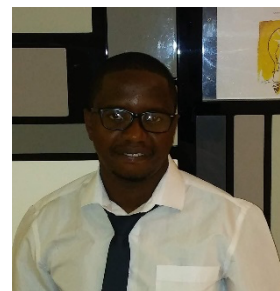


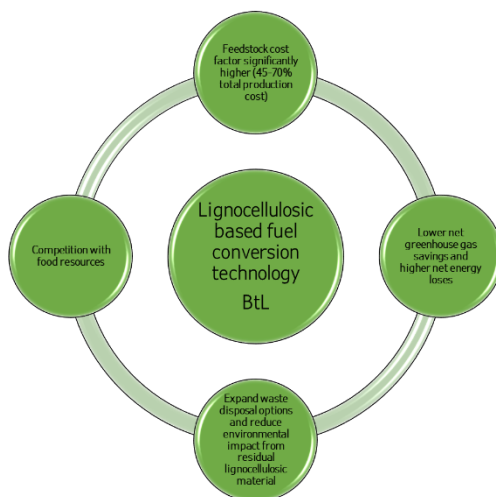
CATALYTIC CO-PYROLYSIS OF RESIDUAL WASTE TO DROP-IN HYDROCARBONS



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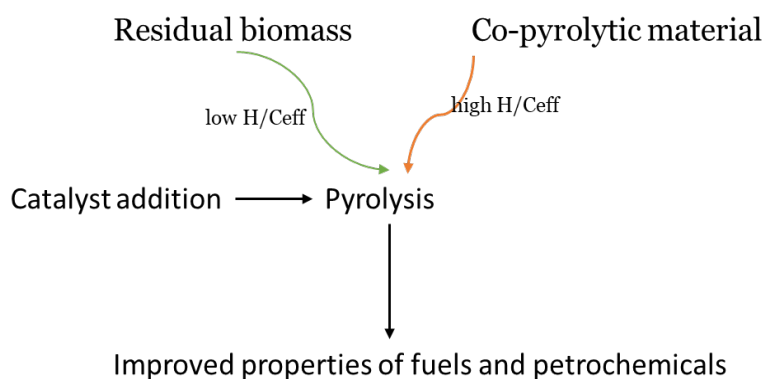
To achieve the desired drop in atmospheric emissions from the transportation sector, there is increasing need to develop and deploy increasing volumes of renewable transport fuels. The transition towards low carbon economies as set out in the 2015 Paris agreement, upon which the European Union chartered a new course to lower the environmental footprint of the transportation sector through the implementation of the RED II and SET-plan. The increased controversy surrounding the use of food resources as feedstocks for fuels has seen the EU set a max. threshold of 7% share of biofuels to be derived from food resources with the rest expected to be produced from non-food competing material. The role of advanced biofuels within economies is expected increase within the decade spurred on by sustainable policies that include the valorisation of non-food resources to address the challenges of 1st generation biofuels. This has seen increased scrutiny towards the integrated valorisation of the abundant solid lignocellulosic stream that is more often underutilised (i.e., disposed of as residual waste) due to its recalcitrant nature toward the 1st generation biofuel industries conversion techniques. In order to make use of this abundant renewable carbon source, valorisation technique that can work with the aforementioned drawback are becoming more critical to the growth of the biofuel sector with thermochemical techniques more suited to maximise the utilisation of the biomass matrix completely.



My PhD research project looks at the valorisation of residual biomass via fast pyrolysis with more emphasis being placed on how to improve the quality of the bio-oil to potentially match petroleum derivatives as drop-in alternative hydrocarbons. Despite there being a lot of work that has been done on the optimisation of the fast pyrolysis to produce bio-crude, the greatest challenge for fast pyrolysis has been the low quality of bio-oil requiring significant and costly upgrading before it can be used as a substitute to fossil derivatives. The use of residual biomass offers feedstock variability challenges that affect the conversion efficiency, and naturally the intrinsic properties of lignocellulosic resources are inherently heterogeneous with variable macro-component compositions adding to the complexity of conversion for the solid waste streams that offer increased sustainability benefits to the biofuel industry. The project will seek to explore a two pronged strategy, with one looking to homogenise the physicochemical properties of the biomass prior to pyrolysis and the other one seeking to influence selectivity and deoxygenation of the pyrolysis process.

Within the 1st year of study, experimental work was done on the various biomass resources available which include spruce wood, wheat straw and olive stone. From the preliminary studies, wheat straw offered the greatest challenges due to its low flowability and bulk density which created feeding challenges, also its high ash content influenced primary pyrolysis pathways resulting in the increased production of non-condensable stream. Inherent catalytic properties of ash were very evident as the other two feedstocks with naturally lower ash content produced greater condensable fractions. From the literature, the pyrolytic mechanism that is most widely accepted suggests contributions from the decomposition of some of the weak fractions of hemicellulose contribute more to the formation of undesirable fractions of fast pyrolysis. Therefore, at the end of the 1st year, going into the 2nd year, work was done on torrefaction of biomass in batch mode fluidised bed reactor to partially degrade some of the hemicellulose fraction to study its influence on the properties of bio-oil quality. Olive stone was torrefied at temperatures of between 200 – 300 °C for 10 minutes, using a bed of sand as a heat transfer medium as well as fluidisation media in an anoxic environment with fast recovery and quenching after the lapse of time. Preliminary analysis of the torrefied solid biomass showed that extremely high torrefaction temperature resulted in decreased mass recovery, and upon grinding the torr solid formed a pulverised powder not suitable for pyrolysis and maybe better suited for gasification and combustion operations.

Pyrolysis of torrefied biomass was studied within the 2nd year, with the pyrolysis products characterised via the various analytical techniques available which included thermogravimetry TGA, ultimate and proximate analysis, GC-MS etc, to try and see the synergy of pre-treating with torrefaction as a strategy to improve the quality of hydrocarbons formed. Catalytic pyrolysis was also explored with the use of an in-situ bed made of material such as ZSM-5 and modified γ -alumina to improve selectivity and deoxygenation which are critical if we are to produce fuel grade hydrocarbons, the results showed that olive stone yielded most phenolic derivatives due to its high lignin content in contrast to residual feedstocks such as wheat straw. The stream of phenolic derivations has potential to substitute for some of the petroleum derived petrochemical feedstocks which aids in improving the potential profitability of the biorefinery as petrochemical are high value material. What became clear from the catalytic pyrolysis studies is that with biomass feedstock inherently hydrogen deficient, deoxygenation occurs at the expense of yield despite the selectivity towards much more deoxygenated hydrocarbons increasing. To compensate for this inherent low hydrogen content, co-pyrolysis with polyolefins which form part of the bulk of waste plastic streams in the form of LDPE and PP is still ongoing to study potential synergistical benefits that include hydrogen transfer which should aid deoxygenation and improve on the quality and yield. To date, this work has been presented at some renowned conference proceedings and work is on-going to publish some articles related to this project.



Conference presentations:

- Integration of different strategies to increase the bio-oil quality and yield during fluidized bed fast pyrolysis of lignocellulosic biomass, 20th CIRIAF National Congress April 2020.
- High-quality bio-oil production via fluidized bed fast pyrolysis of biomass, 8th International symposium on energy from biomass and waste (Venice virtual) / 16 - 19 November 2020.
- Torrefaction and catalytic pyrolysis of olive stone to produce high quality bio-oils, European Combustion Meeting 2021/ 14-15 April 2021
- Catalytic co-pyrolysis of residual biomass and waste plastics to produce drop-in alternative hydrocarbons, 29th European Biomass Conference & Exhibition/ 26-29 April 2021.

Elvis Tinashe Ganda, PhD student XXXIV cycle, May 2021