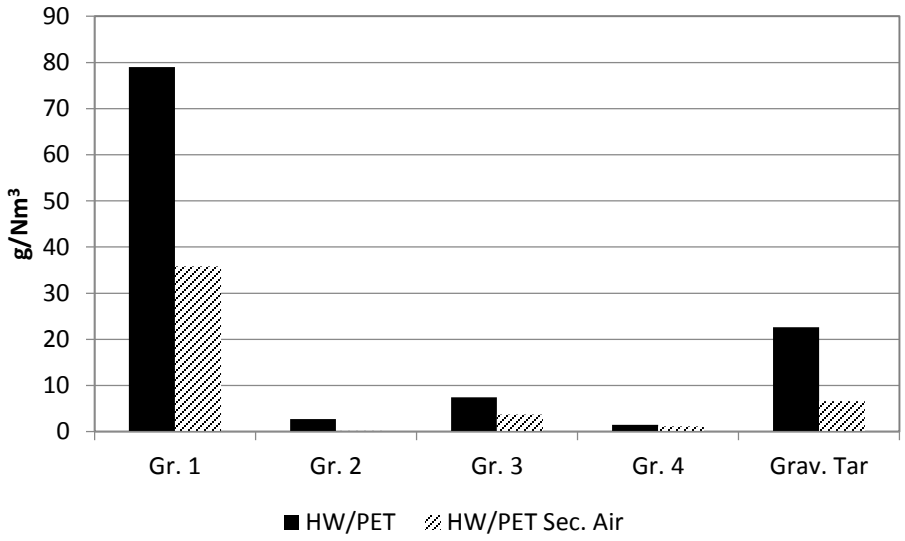


Figure 4.8 Comparison tar concentrations from gasification of hardwood-PET pellets at 800°C with and without addition of secondary air

4.4 Discussion

4.4.1 Co-pelletization

When the gasifier was fed a 50:50 mixture of PET pellets and hardwood pellets the gasifier became fouled with coke, but when the gasifier was fed composite pellets made from a 50:50 mixture of hardwood and PET problems with coking were not encountered. The intimate contact between the PET and hardwood in the pellets is suspected to cause some interaction between the two materials, which prevents the formation of coke above the bed.

4.4.2 Produced Gases

At any given temperature condition, the heating values of produced gases from hardwood-PET pellets had a heating value only about 10% lower than those from hardwood pellets. Gases produced from hardwood-PET pellets had greater concentrations of nitrogen and carbon dioxide than the gases produced from hardwood pellets, but this was partially offset by higher concentrations of C2, C3-hydrocarbons, which have relatively high heating values on a molar basis. Differences in the concentrations of tar were much more significant. All of the produced gases contained much more tar than would be tolerated by an internal combustion engine.

The gases produced from hardwood-PET pellets had lower heating values than gases produced from hardwood pellets. Gas heating values influence the volumetric energy density of fuel-air mixtures delivered to an engine. The heating values of the raw gases may be quite different than the heating values of the gases after tar destruction. This is especially true when comparing the gases from hardwood pellets to the gases produced from hardwood-PET pellets, because of the relatively large amount of tar in the hardwood-PET pellets.

Tinaut et al. [26] developed the Equivalent Fuel Quality (EFQ) parameter, to be used as a simple predictor of internal combustion engine performance. This parameter is the volumetric heating value of a stoichiometric fuel-air mixture. Engines have a fixed volumetric displacement, so the power produced by an engine, at a given engine speed, is heavily dependent on the volumetric heating value of the air-fuel mixture. The alternative EFQ is to the conventional EFQ what the engine power while operating on the alternative fuel is to the engine power while operating on the conventional fuel.

Figure 4.9 contains the EFQs of the produced gases and the approximate engine power de-ratings, which would occur at 100 % replacement of diesel fuel. A diesel EFQ of 3500 kJ/Nm^3 was assumed. This value is obtained if it is assumed that diesel fuel has a molar H:C ratio of 1.8 and a lower heating value of 43 MJ/kg. At each temperature condition gases produced from hardwood pellets had greater EFQs than gases produced from hardwood-PET pellets. For both types of pellets the drop in EFQ was greater when the temperature of the gasifier was increased from 800°C to 875°C, than when the gasifier temperature was increased from 725°C to 800°C. The approximated engine power de-ratings range between 36 % and 48 %. This would tend to suggest that a diesel generator unit with a normal capacity of approximately 160-195 kW would be required to provide 100 kW of power. Power generation systems contain multiple engine-generator units to meet varying load conditions [27]. Producer gas might be most appropriate for use during low load conditions when excess engine capacity is at a maximum.

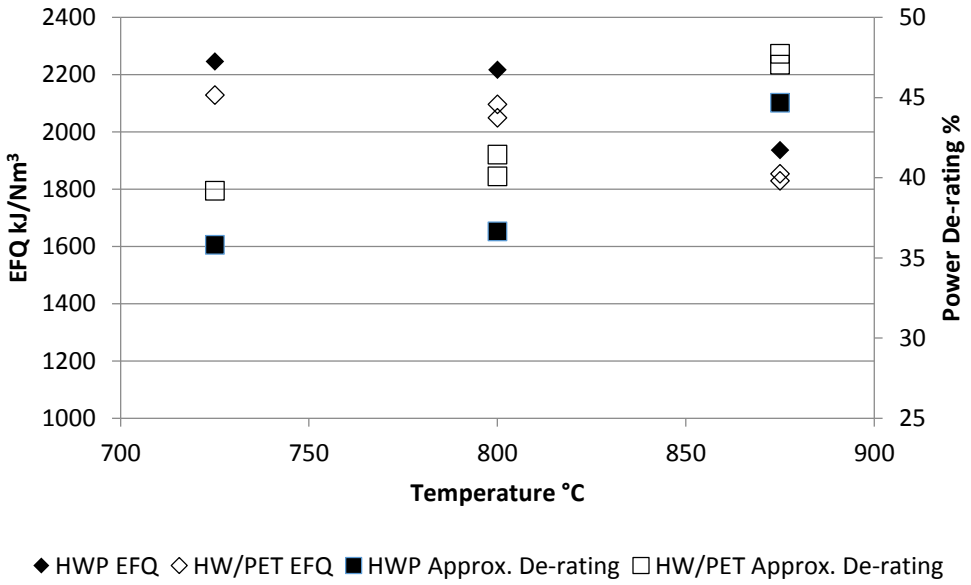


Figure 4.9 EFQs of dry gases produced from hardwood and hardwood-PET pellets

4.4.3 Tar

The most significant difference between gasification of the two different types of pellets is the concentration of tar in the produced gases. The gases produced from hardwood-PET pellets contained much higher concentrations of tar than the gases produced from hard wood pellets. This would be most important if a system operating in a remote northern community was to be switched between the two types of fuels. A tar removal system designed to clean gases produced

from hardwood pellets might be overwhelmed by the much greater tar concentration of the hardwood-PET gases.

Asadullah [28] has reviewed matters related to producer gas cleaning. For tar, hot and cold, gas cleaning methods exist. Cold methods involve condensation and separation of tar, while hot methods involve thermal or catalytic destruction of tar. Cold methods are often used to cleanup producer gas from downdraft gasifiers. Thermal destruction of tar is typically accomplished at temperatures ranging from 1000°C to 1300°C. Catalytic tar destruction is conducted over a catalyst at lower temperatures than thermal tar destruction.

4.4.4 Cold gas cleaning

Cold gas cleaning takes place at a temperature below the tar dew point allowing for mechanical separation of tar along with particulate matter. These units either scrub the gas of tar and other particulate matter using a fluid or they filter tar and other particulate matter using a solid filter [29]. When scrubbing is employed water is most often the scrubbing medium though other media such as oil have been employed [29]. Units such as spray towers, Venturi scrubbers, cyclone scrubbers, and rotating particle scrubbers have been employed for scrubbing biomass producer gas [29]. Sand beds, cotton, sawdust, paper filters and charcoal have all been employed as filters or in the case of charcoal adsorbents for biomass producer gas cleaning [29].

Scrubbing has proven to be an effective means of cleaning producer gas for engine applications. The most glaring problem with scrubbing is the creation of a stream of dirty water. Dasappa et al. [30] report details of a 100 kW_e downdraft gasification power station which employs scrubbing the clean producer gas before it was used in engines. Scrubbing was accomplished using a series of wet cyclones. A total circulation rate of 50 m^3/ h was required for operation of the scrubbers, and 20 m^3 of water must be treated each day to maintain the water quality at a level suitable for scrubber operation.

Jorapur and Rajvanshi [31] investigated the operation of a 15 kW_e downdraft gasification power generation system. Wet scrubbing was used as a means of removing tar and particulate matter from the gas. Water from the scrubbing system was used to water sunflower and mustard seed crops. The dirty water did not kill the crops.

Ghosh et al. [32] reported experience with a 500 kW gasification installation. Five 100 kW downdraft gasifiers were employed. Produced gases were scrubbed in a tower, then passed

through a sawdust filter, and then passed through a cotton filter. Water is circulated to a spray tower at a rate of 2880 L / h. The total amount of water in the system was not specified but it must be replaced every 220 h. Water treatment and disposal is not discussed. The sawdust and cotton filters must be replaced after 48-50 h of engine operation. Even with the intervening gas cleaning measure the engine turbo-chargers must be cleaned and the engine oil must be replaced after 225 h of operation.

The use of mechanical barriers like filters is not recommended for raw gas cleaning since they tend to become clogged very quickly with tar that is difficult to remove [29]. Filters should probably be employed downstream from a more appropriate gas cleaning train. In this way they may serve as a last line of defence in the cases of a process upset which causes tar or other contamination to pass the gas cleanup train.

Fluidized bed gasifiers often produce a gas that has a tar concentration which is roughly an order of magnitude greater than downdraft gasifiers [33]. Scrubbing the gas from a fluidized bed gasifier would require a greater circulation rate and would lead to the creation of more contaminated water than it would with a downdraft gasifier. Use of cold gas cleaning for producer gas cleanup in a remote northern community would require some means of treating the contaminated water, because it would not be acceptable to emit a stream of dirty water into the environment. It seems unlikely that the extra complexity could be borne by a small system operation in a remote location. Hot gas cleaning methods are likely to be the appropriate option since these methods cause the destruction of tar within the process thus avoiding the problem of heavily contaminated water or filter materials.

4.4.5 Thermal Tar Cracking

The use of thermal cracking to destroy the tar present in the produced gases was investigated. For simplicity the thermal cracking kinetics of naphthalene were used to approximate the conversion of tar. Use of naphthalene in this way is recommended since naphthalene is a relatively stable tar compound [34]. First order kinetics with an Arrhenius constant of 10^{16} s^{-1} and, activation energy of 434 kJ mol^{-1} was used to describe the cracking of naphthalene in producer gas [34].

The required conversion for each of the producer gases was calculated assuming that the total content of tar, excluding the content of group 1 tar compounds, in the cleaned gas would be 100 mg/Nm^3. Group 1 tar compounds were excluded since they are too light to interfere with engine

operation. Table 4.4 contains the required conversions. The gas produced from hardwood pellets at 875°C was the only gas which required less than 99 % conversion. Gases produced at lower temperatures require more conversion than gases produced at higher temperatures and most of the gases produced with hardwood-PET pellets require more conversion than gases produced with hardwood pellets.

Heat for thermal cracking of tar would be supplied by addition of air or oxygen. The thermal cracking of the tars in the produced gases was compared by estimating a unique thermal cracking operating temperature for each gas seen in Table 4.4. The temperatures were determined by assuming that 30 % of stoichiometric air supplied at 25°C was adiabatically mixed with each of the produced gases supplied at the temperature at which each gas was produced. The total tar content, including group 1 compounds, was assumed to have the elemental composition of naphthalene and included in the calculation of stoichiometric air. Group 1 compounds were included here since their heating value affects the heating value of the raw gas.

Table 4.4 Simulated thermal cracking of tar in gases produced from hardwood and hardwood-PET

	Hardwood Pellets			**Hardwood-PET pellets**				
Gasification Temperature (°C)	725	800	875	725	800	800	875	875
Required Conversion (%)	99.66	99.15	96.95	99.88	99.62	99.71	99.58	99.48
Simulated Cracker Temperature (°C)	1077	1189	1121	1144	1180	1163	1143	1134
Residence Time (s)	35.3	1.5	6.4	6.7	2.2	3.6	5.6	6.8
Cracker volume (m^3) based on 500 kW gas lower heating value	30.3	2.0	7.4	5.2	1.8	3.0	4.5	5.9
Treated Gas lower heating value (MJ/Nm^3)	3.1	2.1	2.3	3.3	3.4	3.2	3.3	3.0

Unisim™ was used to approximate the addition of secondary air to each of the gases. A Gibb's reactor was used to determine the temperature resulting from addition of air. The Gibb's reactor determines a temperature and composition which minimizes the Gibb's free energy of the input streams. It should be noted that this does not account for non-molecular species which are present at high temperatures. This should tend to make the predicted temperatures higher than actual temperatures. Heat loss from the cracker was also left aside and this would also tend to make the predicted temperatures higher than real temperatures.

For both types of pellets gases produced at 800°C gave the highest predicted temperatures when addition of 30 % of stoichiometric air was modelled. Gases produced at lower temperatures have higher heating values than gases produced at higher temperatures. The differences in heating values between gases produced at 800°C and gases produced at 875°C were more than enough to make up for the 75°C difference in temperature. The differences in heating values between gases produced at 725°C and 800°C were not enough to make up for the 75°C temperature difference. Predicted temperatures were used to calculate the residence time needed to achieve the required conversion. Residence times ranged from 1.5 s to 35 s (Table 4.4). Gases produced at 800°C required the lowest residence times.

Reactor volumes to provide the required tar conversion for a throughput of 500 kW of cleaned gas lower heating value were calculated. This throughput could conceivably supply a small engine-generator with an electrical output of about 125 kW. The reactor volumes, seen in Table 4.4, range from 1.8 to 30 m^3.

The predicted compositions at the outlet of the tar cracker were used to calculate lower heating values of the dry gases after thermal cracking. These heating values ranged from 2.1 to 3.3 MJ/Nm^3 (Table 4.4). For each gasification temperature condition, gases produced from hardwood-PET pellets yield gases with greater heating values, after simulated thermal cracking, than gases produced from hardwood pellets. This is because of the very high concentrations of tar in the gases produced from hardwood-PET pellets.

The results of simulated thermal tar cracking indicate that cracking of the tars present in the produced gases would require very large reactor volumes. The best results were had when thermal cleanup of gases produced at 800°C was considered. For hardwood pellets results indicate that to obtain a throughput of 500 kW of gas lower heating value a reactor with a volume of 2 m^3, would be

required, and the produced gas would have a lower heating value of 2.1 MJ/Nm^3. For the hardwood-PET pellets a reactor volume of 1.8 m^3 would be required and a gas with a lower heating value of 3.5 MJ/Nm^3 would be produced. The simulated results do not include the influence of heat transfer from the cracker, and they do not include the effect of non-molecular species on the calculation of the temperature obtained by addition of air to the raw gases. Even more air would have to be added to achieve the simulated temperatures and this would further decrease the heating values of the produced gases.

This is borne out by the temperatures which were actually achieved during experiments with secondary air. When the gasifier was operated at 800°C using hardwood pellets, and 0.0022 kg/s (100 SLPM) of secondary air was injected above the bed, the highest temperature measured above the bed was 885 °C. The overall equivalence ratio for this experiment was 0.49. Given that the bed was fed 0.0038 kg/s (175 SLPM) of air, the secondary air is approximately 35 % of the stoichiometric air for combustion of the effluent from the bed. Using hardwood-PET pellets under the same conditions, with an overall equivalence ratio of 0.40 the highest temperature measured above the bed was 929°C. In this case the secondary air was approximately 28 % of the stoichiometric air for combustion. The simulated results, for 30 % of stoichiometric air, would suggest that temperatures over 1000 °C should have been obtained in both cases.

The required conversion for each of the gases was calculated assuming that 100 mg/Nm^3 [33] is an acceptable concentration of tar for engine operation. Some recommendations are as low as 10 mg/Nm^3 [33]. A more stringent tar specification would require even greater reactor volumes or higher temperatures. Another factor which must be considered is the inorganic contaminates in the gas. Produced gases contain inorganic contaminates such as alkali metals, hydrogen chloride, and hydrogen sulfide. Allowing these contaminants to pass into the high temperature environment of a thermal cracker may tend to exasperate corrosion [35]. Reducing the temperature of the raw gas would facilitate removal of inorganic contamination [36]. If the raw gas temperature is reduced before the tar cracker than the temperature achieved for a given fraction of stoichiometric air will be lower and the residence time to achieve the required conversion will be longer.

Use of a thermal tar cracker without access to oxygen, would probably require the inclusion of high temperature gas-gas heat exchangers. These could be used the recuperate heat from the cleaned gas. Recuperation of heat might allow the thermal cracker to be maintained at a high temperature without burning too much of the caloric value out of the gas. Inclusion of heat transfer surfaces

complicates the overall system and introduces the possibility of corrosion and fouling issues, which are likely to occur in high temperature equipment especially when the material stream contains inorganic contamination. Expensive and exotic materials, like nickel or chromium alloys, or ceramics, which detract from the economic feasibility of a system, might be required [37].

4.4.6 Catalytic Tar removal

Nickel steam reforming catalysts have been found to be quite effective for destroying tar in hot producer gas [38]. Depending on reactor conditions, coking may be severe when these catalysts are employed. For air blown gasification the concentration of tar over a nickel reforming catalyst should not exceed 2 g/Nm^3 [38]. This tar concentration may be achieved by use of a guard bed of a less effective and less expensive mineral catalyst such as dolomite [38].

Orio et al. [39] investigated the use of different dolomites for hot tar removal using raw gas from an air-blown fluidized bed gasifier. Conversions of 0.778 to 0.968 were obtained at temperatures ranging from 760 to 850°C using space time ranging from 0.052 to 0.072 kg h/m^3. Apparent first order kinetics for tar destruction was derived from this data. The pre-exponential factor was 1.51 x 10^6, and the activation energy was 100 kJ/mol [39]. Since the apparent kinetics includes the effects of external and internal mass transfer resistance, they should provide more realistic estimates of the required catalyst bed mass.

As can be seen in Table 4.5, for gas flow rates equivalent to 500 kW of gas lower heating value, the required bed masses are between 68 and 363 kg. Except for the 725°C temperature condition, the gases produced from hardwood-PET pellets at a given temperature required a greater catalyst bed mass than gases produced from hardwood pellets. That the gases produced from hardwood-PET pellets would require more catalyst is not surprising since these gases contain more tar. The tar content of the gases was included when determining the flow rate of gas required providing 500 kW of lower heating value. The gas produced from hardwood-PET pellets at 725°C is much richer than the gas produced from hardwood pellets at the same temperature. This reduces the volumetric flow rate required for 500 kW of gas lower heating value and this reduction in flow rate is enough to make the hardwood-PET pellets require less catalyst than the hardwood pellets despite the gas from the hardwood-PET pellets requiring a greater degree of conversion.

Table 4.5 Destruction of tar over dolomite using apparent kinetics influenced by mass transfer

Fuel	Hardwood Pellets			Hardwood-PET pellets				
Gasification/Reformer Temperature (°C)	**725**	**800**	**875**	**725**	**800**	**800**	**875**	**875**
Required Conversion	0.943	0.903	0.775	0.986	0.986	0.982	0.979	0.969
K (m^3/kg h)	8.70	20.24	42.15	8.70	20.24	20.24	42.15	42.15
Catalyst Mass (kg)	363	149	68	329	153	167	100	106
Space Time (kg h/m^3)	0.33	0.12	0.04	0.49	0.21	0.20	0.09	0.08
Make up rate (kg/h)	18.17	7.47	3.41	16.45	7.70	8.37	5.01	5.32

Hartman et al. [40] studied the attrition rate of dolomite in a high temperature fluidized bed. An expression for calculation of the bed weight at a given time after start-up based on particle size, minimum fluidization velocity, and superficial bed velocity was derived from experimental results [40]. The expression was used to estimate the attrition rate from a dolomite bed with a mean particle size of 1.6 mm, a minimum fluidization velocity of 0.35 m/s, operated at a superficial velocity of 0.63 m/s. These conditions were drawn from the experimental conditions presented by Orio et al [39]. Without any catalyst make up, the bed mass would be reduced to 75 % of its original mass after five hours of operation. The approximate make up rate to maintain the mass of the bed would be approximately 5 % per hour.

The estimated make up rates are presented in Table 4.5. Between 3.41 and 18.17 kg of dolomite per hour would be required. For 1000 h of operation between 3 and 18 tonnes of dolomite would be required. The make-up rate depends heavily on the fluidization gas velocity. The attrition rate could be reduced by operation at a lower gas velocity but the bed diameters would be larger. Achieving a bed superficial velocity of 0.63 m/s, while producing 500 kW of gas lower heating value, would require a vessel diameter of 0.61 m to 1.04 m (Table 4.6). Reducing the superficial velocity to lower the estimated attrition rate would require even wider vessels.

Table 4.6 Dolomite bed diameters for a superficial velocity of 0.63 m/s

Fuel	Hardwood Pellets			Hardwood-PET pellets				
Gasification Temperature (°C)	725	800	875	725	800	800	875	875
Fluidized Bed Diameter (m)	0.79	0.85	1.04	0.61	0.64	0.69	0.78	0.85

A bed of nickel based reforming catalyst would be used to clean the gas from the dolomite bed to a tar concentration of <100 mg/Nm^3. Narvaez et al. [21], found that a bed of BASF G1-25 reforming catalyst was capable of reducing tar content to well below 100 mg/Nm^3 at space times of 0.14 kg h/Nm^3 and temperatures of 650 and 720°C. If this value of space time is assumed, as shown in Table 4.7 between 27 and 69 kg of catalyst would be required. Richer gases require less catalyst because the volumetric flow rate for 500 kW of gas lower heating value is lower.

Table 4.7 Mass of nickel catalyst required for final tar removal

Fuel	**Hardwood Pellets**			**Hardwood-PET pellets**				
Temperature (°C)	725	800	875	725	800	800	875	875
Volumetric Flow (500 kW) (Nm^3/h)	322	351	491	195	198	228	278	328
Catalyst Mass (kg)	45	49	69	27	28	32	39	46

4.5 Conclusion

Gasification of mixtures of hardwood pellets and PET pellets was found to cause coking above the bed. When pellets were formed from a blend of ground hardwood and PET, coking was not encountered during the gasification.

It seems that intimate contact between the hardwood and PET in the hardwood-PET pellets prevents the formation of coke above the bed. Gasification of the hardwood-PET pellets yielded gases with much higher tar concentrations than gasification of hardwood pellets. Addition of air into the freeboard (secondary air addition) was investigated as a means to reduce the tar at the middle bed temperature tested (800°C), which it did for both hardwood pellets and hardwood-PET pellets. Despite the reduction, the tar concentration was still far too great for direct engine application and the secondary air addition led to a clear decrease in gas heating. The greater concentration of tar in the gases produced from hardwood-PET pellets did not have a marked effect on simulation of thermal tar cracking. The cracking temperature governs the thermal tar destruction process and use of thermal cracking requires that the gases be heated to very high temperatures. This might be practically difficult to achieve in a remote community. The use of a dolomite guard bed followed by a nickel reforming catalyst appears to be an appropriate means of cleaning raw producer gas for engine use in a small remote northern community. The greater concentration of tar in the gases produced from hardwood-PET pellets does influence the mass of

dolomite which is required to reduce the tar concentration to 2 g/Nm^3. For catalytic tar reforming approaches, more work needs to be performed to determine what space time is required under practical operating conditions as well as the dolomite attrition rate.

References

[1] Government of Canada, "Status of Remote/Off grid Communities in Canada," Government of Canada, 2011.

[2] M. Arriaga, C. A. Canizares and M. Kazerani, "Renewable Energy Alternative for Remote Communities in Northern Ontario, Canada," *Transactions on sustainable energy,* 2012.

[3] A. Verma and G. Weisgerber, "Wood Gasification for Gas and Power," in *Thermal Conversion of solid Wastes and Biomass*, Washington DC, American Chemical Society, 1980, pp. 379-394.

[4] A. Verma and G. Weisgerber, "Wood Gasification for Heat and Power Generation," in *Thermal conversion of wastes and biomass*, Washington, DC, American Chemical Society , 1980, pp. 381-394.

[5] T. Robinson, B. Bronson, P. Gogolek and P. Mehrani, "Air-blown bubbling fluidized bed co-gasification of woody biomass and refuse derived fuel," *To be submitted to Biomass and Bioenergy,* vol. TBA, p. TBA, 2015.

[6] F. Pinto, F. C, R. Andre, M. Miranda, I. Gulyurtlu and C. I, "Co-gasification study of biomass with plastic waste," *Fuel,* vol. 81, pp. 291-297, 2002.

[7] P. Garcia-Bacaicoa, J. Mastral, J. Ceamanos, C. Berrueco and S. Serrano, "Gasification of biomass/high density polyethylene mixtures in a downdraft gasifier," *Bioresource Technology ,* vol. 99, pp. 5485-5491, 2008.

[8] G. Ruoppolo, P. Ammendola, R. Chirone and F. Miccio, "H2-rich syngas production by fluidized bed gasification of biomass and plastic fuel," *Waste Management ,* vol. 32, pp. 724-732, 2012.

[9] R. A. Mogadam, S. Yusup, Y. Uemura, B. L. F. Chin, H. L. Lam and A. Al Shoaibi, "Syngas production from palm kernal shell and polyethylene waste blend in fluidized bed catalytic steam co-gasification process," *Energy ,* vol. 75, pp. 40-44, 2014.

[10] P. Brachi, R. Chirone, F. Miccio, M. Miccio, A. Picarelli and G. Ruoppolo, "Fluidized bed co-gasification of biomass and polymeric wastes for a flexible end-use syngas: Focus on bio-methanol," *Fuel,* vol. 128, pp. 88-98, 2014.

[11] M. Narobe, J. Golob, D. Klinar, V. Francetic and B. Likozar, "Co-gasification of biomass and plastics: Pyrolysis kinetics studies, experiments on 100 kW dual fluidized bed pilot plant and development of thermodynamic equilibrium model and balances," *Bioresource Technology ,* vol. 162, pp. 21-29, 2014.

[12] G. Lopez, A. Erkiaga, M. Amutio, J. Bilbao and M. Olazar, "Effect of polyethylene co-feeding in the steam gasification of biomass i a conical spouted bed reactor," *Fuel,* vol. 153, pp. 293-401, 2015.

[13] S. Martinez-Lera, J. Torrico, J. Pallares and A. Gil, "Thermal valorization of post consumer film in a bubbling fluidized bed reactor," *Waste Management,* vol. 33, pp. 1640-1647, 2013.

[14] J.-W. Kim, T.-Y. Mun, J.-O. Kim and J.-S. Kim, "Air gasification of mixed plastic wastes using a two-stage gasifier for the production of producer gas with low tar and high caloric value," *Fuel,* vol. 90, pp. 2266-2272, 2011.

[15] R. Xiao, B. Jin, H. Zhou, Z. Zhong and M. Zang, "Air gasification of polypropylene plastic waste in a fluidized bed gasifier," *Energy Conversion Management,* vol. 48, pp. 778-786, 2007.

[16] U. Arena and F. Di Gregorio, "Energy generation by air gasification of two industrial plastic wastes in a pilot scale fluidized bed reactor," *Energy,* vol. 68, pp. 735-743, 2014.

[17] Biomass Energy Centre, "Biomass Energy Centre," 2008. [Online]. Available: http://www.biomassenergycentre.org.uk/portal/page?_pageid=75,17300&_dad=portal&_schema=portal. [Accessed 17 August 2015].

[18] Ireland's Environmental Protection Agency, "EPA," 2013. [Online]. Available: testweb.epa.ie/pubs/.../Waste%20Wood%20Postition%20Paper.pdf. [Accessed 17 August 2015].

[19] J. Matsunami, S. Yoshida, O. Yokota, M. Nezuca, M. Tsuji and Y. Tamaura, "Gasifiation of waste tyre and plastic (PET) by solar thermochemical process for solar energy utilization,"

Solar Energy, vol. 65, no. 1, pp. 21-23, 1999.

[20] M. Gil, J. Formoso, C. Pevida, J. Pis and F. Rubiera, "Intrinsic char reactivity of plastic waste (PET) during CO2 gasification," *Fuel Processing Technology,* vol. 91, pp. 1776-1781, 2010.

[21] P. Kannan, A. Al Shoibi and C. Srinivasakannan, "Energy recovery from co-gasification of waste polyethylene and polyethylene terephthalate blends," *Computers and Fluids ,* vol. 88, pp. 38-42, 2013.

[22] National association for PET container resources, "Post Consumer PET container recycling activity in 2012," 2012. [Online]. Available: www.napcor.com/pdf/NAPCOR_2012RateReport.pdf. [Accessed 13 07 2015].

[23] J. Smith, "Ottawa sends $2M in bottled water to First Nation," *The Syar,* 14 February 2014.

[24] Y. Pan, X. Roca, E. Velo and L. Puigjaner, "Removal of tar by secondary air in fluidised bed gasification of residual biomass and coal," *Fuel,* vol. 78, pp. 1703-1709, 1999.

[25] I. Narvaez, A. Orio, M. P. Aznar and J. Corella, "Biomass gasification with air in an atmospheric bubbling fluidized bed. Effect of six operational variables on the quality of the produced gas," *Ind. Eng. Chem. Res.,* vol. 35, pp. 2110-2120, 1996.

[26] F. V. Tinaut, A. Melgar, A. Horrillo and A. de la Rosa, "Method for predicting the performance of an internal combustion engine fuelled by producer gas and other low heating value gases," *Fuel Processing Technology,* vol. 87, pp. 135-142, 2006.

[27] M. Arriaga, C. A. Canizares and M. Kazerani, "Northern Lights," *IEEE Power and Energy Magazine,* pp. 50-59, 17 June 2014.

[28] M. Asadullah, "Barriers of commercial power generation using biomass gasification gas: A review," *Renewable and Sustainable Energy Reviws,* vol. 29, pp. 201-215, 2014.

[29] S. Anis and Z. Zainal, "Tar reduction methods in biomass producer gas via mechanical, catalytic and thermal methods: A review," *Renewable and Sustainable Energy Reviews,* vol. 15, pp. 2355-2377, 2011.

[30] S. Dasappa, D. Subbukrishna, K. Suresh, P. Paul and G. Prahu, "Operational experience on a grid connected 100 kWe biomass gasification power plant in Karnataka, India," *Energy for Sustainable Development,* vol. 15, pp. 231-239, 2011.

[31] R. M. Jorapur and A. K. Rajvanshi, "Development of a sugarcane leaf gasifier for electricity generation," *Biomass and Bioenergy,* vol. 8, pp. 91-98, 1995.

[32] S. Ghosh, T. K. Das and T. Jash, "Sustainability of decentralized woodfuel-based power plant: an experience in India," *Energy,* vol. 29, pp. 155-166, 2004.

[33] T. Milne, R. Evans and N. Abatzoglou, "Biomass Gasifier "Tars" Their Nature, Formation, and Conversion," National Renewable Energy Laboratory, Golden, Colorado, 1998.

[34] B. Vreugdenhil and R. Zwart, "Tar formation in pyrolysis and gasification," Energy Reseach centre of the Netherlands (ECN), 2009.

[35] R. A. Antunes and M. C. Lopes de Oliveira, "Corrosion in biomass combustion: A materials selection analysis and its interaction with corrosion mechanism and mitigation strategies," *Corrosion Science,* vol. 76, pp. 6-26, 2013.

[36] M. Blander, "Biomass gasification as a means for avoiding fouling and corrosion during combustion," *Journal of molecular liquids,* vol. 83, pp. 323-328, 1999.

[37] K. Al-attab and Z. Zainal, "Performance of high temperature heat exchangers in biomass fuel powered externally fired gas turbine," *Renewable Energy,* vol. 35, pp. 913-920, 2010.

[38] I. Narvaez, J. Corella and A. Orio, "Fresh tar (from a biomass gasifier) elimination over a commercial steam reforming catalyst kinetics and effect of different variables of operation," *Ind. Eng. Chen Res.,* vol. 36, pp. 317-327, 1997.

[39] A. Orio, J. Corella and I. Narvaez, "Performance of different dolomites on hot raw gas cleaning from biomass gasification with air," *Ind. Eng. Chem. Res.,* vol. 36, pp. 3800-3808, 1997.

[40] M. Hartman, K. Svoboda, M. Pohorely, M. Syc and M. Jeremias, "Attrition of dolomitic lime in a fluidized bed reactor at high temperatures," *Chemical Papers,* vol. 67, no. 2, pp. 164-172, 2013.

Chapter 5 Conclusion

TGA has been used for the analysis RDF by many investigators in the past. The extreme heterogeneity of RDF combined with the small sample sizes which are typical of TGA, make sample preparation very important when applying TGA to RDF. Potential difficulties include a lack of repeatability and sample preparation error. Cryo-ball milling was found to be an acceptable means of preparing RDF samples for analysis by TGA. Experiments using 10 mg samples were found to be repeatable when cryo-ball milling was applied. The nature of the cryo-ball milling process makes sample preparation error unlikely. The same cannot be said for ultra-centrifugal milling, which employs a screen, which appears to discriminate against some components of RDF.

TGA might be used as a means of distinguishing between the biogenic or renewable fraction of RDF and the fossil or non-renewable fraction. Though TGA is an indirect way of making such a determination it might still compete with the current means for making such determinations. The indirectness of the TGA method is similar to the indirectness of the selective dissolution method, since both methods rely on biogenic materials being easier to chemically decompose than fossil materials. Even AMD cannot provide a direct means of distinguishing between biogenic and renewable materials, since atomic weapons testing has caused the amount of C^{14} in the atmosphere to vary with time and this has made the ratio of C^{14} to C^{12} in biogenic material to vary. Despite the fact that preparing samples of RDF for TGA is difficult and requires extreme measures such as cyro-milling, results could still be obtained faster than if the selective dissolution method was used. Additionally there would be far less laboratory waste to be disposed. Compared the AMD TGA is more accessible and due to the need to graphitize samples for AMD, far less time consuming.

Co-gasifying mixed waste with biomass in a fluidized bed gasifier to supply electrical energy to a remote northern community via a dual fuel operation of existing diesel engines was not found to be appropriate. Even commercially produced RDF, which was created with a sophisticated large scale industrial process, contains substantial quantities of materials like silica which cause bed agglomeration. This would limit the operating temperature of the gasifier to a range which is not optimal for conversion of biomass. The char from the unconverted biomass would be contaminated

with the solid residue from the mixed waste and this would complicate the disposal of the solid residue which originates from the biomass.

A more appropriate option for a remote community might be to target certain waste materials for co-gasification along with biomass. Plastics could be targeted since they are non-biodegradable, have low moisture content, contain very small amounts of inorganic materials, and have high energy content. Plastics do not undergo significant bio-degradation in landfill. Diverting these materials frees up landfill space and increases landfill lifetime. Biodegradable materials could be composted or otherwise digested further increasing landfill lifetime. Unlike paper and textiles, plastic does not soak up large quantities of water. This simplifies processing and storage. Many plastics are nearly free of inorganic materials. Inorganics are converted to ash during thermal processing and this ash must be disposed. Using filler free plastics avoids the need to dispose of ash. The high energy content of plastic means that a relatively large amount of salable power could be generated from a relatively small quantity of material, which should help offset the cost of processing and converting the plastic.

With this in mind, co-gasification of hardwood pellets and PET was undertaken. Attempts to co-gasify mixtures of hardwood pellets and PET pellets in a bubbling fluidized bed gasifier failed due to the formation of coke above the bed. This operational issue was solved by co-pelletizing hardwood and PET, making hardwood-PET pellets. Compared to gasification of hardwood pellets the gasification of hardwood pellets yields substantially more tar. For either hardwood pellets or hardwood-PET pellets catalytic destruction of tar appears to be the most appropriate means of cleaning tar from the raw produced gas, so that the gas may be used for dual fuel operation of diesel engines.

Further work needs to be completed. A system for cleaning the raw gas needs to be designed and validated with long-term testing to ensure stable operation in a remote community is possible. It is also necessary to explore the transient behavior of the gasifier and process control strategies as a gasifier coupled to a power generation system would experience a variable load. Specifically, it needs to be determined how step changes in demand influence the operation of gas cleaning equipment and dual fuel engine operation.

It would be necessary to first design and construct a pilot scale gas cleaning system, so its operation could be validated during steady state and transient operation. Once a suitable gas cleaning system

was settled upon it would then be necessary to couple the gasifier and gas cleaning system to a diesel engine equipped with a simulated mechanical load. This would allow for development of process control strategies for the system as a whole.

Acknowledgements

Completion of this work would not have been possible without the hard work and direction of my supervisor Dr. Poupak Mehrani. Thank you for all the time and effort which you have given to this work and my education as a whole.

I would like to thank Benjamin Bronson and Dr. Peter Gogolek for the advice and direction which they have provided during the completion of this work.

I would like to thank Dave Wambolt, Bart Young, Vivian Ko, and Penny McDonald for their help in preparing materials and performing characterization.

I would also like to acknowledge the love and support of my parents Ken and Sharon Wylie. None of this could even have been undertaken without the years of love and support which they have provided. Thank you.