MICROWAVE-INDUCED PYROLYSIS OF WASTE AUTOMOTIVE OIL

UNIVERSITY OF CAMBRIDGE

SU SHIUNG LAM

DOCTOR OF PHILOSOPHY (PhD)
IN
CHEMICAL ENGINEERING

2011

Microwave-induced Pyrolysis of Waste Automotive Oil

Su Shiung Lam

Clare Hall College

A Dissertation Submitted for the Degree of Doctor of Philosophy

Department of Chemical Engineering and Biotechnology

University of Cambridge

December 2011

Kate Maxwell PhD
Secretary of the Board of Graduate Studies

Mr S.S. Lam
Universiti Malaysia Terengganu
Department of Engineering Science
Faculty of Science and Technology
Kuala Terengganu
Trengganu
21030
Malaysia

UNIVERSITY OF CAMBRIDGE
Board of Graduate Studies

May 8, 2012

When replying please quote:
300818398/ccltrb02/resa1

Dear Mr Lam

Approval for the PhD Degree

I am delighted to tell you that the Board of Graduate Studies, on the recommendation of the Degree Committee for the Faculty concerned, have agreed to approve you for the PhD Degree.

Please note that you will not actually receive the degree until it has been conferred on you, either in person or in your absence, at a Congregation of the Regent House. You should therefore get in touch as soon as possible with the Praelector of your College to arrange for this to be done. Your degree certificate will be issued only after the degree has been conferred.

I enclose a copy of your Examiners' reports which have also been sent to your Supervisor.

May I extend my warmest congratulations.

Yours sincerely

Kate Maxwell
Secretary of the Board of Graduate Studies

Copy to: Supervisor: Professor H.A. Chase
Department of Chemical Engineering
New Museums Site
Pembroke Street
Cambridge
CB2 3RA

4 Mill Lane, Cambridge CB2 1RZ
Telephone: +44 1223 766302
Fax: +44 1223 338398
student.registry@admin.cam.ac.uk
http://www.admin.cam.ac.uk/offices/gradstud/exams/

FORM PhD2
for use on first examination of a PhD thesis

UNIVERSITY OF CAMBRIDGE
Board of Graduate Studies

Examiners' joint report and recommendation

(to be completed *after* the oral examination)

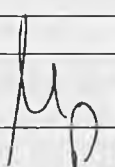
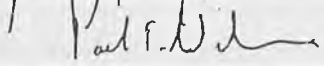
Candidate	Examiners	Date of report
Su Shiung Lam	Prof Markus Kraft PROF PAUL T. WILLIAMS	8/Mar/2012

1. Please write your **Joint Report** of the Oral examination below; if you prefer to attach the report on a separate sheet, please sign and date the sheet.
2. Please complete the **Recommendation** form overleaf

Both examiners agreed in their individual reports that the dissertation represents a solid piece of work, which shows novelty and originality. It clearly satisfies the requirements for a PhD. During the viva Mr Lam demonstrated that he conducted the work described in his thesis himself. He was able to answer the majority of the examiners' questions to their full satisfaction.
He defended his work well in all respects. In conclusion we recommend that the candidate be approved for the degree of PhD.

If your have written your report on this sheet, please now **sign and date** this form and submit it, together with your independent reports and other papers to the Degree Committee office after the oral examination.

This Form **will be made available to the candidate and their supervisor** when the Board of Graduate Studies communicates the result to the candidate.

Signed		Date
Internal Examiner		8/Mar/2012
External Examiner		8/3/12

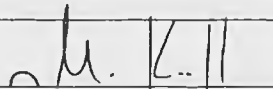
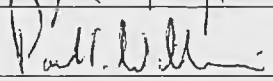
Please turn over

Joint Recommendation

Please indicate your joint recommendation by circling the appropriate number on the table below; you may wish to refer to the *Guide to Examiners* for guidance.

N.B. If you do not agree in your recommendation, or if this recommendation differs from those in either of your Independent Reports, please see the *Guide to Examiners* for instructions on how to proceed.

The thesis is satisfactory for the award of the Ph.D. Degree	
(1)	*Approved* for the Ph.D. Degree *without correction* ✓
2	Approved for the Ph.D. Degree subject to *minor or straightforward corrections* • If the corrections have already been made to your satisfaction, please initial and date here (either or both Examiners) [ ] • If corrections are to be completed in future, please indicate which Examiner(s) will be responsible for checking them: Internal/External/both (delete as appropriate)
3	*Approved* for the Ph.D. Degree subject to *more substantial, or less straightforward, corrections* • Please indicate which Examiner(s) will be responsible for checking them: Internal/External/both (delete as appropriate)
The thesis requires revision such that we are unable to recommend the awarding of the Ph.D. Degree without a fresh examination of a revised thesis	
4	*Allowed to Revise and resubmit* the thesis for examination for the *Ph.D. Degree*
5	*Allowed to Revise and resubmit* the thesis for examination for the *Ph.D. Degree* or *accept the MSc./M.Litt. Degree without further revision* • Please indicate whether *corrections* are required for the awarding of the lesser degree and which examiner(s) will be responsible for checking them: corrections are/are not required Internal/External/both (delete as appropriate)
The candidate is not to be approved for the Ph.D. Degree and not allowed to submit a revised thesis for the Ph.D. Degree *(the following recommendations should be used only in very exceptional cases on a first examination)*	
6	*Not be allowed to revise the thesis for the Ph.D. Degree* but offered the *MLitt or MSc without further revision or examination of the thesis* • Please indicate whether *corrections* are required for the awarding of the lesser degree and which examiner(s) will be responsible for checking them: corrections are/are not required Internal/External/both (delete as appropriate)
7	*Not be allowed to revise the thesis for the Ph.D. Degree* but to be allowed to *revise the thesis for the MLitt or MSc* only
8	*Not be approved nor allowed to revise the thesis for* any *degree* - outright failure

Signed		Date
Internal Examiner		8/Mar/2012
External Examiner		8/3/12

FORM PhD1
for use on first examination of a PhD thesis

UNIVERSITY OF CAMBRIDGE
Board of Graduate Studies

Examiner's independent report and recommendation

(to be completed *before the* oral examination)

Candidate	Examiner	Date of report
Su Shiung Lam	Prof Markus Kraft	7/Mar 2012

1. Please attach this form to your **Independent Report** on the thesis; please sign and date the report. Please note that **your report will be made available to the candidate and their supervisor** when the Board of Graduate Studies communicates the result to the candidate

2. Please indicate your pre-oral recommendation by circling the appropriate number on the table below; you may wish to refer to the *Guide to Examiners* for guidance.

The thesis is satisfactory for the award of the Ph.D. Degree	
(1)	*Approved* for the Ph.D. *without correction*
2	*Approved* for the Ph.D. subject to *minor or straightforward corrections*
3	*Approved* for the Ph.D. subject to *more substantial, or less straightforward, corrections*
The thesis requires revision such that I am unable to recommend the awarding of the Ph.D. Degree without a fresh examination of a revised thesis	
4	*Allowed to Revise and resubmit* the thesis for examination for the Ph.D. Degree
5	*Allowed to Revise and resubmit* the thesis for examination for the Ph.D. Degree **or** *accept the MSc./M.Litt. Degree* without further revision
The candidate is not to be approved for the Ph.D. Degree and not allowed to submit a revised thesis for the Ph.D. Degree	
6	*Not be allowed to revise the thesis for the Ph.D. Degree but offered the MLitt or MSc without further revision or examination of the thesis*
7	*Not be allowed to revise the thesis for the Ph.D. Degree but to be allowed to revise the thesis for the MLitt or MSc only*
8	*Not be approved nor allowed to revise the thesis for* any *degree* - outright failure
9	**I wish to reserve judgement on the outcome till after the oral examination**

Please now **sign and date** this form and submit it, together with the other papers, to the Degree Committee office after the oral examination.

Signed	Date 7/Mar/2012

Examiner's Report on the PHD Thesis of Su Shiung Lam : Microwave-induced Pyrolysis of Waste Automotive Oil

Examiners Report:

The thesis deals with the development and investigation of microwave pyrolysis for the recycling of used automotive engine oil in the presence of a bed of particulate carbon.

Chapter 1 motivates the work discussing the current disposal methods of automotive engine oil and microwave pyrolysis. The chapter ends by stating the objectives and describing the structure of the thesis. **Chapter 2** reviews the literature. Aspects of automotive engine oil, pyrolysis of waste oils and microwave heating that are relevant to the study are discussed. **Chapter 3** reports on a detailed study of waste oil pyrolysis in semi-batch operation. The experimental procedure and the analytic methods are described in some detail. The reaction products are characterised with respect to product yield and composition. In particular the role of temperature is discussed. The investigations serve as a pre-study for the continuous operation which is investigated in **Chapter 4.** First the modification and improvement of the experimental rig for continuous operation are described. Methods and materials are similar to the semi-batch operation. However, the role of PAHs and metallic particles present in the oil are studied in more detail. A sensitivity study of the effect of the process parameters on yield and composition of the pyrolysis products complete this chapter. **Chapter 5** focuses on the role of the carbon reaction bed on the pyrolysis. In particular, the catalytic effects of carbon are investigated. These effects result in a shift to smaller pyrolysis products. The product yield is investigated with respect to the amount of particulate carbon in the bed and the presence of pyrolysis char.

Chapter 6 contains a general discussion of the results. Possible reaction mechanisms for the thermal decomposition of waste oil as well as heterogeneous reaction mechanisms for the production of gaseous products are discussed. In addition the microwave pyrolysis is compared to electrically heated conventional pyrolysis and an energy balance is derived.

In **Chapter 7** the project is reviewed and future work is discussed.

The thesis is well written and contains very few spelling mistakes or formal errors. The PhD represents a solid piece of chemical engineering. It contains novel aspects and it is original. The pyrolysis of waste oil has been carefully investigated and the operation in the bench apparatus is now understood well enough to be taken to a pilot level. Modifying the rig to continuous operation is the most important engineering contribution described in the thesis. There are attempts to understand the underlying chemical process of the pyrolysis reactions. However, there is wealth of information which has not been considered.

In conclusion I think that the candidate contributed significantly towards the understanding of microwave based pyrolysis of waste oils and should be awarded with a PhD subject to a satisfactory oral examination.

Professor Markus Kraft

Wednesday, 07 March 2012

Department of Chemical Engineering and Biotechnology
University of Cambridge
Pembroke Street
Cambridge CB2 3RA
UK
Tel. +44 (0)1223 762784
Email: mk306@cam.ac.uk

FORM PhD1
for use on first examination of a PhD thesis

UNIVERSITY OF CAMBRIDGE
Board of Graduate Studies

Examiner's independent report and recommendation
(to be completed *before the* oral examination)

Candidate	Examiner	Date of report
SU SHIUNG LAM	PROFESSOR PAUL T. WILLIAMS	6/3/12

1. Please attach this form to your **Independent Report** on the thesis; please sign and date the report. Please note that **your report will be made available to the candidate and their supervisor** when the Board of Graduate Studies communicates the result to the candidate

2. Please indicate your pre-oral recommendation by circling the appropriate number on the table below; you may wish to refer to the *Guide to Examiners* for guidance.

The thesis is satisfactory for the award of the Ph.D. Degree	
1	*Approved* for the Ph.D. *without correction* ✓
2	*Approved* for the Ph.D. subject to *minor or straightforward corrections*
3	*Approved* for the Ph.D. subject to *more substantial, or less straightforward, corrections*
The thesis requires revision such that I am unable to recommend the awarding of the Ph.D. Degree without a fresh examination of a revised thesis	
4	*Allowed to Revise and resubmit* the thesis for examination for the Ph.D. Degree
5	*Allowed to Revise and resubmit* the thesis for examination for the Ph.D. Degree **or** *accept the MSc./M.Litt. Degree* without further revision
The candidate is not to be approved for the Ph.D. Degree and not allowed to submit a revised thesis for the Ph.D. Degree	
6	*Not be allowed to revise the thesis for the Ph.D. Degree but offered the MLitt or MSc without further revision or examination of the thesis*
7	*Not be allowed to revise the thesis for the Ph.D. Degree but to be allowed to revise the thesis for the MLitt or MSc only*
8	*Not be approved nor allowed to revise the thesis for* any *degree* - outright failure
9	**I wish to reserve judgement on the outcome till after the oral examination**

Please now **sign and date** this form and submit it, together with the other papers, to the Degree Committee office after the oral examination.

Signed	Date 6/3/12

Dissertation Title: Microwave-induced pyrolysis of waste automotive oil.

Candidate: Su Shiung Lam

PhD Thesis Report

The thesis describes research on the use of microwave pyrolysis of waste automotive oil to produce a product pyrolysis oil of potential use as a transport grade fuel. The investigation was an experimental study using a batch microwave pyrolysis reactor, followed by development of a continuous microwave pyrolysis system. A range of process parameters were investigated to determine their influence on the product yield and composition from the microwave pyrolysis of used automotive engine oil.

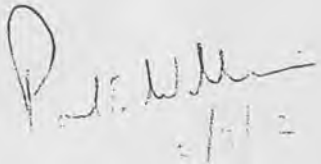
The introduction sets the scene well and is followed by a concise literature review of the pyrolysis process and microwave processing. The experimental chapter is comprehensive explaining the steps involved in the development of the batch and continuous microwave systems and the range of analytical systems used. The later chapters present and discuss the results obtained, including a research outcomes overview and comprehensive and detailed proposals for future research.

The work is original and advances the field of research by detailing the influence of the various process parameters on the products, particularly the pyrolysis oil, derived from the microwave process. The work shows for the first time the range of gases produced and the their yield and composition from microwave pyrolysis under a range of temperatures, oil feed rates, and nitrogen purge rates. The main product pyrolysis oil is analysed in detail using a range of fuel testing and analytical chemistry techniques and the composition of the oil and influence of the various process parameters is reported for the first time in the literature. The oil analysis also includes an analysis of the hazardous polycyclic aromatic hydrocarbons and trace metals present in the pyrolysi oil and an assessment of the hazard involved. The results are discussed in detail and set in context and compared with the composition of products form 'conventional' thermal pyrolysis. The detailed discussion of the data also includes an in-depth analysis and discussion of the fundamental mechanisms involved in the formation of the chemical species present in the product oils. Also investigated and reported is a full energy balance for the process. The work has developed a bench scale continuous microwave pyrolysis process using a novel carbon reaction bed and has demonstrated the potential of the process for scale-up.

There is very little in the existing literature on the microwave pyrolysis of waste engine oils and a demonstration of the novelty and originality of the work is the publication of 6 journal papers and 9 oral/poster conference presentations. The work is published in high impact journals in the field, such as, Energy, International Journal of Hydrogen Energy, Fuel, Industrial & Engineering Chemistry Research. This is a remarkable output for an engineering PhD!

The thesis is very well structured and presented and well written with a very good logical and literary style.

Overall this is an excellent PhD thesis, the research is of the highest academic standard and the candidate demonstrates a thorough understanding of the area of research. The overall discussion of the results obtained and the future work proposed to take the research forward was very considered and showed academic insight of high quality.



Summary

This dissertation describes the development and analysis of the use of microwave heating to power a pyrolysis process (termed "microwave pyrolysis") for the recycling of used automobile engine oil. By pyrolysing the waste oil in a modified microwave oven in the presence of a bed of particulate-carbon as the microwave-absorbent, hydrocarbons (of smaller molecular size than those present in the waste oil) and H_2 are generated and these have potential for use as either an energy source or industrial feedstock. The method was examined for its suitability for processing waste oil by investigating the effects of various process parameters on the yields and properties (chemical and physical) of the products formed.

The pyrolysis generated a high yield of a condensable oil product that contains substantial concentrations of potentially valuable light aliphatic and aromatic hydrocarbons, and with fuel properties comparable to transport-grade fuels. The oil product showed a high recovery of the calorific value present in the waste oil, is relatively contaminant free with a low content of sulphur, oxygen, polycyclic aromatic hydrocarbons, and residue, and is almost entirely free of metals. The process also produced an incondensable gaseous product that contains light aliphatic hydrocarbons and syngas that could potentially be used as gaseous fuel. Additionally, the pyrolysis generated a char product with a high surface area and contained the majority of metals originally present in the waste oil, providing a convenient opportunity for the efficient recovery of these metals. The char can be readily separated from the particulate-carbon particles by sieving, and the particulate-carbon bed can be repeatedly re-used. The microwave apparatus was operated with an electrical power input of 7.5 kW and was capable of processing waste oil at a flow rate of 1 kg/h with a positive energy ratio of 4 (energy content of hydrocarbon products/electrical energy supplied for microwave heating).

The product compositions, which are different to those formed in conventional pyrolysis of oils, can be attributed to the unique heating mode and the chemical environment present during microwave pyrolysis, and chemical mechanisms for the production of the various products are proposed. Overall, this study demonstrates that microwave pyrolysis offers an exciting new approach to treat and transform the waste oil into valuable hydrocarbon feedstocks and gases.