Rumpun Ilmu	: Teknik Kimia
Bidang Kepakaran	: Chemical Engineering
Jenis Riset	: Dasar

LAPORAN AKHIR
SKEMA PENELITIAN DASAR

PENGEMBANGAN BIOFUEL DAN CHEMICALS DARI PIROLISIS LIMBAH PADAT PENGOLAHAN KELAPA SAWIT (LPPKS) UNTUK PENGUATAN GREEN ECONOMY DALAM MENDUKUNG KEMANDIRIAN ENERGI DAN PENYEDIAAN BAHAN KIMIA

TIM PENELITI :

Ketua : SITI JAMILATUN, Dr. Ir., M.T.

Anggota : 1. Dr. Dhias Cahya Hakika, S.T., M.Sc.

Mahasiswa Terlibat : 1. Dwita Sarah (1900020090)
2. Joko Pitoyo (2107054001)
3. Anggun Puspitasari (1900020093)

TEKNIK KIMIA
TEKNOLOGI INDUSTRI
UNIVERSITAS AHMAD DAHLAN
JANUARI 2023

COVER LETTER
LAPORAN KEMAJUAN PENELITIAN TA. 2022/2023

Ketua Peneliti   :   SITI JAMILATUN, Dr. Ir., M.T.

Judul Penelitian   :   Pengembangan Biofuel dan Chemicals dari Pirolisis Limbah Padat Pengolahan Kelapa Sawit (LPPKS) untuk Penguatan Green Economy dalam mendukung Kemandirian energi dan Penyediaan Bahan Kimia

Hari, Tanggal Review   :   Senin, 02 Januari 2023

No.	Kriteria (Indikator Penilaian)	Komentar Reviewer	Isi Perbaikan
1.	A. Ringkasan penelitian berisi: (i) latar belakang penelitian, (ii) tujuan penelitian, (iii) tahapan metode penelitian, (iv) luaran yang ditargetkan, (v) uraian TKT penelitian yang ditargetkan serta (vi) hasil penelitian yang diperoleh sesuai dengan tahun pelaksanaan penelitian.	luaran dan hasil penelitian disampaikan sesuai yang dilaksanakan	Sudah ditambahkan
2.	B. Kata kunci maksimal 5 kata kunci. Gunakan tanda baca titik koma (?) sebagai pemisah, dan ditulis sesuai urutan abjad.	Gunakan tanda baca titik koma (;) sebagai pemisah, dan ditulis sesuai urutan abjad	Sudah diperbaiki
3.	C. Hasil pelaksanaan penelitian berisi: (i) kemajuan pelaksanaan penelitian yang telah dicapai sesuai tahun pelaksanaan penelitian, (ii) data yang diperoleh, (iii) hasil analisis data yang telah dilakukan, (iv) pembahasan hasil penelitian, serta (v) luaran yang telah didapatkan. Seluruh hasil atau capaian yang dilaporkan harus berkaitan dengan tahapan pelaksanaan penelitian sebagaimana direncanakan pada proposal. Penyajian data dan hasil penelitian dapat berupa gambar, tabel, grafik, dan sejenisnya, serta pembahasan hasil penelitian didukung dengan sumber pustaka primer yang relevan dan terkini.	Data dan pembahasan variasi jumlah katalis terhadap yield dan komposisi bio-oil (dengan dan tanpa katalis silika-alumina) belum dilaporkan	Sudah ditambahkan
4.	D. Status luaran berisi identitas dan status ketercapaian setiap luaran wajib dan luaran tambahan (jika ada) yang dijanjikan. Jenis luaran dapat berupa publikasi, perolehan kekayaan intelektual, hasil pengujian atau luaran lainnya yang telah dijanjikan pada proposal. Uraian status luaran harus didukung dengan bukti kemajuan ketercapaian luaran sesuai dengan luaran yang dijanjikan. Lengkapi isian jenis luaran yang dijanjikan serta mengunggah bukti dokumen ketercapaian luaran wajib dan luaran tambahan melalui portal penelitian.	Luaran wajib dan tambahan belum tercapai	Sudah disesuaikan
5.	E. Peran Mitra berupa realisasi kerjasama dan kontribusi Mitra baik in-kind maupun in-cash (untuk Penelitian Terapan dan Pengembangan). Bukti pendukung realisasi kerjasama dan realisasi kontribusi mitra dilaporkan sesuai dengan kondisi yang sebenarnya. Bukti dokumen realisasi kerjasama dengan Mitra diunggah melalui portal penelitian.	tidak ada mitra	PD tdk ada mitra

6.	F. Kendala Pelaksanaan Penelitian berisi kesulitan atau hambatan yang dihadapi selama melakukan penelitian dan mencapai luaran yang dijanjikan.	tidak ada kendala	Tidak ada kendala
7.	G. Rencana Tahapan Selanjutnya berisi tentang rencana penyelesaian penelitian dan rencana untuk mencapai luaran yang dijanjikan jika belum tercapai.	menambah data variasi jumlah katalis dan mengusahakan luaran sesuai yang dijanjikan	Sudah ditambahkan
8.	H. Daftar Pustaka disusun dan ditulis berdasarkan sistem nomor sesuai dengan urutan pengutipan. Hanya pustaka yang disitasi/diacu pada laporan kemajuan saja yang dicantumkan dalam Daftar Pustaka.	sesuai	Sudah sesuai

Penilaian/Review Luaran Penelitian

No.	Komponen	Kriteria	Komentar Reviewer
1.	Identitas Luaran	Lengkap / Tidak lengkap	
2.	Status Luaran	Memenuhi / Tidak	
3.	Bukti Status Luaran	Ada / Tidak	
4.	Bukti Luaran / File	Ada / Tidak	
5.	URL / Link Luaran	Dapat diakses menuju luaran/tidak	

PENELITIAN DANA INTERNAL UAD
TAHUN AKADEMIK 2022/2023

A. DATA PENELITIAN

1. Identitas Penelitian

a. NIY/NIP : 60960133

b. Nama Lengkap : Dr. Ir. SITI JAMILATUN, M.T.

c. Judul : Pengembangan Biofuel dan Chemicals dari Pirolisis Limbah Padat Pengolahan Kelapa Sawit (LPPKS) untuk Penguatan Green Economy dalam mendukung Kemandirian energi dan Penyediaan Bahan Kimia

d. Lokasi Penelitian : Laboratorium Proses Teknik Kimia UAD

e. Lama Penelitian : 7 Bulan

f. Tanggal Mulai : 02 Juli 2022

g. Tanggal Rencana Selesai : 31 Januari 2023

2. Skema Penelitian

a. Skema Penelitian : Internal - Penelitian Dasar

b. Jenis Riset : Dasar

c. Tingkat Kesiapterapan Teknologi (TKT) : 3

d. Tujuan Sosial Ekonomi (TSE) : 06.02-Renewable energy

e. Bidang Kepakaran : Chemical Engineering

f. Bidang Fokus : Energi Terbarukan dan Lingkungan

g. Tema Penelitian : Waste to Energy

h. Topik Penelitian : Kajian energi dan lingkungan produk subtitusi bahan bakar (biomassa padat maupun cair)

i. Renstra Penelitian : Program Studi

j. Rumpun Ilmu : Teknik Kimia

B. SUBSTANSI PENELITIAN

Data Mitra

a. Nama Mitra :

b. Alamat Mitra :

C. ANGGOTA PENELITIAN

1. Anggota Internal

Nama Anggota Internal : 1. Dr. Dhias Cahya Hakika, S.T., M.Sc.

2. Anggota Mahasiswa

Nama Anggota Mahasiswa : 1. Dwita Sarah (1900020090)
2. Joko Pitoyo (2107054001)
3. Anggun Puspitasari (1900020093)

3. Anggota Eksternal

Nama Anggota Eksternal : -

LAPORAN AKHIR PENELITIAN

Ringkasan Penelitian, **terdiri dari 250-500 kata,** berisi: latar belakang penelitian, tujuan penelitian, tahapan metode penelitian, luaran yang ditargetkan, uraian TKT penelitian yang ditargetkan serta hasil penelitian yang diperoleh sesuai dengan tahun pelaksanaan penelitian.

RINGKASAN

Target pemerintah untuk menjaga cadangan energi dengan bauran energi baru terbarukan (EBT) pada tahun 2025 sebesar 23%, seperempatnya direncanakan dari bahan bakar nabati (BBN)[1-3]. Produksi EBT berupa bahan bakar nabati banyak bergantung pada pengolahan kelapa sawit, merupakan salah satu komoditas perkebunan yang memiliki peran strategis dalam pembangunan ekonomi Indonesia [1-2]. Sebagai penghasil kelapa sawit terbesar di dunia, maka dalam pengolahannya akan menyisakan limbah cair dan limbah padat yang sangat besar yakni lebih dari 45 % dari kelapa sawit yang diolah. Pemanfaatan limbah padat pengolahan kelapa sawit (LPPKS) berupa tandan kosong dan LPPKS melalui proses pirolisis dapat menghasilkan bahan-bahan kimia (chemicals) dan biofuel (bio-oil, gas dan char) [4-6]. Bio-oil dapat diolah menjadi chemicals dan bahan bakar, gas sebagai bahan bakar, sedangkan char dapat diolah sebagai adsorben untuk berbagai macam keperluan [7]. Dalam aplikasinya sebagai bahan bakar maka bio-oil perlu di upgrading dengan cara pirolisis menggunakan katalis [8-10]. Pengurangan senyawa oksigenat dalam bio-oil akan meningkatkan potensinya untuk diolah lebih lanjut menjadi bahan bakar. Adapun komposisi senyawa dalam bio-oil hasil pirolisis tanpa katalis dan dengan katalis sangat menentukan penggunaan selanjutnya [11-12].

Tujuan penelitian ini adalah (1) untuk mengetahui pengaruh suhu dan jumlah katalis berbasis Nickel dalam pirolisis terhadap yield produk dan komposisi senyawa dalam bio-oil. (2) Produk pirolisis LPPKS berupa bio-oil perlu dianalisis ultimate, proksimate, dan nilai kalor. (3) Tujuan lainnya adalah untuk mengidentifikasi *chemicals* dalam bio-oil yang berpotensi dimanfaatkan untuk keperluan di industri kimia.

Metode Penelitian meliputi empat Langkah. (1) Persiapan bahan baku. Menghaluskan LPPKS, mengayak dengan ukuran 80-100 mesh kemudian mengeringkan dalam oven pada suhu 105 ∘C selama 2 jam dan dianalisis proksimate, ultimate, nilai kalor. (2) Persiapan peralatan pirolisis. Reaktor pirolisis adalah reaktor *fixed-bed* berbentuk silinder vertikal terbuat dari stainless steel dengan pemanas yang terbuat dari kawat nikel yang dililitkan pada bagian luar reaktor. Reaktor dilengkapi *thermocouple* dan *temperature control*. (3) Proses pirolisis dilakukan dengan memasukkan LPPKS dan katalis ke dalam reaktor dengan kisaran berat katalis 5 - 25 wt.%, kemudian dilakukan pemanasan. (4) Analisis produk: Produk bio-oil dianalisa dengan GC-MS, dan *Bomb Calorimeter*.

Dari hasil penelitian pirolisis LPPKS pada 300-600°C diperoleh produk cair dengan katalis mengandung phenol dan turunannya yang sangat tinggi (60-70%), sedangkan tanpa katalis 23-29,90%. Yield produk cair tanpa katalis lebih tinggi (39-42 wt.%) dibandingkan dengan katalis (23-39 wt.%).

Luaran yang diharapkan. Luaran wajib adalah artikel dalam jurnal Elkawnie Sinta 2 atau yang setara dan luaran tambahan adalah artikel di jurnal Agroindustrial Technology Journal Sinta 5 atau yang setara.

Uraian TKT Penelitian. Dalam penelitian akan dilakukan pirolisis limbah padat pengolahan kelapa sawit dengan pengaruh suhu dan jumlah katalis terhadap yield dan komposisi bio-oil (dengan dan tanpa katalis berbasis Nickel). Hasilnya adalah penentuan yield tertinggi dan komposisi senyawa dalam bio-oil dengan TKT Level 3.

> **Kata kunci** maksimal 5 kata kunci. Gunakan tanda baca titik koma (;) sebagai pemisah dan ditulis sesuai urutan abjad.

Kata kunci 1; Limbah padat pengolahan kelapa sawit 2; Pirolisis 3; Bio-oil 4; Energi Baru Terbarukan 5; *Chemicals*

> **Hasil dan Pembahasan Penelitian**, **terdiri dari 1000-1500 kata,** berisi: (i) kemajuan pelaksanaan penelitian yang telah dicapai sesuai tahun pelaksanaan penelitian, (ii) data yang diperoleh, (iii) hasil analisis data yang telah dilakukan, (iv) pembahasan hasil penelitian, serta (v) luaran yang telah didapatkan. Seluruh hasil atau capaian yang dilaporkan harus berkaitan dengan tahapan pelaksanaan penelitian sebagaimana direncanakan pada proposal. **Penyajian data** dan **hasil penelitian** dapat berupa gambar, tabel, grafik, dan sejenisnya serta didukung dengan sumber pustaka primer yang relevan dan terkini.

HASIL DAN PEMBAHASAN PENELITIAN
1. Karakterisasi bahan baku

LPPKS didapatkan dari perkebunan kelapa sawit di Kalimantan Barat. LPPKS dicuci menggunakan air bersih untuk menghilangkan pengotor. Selanjutnya dijemur di bawah sinar matahari selama 2 hari. LPPKS yang sudah dijemur selanjutnya dioven selama 24 jam untuk menghilangkan kandungan airnya sehingga didapatkan kadar air kurang dari 10%. LPPKS selanjutnya dihaluskan dengan hammer mill kemudian diayak sampai didapatkan ukuran butir 10-40 mesh. Proximat analisis dan ultimat analisis LPPKS dapat dilihat pada table 1. Sampel LPPKS terdiri dari 33.04 wt.% selulosa, 23.82 wt.% hemiselulosa, dan 45.59 wt.% lignin [10].

Tabel 1. Analisis proksimat dan ultimat LPPKS

Analisa Proksimat	Nilai (wt%)					Analisa Ultimat	Nilai (wt%)				
Moisture	5.69	7.96	12.69	9.4	11	Carbon	46.92	50.01	51.56	44.56	48.99
Volatile	69.10	72.47	75.14	82.5	67.2	Hydrogen	8.95	6.85	6.31	5.22	6.6
Fixed Carbon	23.49	18.7	22.05	1.4	19.7	Nitrogen	1.15	1.90	0.7	0.4	0.37
Ash	1.72	1.1	2.81	6.7	2.1	Sulfur	2.35	-	0.1	0.05	0.08

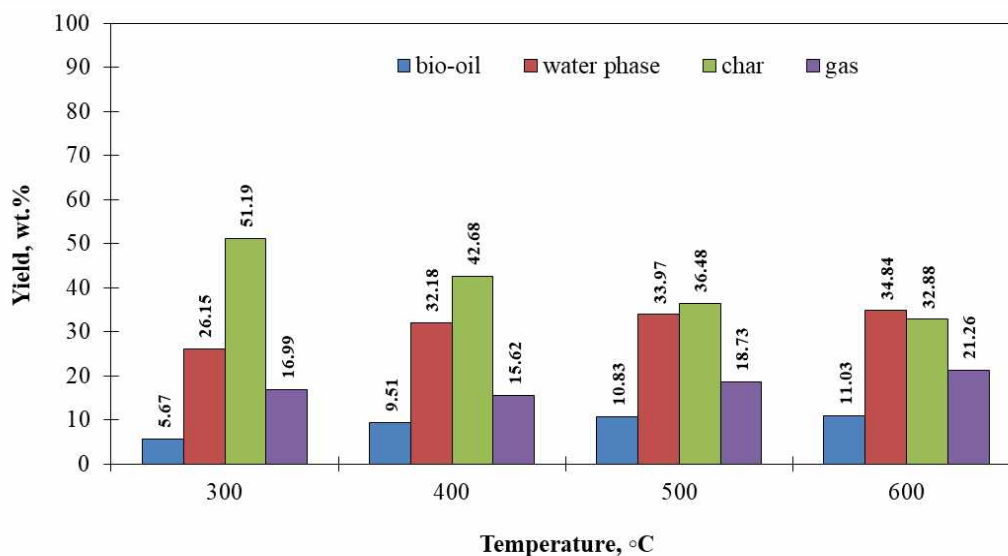|						Oksigen	40.63	41.15	41.33	49.77	43.96
Ref.	[14]	[15]	[16]	[10]	[17]		[14]	[15]	[16]	[10]	*

*Data dari penelitian ini

1. Product Yield

Penelitian ini dilakukan untuk mempelajari pengaruh suhu terhadap yield dan selektivitas komponen *phenolic* pada bio-oil [15]. LPPKS dan produk bio-oil ditunjukkan pada gambar 1, sedangkan pengaruh suhu terhadap yield ditunjukkan pada gambar 2.

Gambar 1. LPPKS dan bio-oil hasil pirolisis

Gambar 2. Produk pirolisis pada berbagai suhu

Pirolisis LPPKS pada suhu 300 sampai 600°C menghasilkan bio-oil yang meningkat dari 5.67 – 11.03 wt.%, water phase meningkat, dan produk arang yang menurun dari 51.19 pada 300°C

menjadi 32.88 wt.% pada 600°C. Sementara itu hasil gas meningkat dari 16.99 pada 300°C menjadi 21.26 wt.% pada 600°C. Kecepatan pembentukan bio-oil semakin menurun, sementara itu kecepatan pembentukan gas semakin tinggi pada suhu diatas 500°C. Hal ini disebabkan adanya reaksi pirolisis sekunder yang mengubah uap hasil reaksi cracking primer menjadi non-condensable gas (CH$_4$, CO$_2$, CO) sehingga menyebabkan turunnya jumlah bio-oil dan meningkatnya pembentukan gas [16]–[21].

2. Karakterisasi bio-oil tanpa katalis

Komposisi bio-oil hasil pirolisis LPPKS pada kisaran suhu 300 – 600°C ditunjukkan pada table 2. Hasil analisis GC-MS menunjukkan bahwa bio-oil hasil pirolisis LPPKS pada suhu 300°C tersusun atas komponen phenolic (dengan komponen utama phenol dan guaiacol), asam (dengan komponen utama 9-Octadecenoic acid, 2-(octadecyloxy) ethyl ester dan 9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester), dan komponen lain (dengan komponen utama Triethylene glycol monododecyl ether). Pirolisis pada suhu 400 C menghasilkan komponen phenolic (dengan komponen utama phenol, syringol dan guaiacol), asam (dengan komponen utama asam laurat, asam myristat, dan asam palmitat), dan komponen lain (dengan komponen utama berupa hidrokarbon aromatic seperti 1,2,4- Trimethoxybenzene dan Benzene, 1,2,3-trimethoxy-5-methyl). Pirolisis pada suhu 500°C menghasilkan komponen phenolic (phenol, syringol, guaiacol, eugenol, cresol dan xylenol), asam (dengan komponen utama asam laurat, asam palmitat dan asam oleat), dan komponen lain (dengan komponen utama berupa hidrokarbon aromatic seperti 1,2,4-Trimethoxybenzene dan Benzene, 1,2,3-trimethoxy-5-methyl- dan Benzofuran, 2-methyl-). Sedangkan pirolisis pada suhu 600°C menghasilkan komponen phenolic (phenol, syringol, guaiacol, eugenol, cresol, dan xylenol), asam (dengan komponen utama asam laurat, asam palmitat dan asam oleat), dan komponen lain (dengan komponen utama 1,2,4-Trimethoxybenzene, Ethanone, 1-(2,6-dihydroxy-4-methoxyphenyl)-, Benzofuran, 2-methyl- dan terdeteksi juga hidrokarban aliphatic seperti heptadecane dan octadecane) [22].
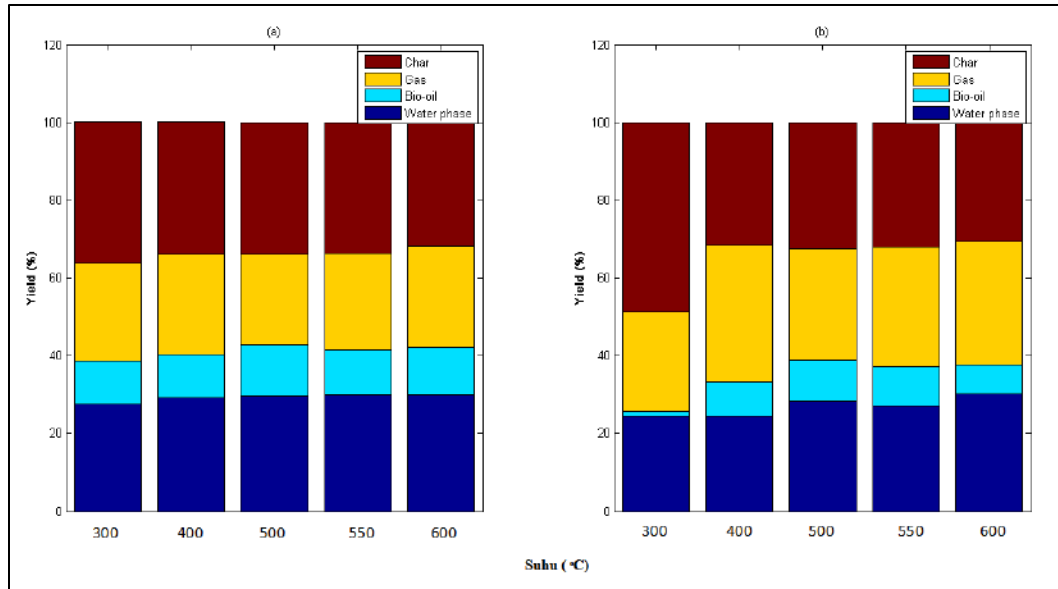
Tabel 2. Komposisi bio-oil pada berbagai suhu

Komponen (% area)	Suhu			
	300	400	500	600
Phenolics	**25.32**	**52.93**	**50.7**	**49.94**
Phenol	21.4	35.27	35.89	33.79
Phenol, 2-methoxy- (Guaiacol)	2.03	2.88	2.27	2.72
Phenol, 4-ethyl-2-methoxy- (p-Ethylguaiacol)	0.62	3.86	3.08	3.4
2-Methoxy-4-methylphenol (Creosol)	0.58	3.62	2.96	3.22
Phenol, 2,6-dimethoxy- (Syringol)		5.03	4.17	4.39
Phenol, 2,6-dimethoxy-4-(2-propenyl)- (Eugenol)		1.65	1.83	1.82
Phenol, 2-methyl- (o-Cresol)		0.41	0.33	0.39
Phenol, 2,4-dimethyl- (Xylenol)		0.21	0.17	0.21
4-Methoxy-3-(methoxymethyl) phenol	0.69			
Acids	**23.31**	**35.76**	**39.37**	**39.15**
9-Octadecenoic acid, 2-(octadecyloxy)ethyl ester	7.72			

9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester	6.12			
Docosanoic acid	3.25			
9-Octadecenoic acid (Z)-, 2-hydroxyethyl ester	2.69			
Dodecanoic acid (Lauric acid)	0.25	13.75	13.9	14.7
Hexadecanoic acid (Palmitic acid)	3.28	5	5.78	5.6
Tetradecanoic acid (Myristic acid)		5.02	5.22	5.18
Octadec-9-enoic acid (oleic acid)		3.99	5.4	5.35
2,4-Hexadienedioic acid		2.57	2.6	2.69
Octadecanoic acid		1.27	1.83	1.41
komponen lain	**51.38**	**10.11**	**10.04**	**11.35**
2-Butanone, 3,3-dimethyl-	0.62			
Ethanone, 1-(2,6-dihydroxy-4-methoxyphenyl)-	0.46			2.99
Benzofuran, 2-methyl-			1.22	1.15
Benzene, 1,2,3-trimethoxy-5-methyl-		3.06	2.88	
1,2,4-Trimethoxybenzene		5.2	4.41	5.17
1,4,7,10,13,16,19-Heptaoxa-2-cycloheneicosanone	6.87			
1-(5-Hydroxy-6-hydroxymethyl-tetrahydropyran-2-yl)-5-methyl-1H-pyrimidine-2,4-dione	5.31			
1,2-Cyclopentanedione, 3-methyl-	5.15			
1,4,7,10,13,16,19-Heptaoxa-2-cycloheneicosanone	1.87			
2,5-methanothieno[3,2-b]pyridin-3-d-8-ol,	1.24			
d,l-Xylitol, 1-O-dodecanoyl-	2.32			
Triethylene glycol monododecyl ether	10.12			
Di-(9-octadecenoyl)-glycerol	6.04			
Tridecanedial	4.08			
9-Octadecenamide, (Z)-	2.39			
Oxirane, [(hexadecyloxy)methyl]-	1.97			
(1S*,2R*,4S*,8R*)-2-Cyano-8-acetylbicyclo [3.2.1] oct-6-ene	1.57			

3. Pengaruh Suhu dan Katalis terhadap Yield Produk Pirolisis

Pirolisis menghasilkan tiga produk utama yaitu bio-oil, bio-char, dan gas. Penggunaan katalis dalam proses pirolisis akan mempengaruhi distribusi, yield, dan komposisi produk pirolisis. Gambar 3 menunjukkkan yield produk pirolisis pada berbagai suhu baik yang non-katalitik maupun katalitik.

Gambar 3. Distribusi Yield Produk Pirolisis LPPKS a) Non-katalitik b) Katalitik

Gambar 3 menunjukkan yield bio-oil tertinggi didapatkan pada suhu 500 ⁰C untuk pirolisis non-katalitik maupun pirolisis katalitik. Meningkatnya suhu dari 300⁰C menjadi 500⁰C menyebabkan kenaikan yield bio-oil pada pirolisis non-katalitik maupun pirolisis katalitik. Gambar 3 juga menunjukkan bahwa pemanasan pada suhu diatas 500⁰C menyebabkan penurunan yield bio-oil baik pada pirolisis katalitik maupun non-katalitik. Hal ini terjadi karena pemanasa diatas 500⁰C menyebabkan adanya reaksi sekunder yang mengubah komponen volatile (asam, alcohol, levoglukosan, furan) menjadi *non-condensable gas* (CH_4, CO_2, CO) atau karena adanya pemutusan rantai panjang pada komponen organic dan hidrokarbon menjadi rantai pendek sehingga tidak bisa diembunkan [23]. Gambar 3 menunjukkan juga bahwa penggunaan katalis nikel-alumina menyebabkan penurunan yield bio-oil dibandingkan dengan tanpa katalis. Hal ini terjadi karena penggunaan katalis akan menyebabkan terjadinya reaksi sekunder berupa dekomposisi molekul dengan berat molekul yang besar dan komponen organic rantai panjang yang ada dalam bentuk *condensable gas* menjadi molekul dengan berat molekul yang kecil melalui pemutusan ikatan C-C, transfer hidrogen, isomerisasi, pemutusan rantai aromatik, dan deoksigenasi menghasilkan hidrokarbon rantai pendek (C1-C4), H_2O, CO_2, dan CO sehingga akan mengurangi yield bio-oil.
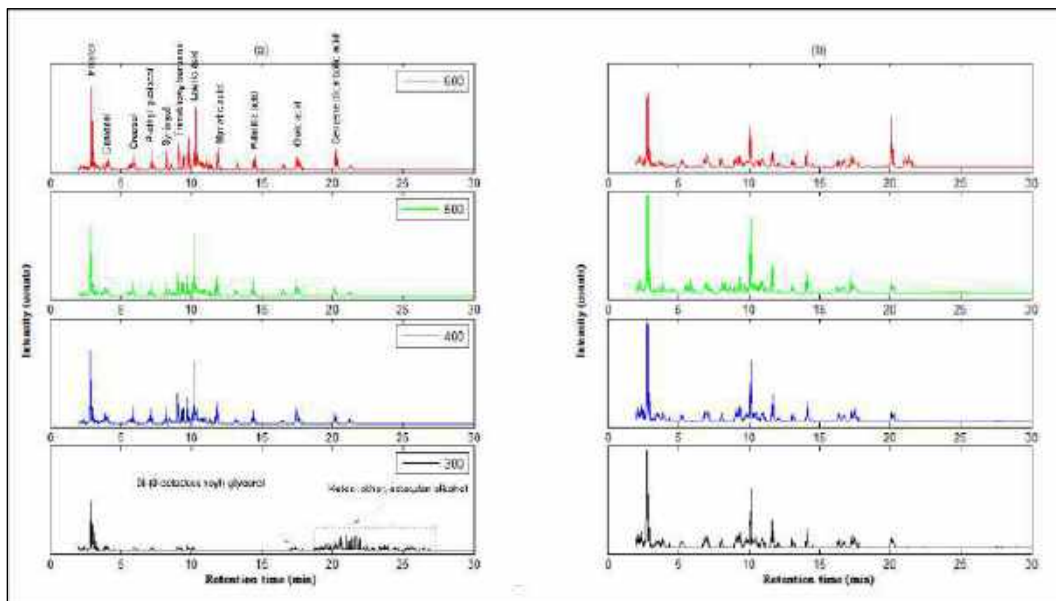
4. Karakteristik Kimia Bio-oil

Bio-oil dikenal juga sebagai *pyrolysis oil, pyrolysis liquid, pyrolysis tar, bio-crude, wood liquid, wood oil*, atau *wood distillate* [18; 19]. Bio-oil berwarna coklat gelap, berbau seperti asap, mempunyai viskositas yang tinggi, umumnya terdiri atas sejumlah besar air (15-35 wt.%) dan banyak mengandung komponen *organic seperti asam, alcohol, keton, aldehyde*, *phenol, ether, ester, furan, furfural, alkane, alkena*, komponen nitrogen dan kompleks oksigenat [19] demikian juga partikel padatan [20]. Gambar 4 menunjukkan bio-oil hasil pirolisis LPPKS.
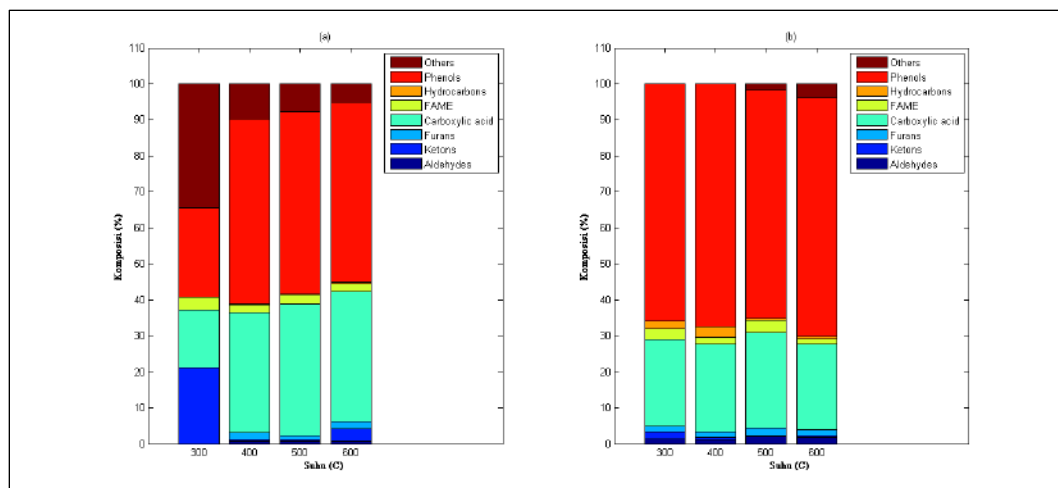
Gambar 4. Bio-oil Hasil Pirolisis dengan Warna Coklat Gelap

Gambar 5 menunjukkan *chromatogram* hasil analisis GC-MS pada suhu 300, 400, 500, dan 600°C baik untuk yang non-katalitik maupun yang katalitik.

Gambar 5. Cromatogram hasil GC-MS pada berbagai suhu a) Non-katalitik b) Katalitik

Berdasarkan Gambar 5, chromatogram menunjukkan pola yang serupa untuk berbagai suhu baik untuk yang non-katalitik maupun yang katalitik kecuali pada suhu 300°C untuk yang non-katalitik yang mana gugus fungsi keton, *ether, ester,* dan alcohol muncul dalam jumlah yang cukup signifikan yang kemudian mengalami penurunan seiring dengan naiknya suhu pirolisis. Pada retention time 2 sampai 8 menit chromatogram menunjukkan penampakan komponen phenolic (*phenol, guaiacol, creosol*, dan *syringol*). Pada retention time 8 sampai 10 menit terdapat komponen turunan phenol seperti *trimethoxy benzene*. Pada retention time 10 sampai 20 terdeteksi komponen asam karboksilat dari jenis fatty acid (asam lemak) seperti asam laurat, asam myristat, asam palmitat, dan asam oleat. Pada retention time 20 sampai 30 menit terdeteksi gugus fungsi keton, ether, ester, alkohol, dan hidrokarbon [21]. Komposisi kimia bio-oil pada berbagai suhu untuk non-katalitik dan katalitik dapat dilihat pada Gambar 6.

Gambar 6. Komposisi Kimia Bio-oil pada Berbagai Suhu a) Non-katalitik b) Katalitik

Komponen phenolik dan asam merupakan komponen yang paling dominan dalam bio-oil hasil pirolisis LPPKS. Phenol merupakan komponen terbesar pada komponen phenolic dengan persentase rata-rata sebesar 72% pada pirolisis non-katalitik dan 92% pada pirolisis katalitik. Sementara asam didominasi oleh asam karboksilat dari jenis asam lemak (*fatty acid*) seperti asam laurat, asam myristat, asam palmitat, dan asam oleat. Pembentukan asam mengalami kenaikan dari suhu 300 menjadi 400 °C, kemudian cenderung sedikit menurun pada suhu di atas 400 °C pada pirolisis non-katalitik. Kenaikan tersebut terjadi karena meningkatnya dekomposisi selulosa dan hemiselulosa melalui depolimerisasi oligosakarida menjadi xylose yang kemudian terdekomposisi lebih lanjut membentuk asam, furfural, dan furan. Penggunaan katalis Ni/Al$_2$O$_3$ meningkatkan pembentukan komponen phenol dengan kenaikan rata-rata sebesar 20% dibandingkan tanpa katalis. Hal ini disebabkan karena penggunaan katalis kemungkinan meningkatkan pemutusan rantai cabang ester asam ferulat pada *xylan* dan polimerisasi komponen rantai pendek tak jenuh (*unsaturated light component*) [22].

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Authors	Siti Jamilatun, Joko Pitoyo, Totok Eka Suharto
Title	Semi-Global Kinetic Model for Predicting Yields of Palm Shell Catalytic Pyrolysis using Fixed Bed Analysis Thermal Gravimetric (FB-TGA)
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Title and Abstract

Title	Semi-Global Kinetic Model for Predicting Yields of Palm Shell Catalytic Pyrolysis using Fixed Bed Analysis Thermal Gravimetric (FB-TGA)

Abstract	Pyrolysis is an eco-friendly and sustainable thermochemical method to convert biomass into biofuel. So far, there is no instant and accepted model for predicting the yield of pyrolysis products (tar, char, and gas) over a variety of pyrolysis conditions. This paper investigated the accuracy of the semi-global kinetic model using multi-component model-fitting techniques in predicting the product yields from palm shell pyrolysis and then develop the model based on obtained kinetic parameters. Palm shell pyrolysis was performed in a fixed-bed thermal gravimetric analysis (FB-TGA) reactor at different experimental temperatures (300, 400, 500, 550, and 600°C) in the range of heating rate of 8-12°C/min. The developed model agreed well with the experimental data both non-catalytic and catalytic. The model validation confirms that the developed model is sufficiently good to predict the yield of pyrolysis products (tar, char, and gas) at the suggested heating rate, with the RMSE value of 1.82 and 1.67 for non-catalytic and catalytic pyrolysis respectively.

Indexing

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Keywords	Pyrolysis; Biofuel; Palm Shell; Kinetic model; Fixed bed
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Semi-Global Kinetic Model for Predicting Yields of Palm Shell Catalytic Pyrolysis using Fixed Bed Analysis Thermal Gravimetric (FB-TGA)

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A B S T R A C T S

Pyrolysis is an eco-friendly and sustainable thermochemical method to convert biomass into biofuel. So far, there is no instant and accepted model for predicting the yield of pyrolysis products (tar, char, and gas) over a variety of pyrolysis conditions. This paper investigated the accuracy of the semi-global kinetic model using multi-component model-fitting techniques in predicting the product yields from palm shell pyrolysis and then develop the model based on obtained kinetic parameters. Palm shell pyrolysis was performed in a fixed-bed thermal gravimetric analysis (FB-TGA) reactor at different experimental temperatures (300, 400, 500, 550, and 600° C) in the range of heating rate of 8-12°C/min. The developed model agreed well with the experimental data both non-catalytic and catalytic. The model validation confirms that the developed model is sufficiently good to predict the yield of pyrolysis products (tar, char, and gas) at the suggested heating rate, with the RMSE value of 1.82 and 1.67 for non-catalytic and catalytic pyrolysis respectively.

A R T I C L E   I N F O

1. INTRODUCTION

High population growth coupled with increased industrial and commercial activity results in reduced fossil fuels, increased environmental pollution, global warming, and worsening health effects (Ali et al., 2017). In order to meet global energy needs in the face of this energy crisis, alternative energy sources must be explored (Ighalo & Adeniyi, 2020). Biomass is thought to be the most significant sustainable and renewable resources for the production of biofuels. It provides 14% of the world's annual energy consumption. (Dai et al., 2019).

The two significant processes for converting biomass into biofuel are biochemical and thermochemical (Van de Velden et al., 2010). The biochemical processes can convert biomass into bio-fuels, including extraction, hydrolysis, fermentation (Damartzis & Zabaniotou, 2011), and anaerobic digestion (Tyagi et al., 2018). Thermochemical processes include combustion, gasification, and pyrolysis that produce energy (Tomić et al., 2017).

Pyrolysis is the thermal decomposition in the absence of oxygen. Pyrolysis is more promising than other thermochemical conversions because it is more flexible in the selection of feedstocks, can be applied under atmospheric pressure and a wide range of temperatures, and produces three types of products (char, liquid (tar), and gas) (Terry et al., 2021). Pyrolysis gas, char, and liquid (tar) can be utilized for various purposes. Char can be used as an adsorbent, while tar and gas can be utilized as biofuel (Jamilatun et al., 2022).

Biomass pyrolysis occurs in two reaction steps, primary decomposition reactions and secondary tar decomposition reactions (**Figure 1**). Condensable gas and solid char compose the initial pyrolysis byproduct. The condensable gas further decomposed into char, liquid (tar), and non-condensable gas. (Basu, 2010).
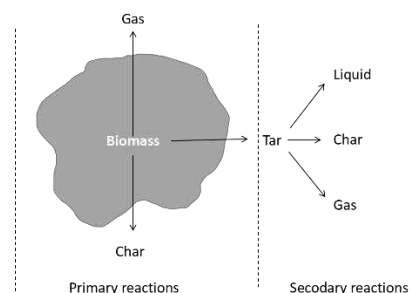

Figure 1. Thermal decomposition of biomass

As pyrolysis is an important process in the thermochemical conversion method. Comprehending the kinetics of pyrolysis is crucial for the improvement of the process, optimization, and efficient design of the reactor (Sand & Bel Fdhila, 2011). There are two basic mathematical methods to determine the kinetic parameters of biomass pyrolysis based on experimental data: iso-conventional methods and model-fitting methods (Vo et al., 2021). Model-fitting methods can be classified into one-component or multi-component mechanisms and into lumped or detailed reaction mechanisms (Di Blasi, 2008). The lumped-kinetic models for pyrolysis can be divided into two categories: global-decomposition models and multi-component decomposition models. The multi-component decomposition models were developed based on the constituents of biomass namely hemicellulose, cellulose, and lignin. Generally, these models use first-order reactions to describe the decomposition of biomass (Vo et al., 2021). A lumped model is sufficient to ascertain the kinetic parameters of pyrolysis reactions (Ranzi et al., 2001).

Semi-global decomposition models are used to explain primary and secondary tar decomposition reactions of biomass through the measurement of the rates of weight loss experimentally. The semi-global models seem to be more suitable for

reactor design and process optimization. These models describe competitive reaction schemes which allow predicting the product distribution on the dependence of reaction conditions (Di Blasi, 2008).

Numerous research have focused in the kinetics of the palm shell pyrolysis. Vo et al. (Vo et al., 2021) conducted thermogravimetry analysis (TGA) palm shell and determine the kinetic parameters using iso-conventional (FWO and KAS) methods at various heating rates (10, 20, 30 and 40° C min^{-1}). Hernowo et al. (Hernowo et al., 2022) performed pyrolysis on palm shell using a volatile state model and determine the kinetic parameters using the modified Kissinger–Akahira–Sunose (KAS) method. Safavi et al. (Safavi & Richter, 2022) carried out pyrolysis on a walnut shell and determine kinetic parameters using a competitive reaction scheme with three reactions and suggest the use of a competitive reaction scheme including secondary reaction to accurately predict the yields.

To our best knowledge, so far no kinetic study has been conducted on palm shell using semi-global reaction models which include secondary reaction mechanisms. Besides, the use of fixed bed thermal gravimetric analysis (FB-TGA) has its novelty value. FB-TGA is a fixed bed modification based on the TGA concept. The principle of the FB-TGA is a measurement of the mass loss of solid, based on the tar and gas formation. Pyrolysis using fixed bed modification based on the TGA concept in different methods has been conducted by a few researchers (Hernowo et al., 2022; Meng et al., 2015; Sand & Bel Fdhila, 2011). Therefore, this work aimed to perform the semi-global kinetic model developed by several authors (Di Blasi, 2008) to precisely calculate the kinetic parameters of palm shell pyrolysis. The purpose of this study were as follows: (1) perform pyrolysis experiments on palm shell using fixed bed thermal gravimetric analysis, (2) determine the kinetic parameters of the palm shell pyrolysis, (3) develop a kinetic model to predict tar, residue (char and remaining solid), and gas yields throughout the experimental temperatures of 300 to 600 °C.

2. METHODS

2.1. Experimental Materials
2.1.1. Palm shell

Palm shell was gathered from PT Perkebunan Nusantara V (PTPN V), Riau. The palm shell was washed using clean water to remove impurities, then dried in the sun for 2 days. The dried palm shell was then oven-dried for 24 hours to get a moisture content of less than 10%. The oven-dried palm shell was then grounded with a hammer mill and then sieved to obtain a grain size of 0.425-2.00 mm. The raw materials' elemental composition was ascertained through ultimate analysis. Before ultimate analysis, the palm shell was grounded to obtain a grain size of less than or equal to 60 mesh. CHN analyzer (Perkin Elmer 2400) was used to perform the ultimate analysis in accordance with ASTM D5291-96, while the oxygen content was determined by difference.

2.1.2. Nickel-alumina catalyst

The catalyst was obtained from PT Pupuk Kujang Cikampek in the pellets form, with a dimensions of 33 mm in diameter and 15 mm in height. The catalyst was crushed using a hammer mill. The refined catalyst was sieved to get a grain size of 0.425-2.00 mm. Catalyst analysis was performed using a Scanning Electron Microscope-Energy Disperse X-Ray (SEM-EDX) to determine the morphology (pore, rough, and shape) and element composition of the catalyst. SEM analysis

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was performed using the JSM-6510 instrument which was operated at an accelerating voltage of 15kV, a working distance (WD) of 11 mm, and a spot size (SS) of 40.

2.2. Experimental setup

2.2.1. Fixed Bed Thermal Gravimetric Analysis (FB-TGA)

The study was performed using a fixed bed thermal gravimetric analysis (FB-TGA) reactor in the form of a vertical stainless steel cylinder with an inner diameter of 40 cm, an outer diameter of 4.4 cm, and a height of 60 cm. A nickel wire-based electric heater was equipped on the reactor, and it was looped spirally around the outer of the reactor. The heating temperature was measured using a thermocouple and the heating rate was regulated using a TGDC regulator of 0.5 kva. The reactor is equipped with two vertical cylinders. The palm shell was placed in the first cylinder (R_1), and the second (R2) was for nickel-alumina catalysts. The pyrolysis gas product from R_1 flowed upward through R_2, containing the catalysts (Jamilatun, 2022).

Figure 2. Fixed bed thermal gravimetric analysis (FB-TGA) equipment

2.2.2. Procedure

Pyrolysis was carried out by placing 50 grams of palm shell into reactor R_1 for non-catalytic pyrolysis and adding 40% w/w nickel-alumina catalyst into reactor R_2 for catalytic pyrolysis. The reactor was heated at a heating rate of 10-12° C/min to the desired temperature (300, 400, 500, and 600° C). Data collection starts after the first drop of tar appears. The result of pyrolysis in the form of condensable gas (tar) was collected in a measuring cup and then weighed. Non-condensable gas flowed into a plastic bag, then the weight and volume were measured. Weighing and measurement of tar and non-condensable gas were carried out every 5 minutes after the appearance of the first drop. Residue (char and remaining solid) yields were determined by the difference. The principle of gas weighing was explained using the air buoyancy concept. Air buoyancy is the upward force applied to an

object which causes the object to weigh less. This force is equivalent to the mass of air displaced by the object. So that the weight of the gas is the sum of the weight of the air displaced by the plastic bag and the weight measured on the scale. The yields of the pyrolysis product were calculated using Equations [1-5].

$$Yt = \frac{Mt}{Ms} \times 100\% \qquad (1)$$

$$Yg = \frac{Mg}{Ms} \times 100\% \qquad (2)$$

$$Mg = Msc + Fa \qquad (3)$$

$$Fa = Vg \times \rho u \qquad (4)$$

$$Yr = 100 - Yt - Yg \qquad (5)$$

Where *Yt, Yg,* and *Yr* are the yield of tar, gas, and residue respectively. *Mt, Mg,* and *Ms* are masses of tar, gas, and solid. *Msc, Fa, Vg,* and *ρu* are mass measured on a scale, air buoyancy force, the volume of gas (plastic bag), and density of air.

2.2.3. Reaction kinetic modeling

To investigate the kinetics parameters of palm-shell pyrolysis in the fixed bed thermal gravimetric analysis (FB-TGA), a semi-global kinetic model was hypothesized. Accordingly, the raw material (palm shell) and products were classified into four lumps, namely solid, char, tar, and gas. The kinetic scheme as shown in **Figure 3** illustrates the process of pyrolysis (primary and secondary) which includes the breakdown of biomass into gas, tar, and char, and the tar continues to break down into char and gases.

Figure 3. The kinetic scheme of the semi-global model

The mass change of the components with time was modeled in the form of ordinary differential equations as shown in Equations [6-10].

$$\frac{dMs}{dt} = -(k1 + k2 + k3)Ms \qquad (6)$$

$$\frac{dMt}{dt} = k2Ms - (k4 + k5)Mt \qquad (7)$$

$$\frac{dMc}{dt} = k3Ms + k5Mt \qquad (8)$$

$$\frac{dMg}{dt} = k1Ms + k4Mt \qquad (9)$$

$$\frac{dMr}{dt} = \frac{dMs}{dt} + \frac{dMc}{dt} \qquad (10)$$

where *Ms, Mt, Mc, Mg,* and *Mr* are the mass (gr) of solid, tar, char, gas, and residue (remaining solid and char), respectively; *k1, k2, k3, k4,* and *k5* are reaction rate constants of reactions (R1), (R2), (R3), (R4), and (R5), respectively. The initial conditions for the kinetic equations are:

t =0, Ms =Mr=Ms0 , Mt=Mc=Mg =0

The reaction rate constant is formulated by Equation [11].

$$ki = Ai \exp\left(\frac{-Ei}{RT}\right) \qquad i{=}1\text{-}5 \qquad (11)$$

Where *A* is the pre-exponential factor (s^{-1}), *E* is the activation energy (kJ·mol^{-1}), *R* is the universal gas constant (kJ·K^{-1}·mol^{-1}), and *T* is the absolute temperature (K).

For non-isothermal conditions, the heating rate (β) is determined using Equation [12], where *dT* is the change of temperature (K) and *dt* is the change of time (s).

$$\frac{dT}{dt} = \beta \qquad (12)$$

On solving Equation [12], with the initial conditions t=0, T=T0 we achieve,

$$T = T0 + \beta t \qquad (13)$$

The system of ordinary differential equations in Equations [6-10] can be

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solved analytically or numerically. The analytical solutions of the kinetic equation give Equation [14-18].

$$Ms = Ms0 \, exp\{-(k1 + k2 + k3)t\} \tag{14}$$

$$Mt = \frac{Ms0 \, k2}{\{(k4+k5)-(k1+k2+k3)\}}[\exp\{-(k1 + k2 + k3)t\} - \exp\{-(k4 + k5)t\}] \tag{15}$$

$$Mc = \frac{Ms0 \, k3}{(k1+k2+k3)}[\exp\{-(k1 + k2 + k3)t\}] - \frac{Ms0 \, k2 \, k5}{\{(k4+k5)-(k1+k2+k3)\}}[\frac{1}{(k1+k2+k3)}[1 - \exp\{-(k1 + k2 + k3)t\}] + \frac{1}{(k4+k5)}[1 - \exp\{-(k4 + k5)t\}] \tag{16}$$

$$Mg = \frac{Ms0 \, k1}{(k1+k2+k3)}[\exp\{-(k1 + k2 + k3)t\}] - \frac{Ms0 \, k2 \, k4}{\{(k4+k5)-(k1+k2+k3)\}}[\frac{1}{(k1+k2+k3)}[1 - \exp\{-(k1 + k2 + k3)t\}] + \frac{1}{(k4+k5)}[1 - \exp\{-(k4 + k5)t\}] \tag{17}$$

$$Mr = Ms + Mc \tag{18}$$

$$F = \min_{p} \sum_{i=1}^{n1} \sum_{T=1}^{n2} \sum_{t}[Mi^{\exp(T,t)} - Mi^{model}(T,t)]^2 \tag{19}$$

$$TSS_{Mi} = \sum_{j=1}^{n3}(Mij - \overline{M_{ij}})^2 \tag{20}$$

$$RSS_{Mi} = \sum_{j=1}^{n3}(Mij - \widehat{M_{ij}})^2 \tag{21}$$

$$R^2{}_{Mi} = 1 - \frac{TSS_{Mi}}{RSS_{Mi}} \tag{22}$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n1} \sum_{T=1}^{n2} \sum_{t}[Mi^{\exp(T,t)} - Mi^{model}(T,t)]^2}{(n1 \, n2 \, n3)}} \tag{23}$$

An optimization tool in the Matlab software package i.e. *fminsearch* function was used to solve the Equations [14-18] simultaneously related to the change of product yields with time across overall the experimental temperatures. The objective of this optimization was to search the set of coefficients p = (A1, A2, A3, A4, A5, E1, E2, E3, E4, and E5) that minimizes the Equations [19]. Where F is the objective function, TSS_{Mi} is the total sum of squares of *Mi*, *n1, n2*, and *n3* are the number of observations of product phase, temperature, and time, respectively. *Mij* is the jth value of *Mi* from the experiment (*j*≤*n3*), $\overline{M_{ij}}$ is the mean value of *Mi* from the experiment, RSS_{Mi} is the residue sum of squares of *Mi*, $\widehat{M_{ij}}$ is the jth predicted value of *Mi* from modeling, $R^2{}_{Mi}$ is the coefficient of determination of *Mi*. *RMSE* is the root mean square error of the predicted model.
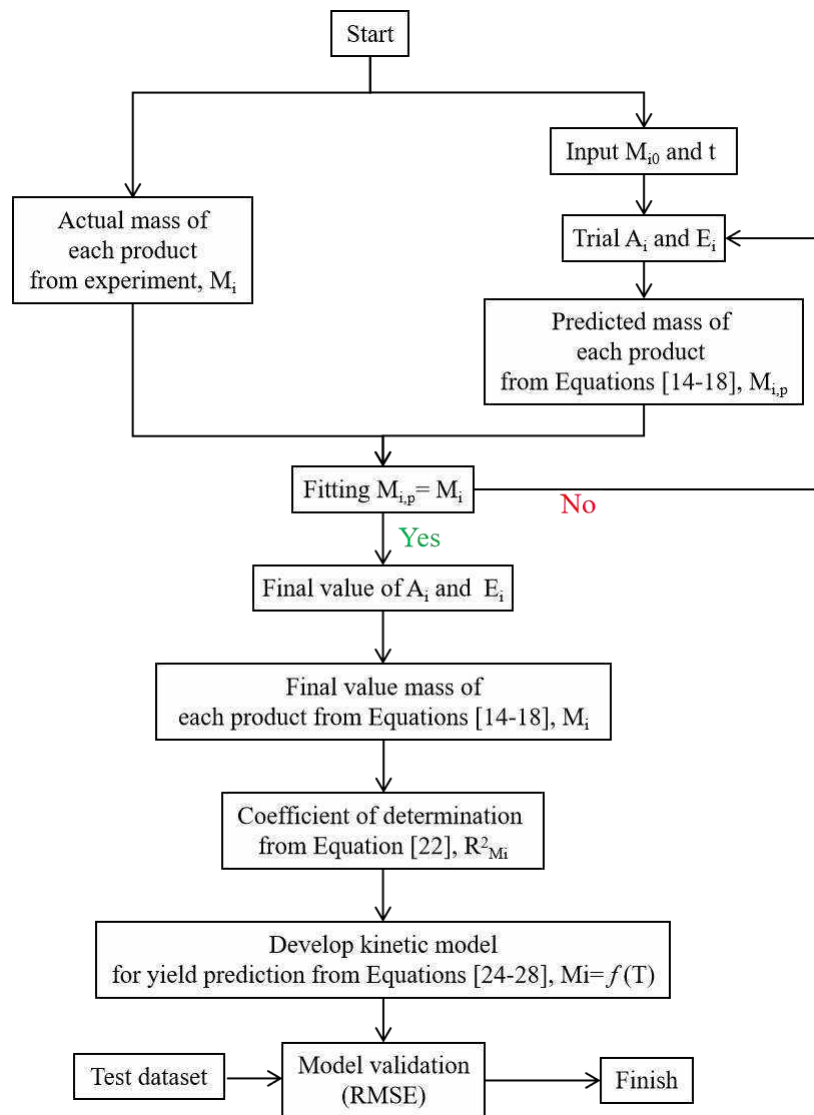
Figure 4. The flowchart to predict yields and to develop a reaction kinetic model

3. RESULTS AND DISCUSSION

3.1. Characteristics of the materials and FB-TGA

3.1.1. Palm shell

Composition, proximate and ultimate analysis of the palm shell was important to estimate the energy content in the palm shell. The result of the analysis of palm shell was shown in **Table 1** and the results of the analysis agree with other literature (Abnisa et al., 2011)(Han-U-Domlarpyos et al., 2015).

Proximate analysis of palm shell shows a high content of volatile materials in palm shell. High volatile matter content will increase the yield of bio-oil produced because high volatile matter content gives high volatility and reactivity to raw materials (Ferreira et al., 2020). The ash content (minerals) in the sample is formed by the presence of alkali metals such as K, Ca, Mg, P, and Si. Ash content has an impact on the yield of bio-oil. The high content of ash will reduce the bio-oil produced and increase the yield of char and gas produced (Pitoyo et al., 2022). High ash content can also reduce the HHV value of biomass (Ferreira et al., 2020).

Table 1. The result of composition and elemental analysis of palm shell

Proximate analysis (wt.%)	
Moisture	11
Volatile matter	67.2
Fixed Carbon	19.7
Ash	2.1
Composition analysis (wt.%)	
Cellulose	27.7
Hemicellulose	21.6
Lignin	44
Ultimate analysis (wt.%)	
C	48.99
H	6.6
N	0.37
S	0.076
O*	43.96
H/C	1.62
O/C	0.67
HHV (MJ/Kg)	24.27

Ultimate analysis of palm shell was performed to determine the chemical composition of palm shell, namely C, H, N, S, and O. The low content of nitrogen (N) and sulphur (S) in palm shell can make palm shell an eco-friendly fuel. The high index of aromatization and carbonization is indicated by the high content of hydrogen (H) and carbon (C) compared to the content of oxygen (O). A low O/C ratio gives a high higher heating value (HHV) (Braza & Crnkovic, 2014). **Table 1** shows that the oil palm shell has H/C, O/C, and HHV of 1.62, 0.67, and 24.27 respectively. The HHV in this study was higher compared to the HHV in other works (Vo et al., 2021)(Han-U-Domlarpyos et al., 2015).

Figure 5 shows the mass evolution and the derivative mass loss of palm shell pyrolysis at a heating rate of 8-12° C/min. According to the figure, palm shell pyrolysis showed a similar mass loss pattern, especially at 400, 500, 550, and 600° C, and little difference related to the value caused by the difference in heating rate, which means the equipment has good performance and more precise heating rate control is recommended. From the figure, it can be seen also that palm shell initial mass loss under five experimental temperatures starts at a range of 190-220° C. This was because the data collection starts after the appearance of the first drop of tar. There was a delay between the actual decomposition temperature and the appearance of the first drop. So the actual decomposition time was less than 190° C.
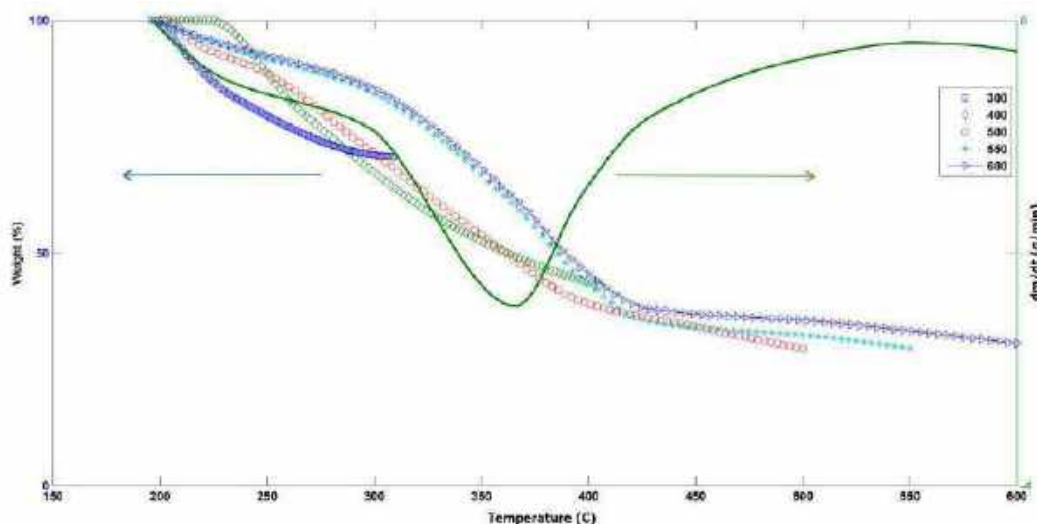

Figure 5. Mass loss evolution and derivative mass loss of palm shell pyrolysis

Palm shell is consist of complex components (cellulose, hemicellulose, and lignin), thus it can be seen that the thermal decomposition of palm shell

occurs over wide temperature range (~190-600° C). The primary temperature range of palm shell decomposition was from 300 to 420° C with the highest decomposition at 365° C. The simultaneous decomposition of cellulose, hemicellulose, and lignin was responsible for the major decomposition peak, and this was reasonable given because the decomposition temperature of hemicellulose is 250-350 ° C, the decomposition temperature of cellulose is 325-400 ° C, and whereas lignin needs a higher decomposition temperature (between 300 and 550 °C) due to its complex structural makeup (K N est al., 2022). At temperatures of 300°C, the decomposition of hemicellulose and the loss of moisture were responsible for the palm shell decomposition. The remaining component of lignin and secondary biochar decomposition might be responsible for the slow decomposition at temperatures higher than 420 C. (Aysu et al., 2016; Yang et al., 2007).

The curve of the derivative mass loss in **Figure 5** confirms the presence of one peak and the tendency to form a second peak at the temperature of 600 C. It indicates that the primary reaction occurs at the range temperature of 200-~600 C, and the secondary tar reaction occurs starting at 550 C. It is relevant to Sand et al. and Park et al., who stated that the secondary tar decomposition reaction in the palm shell and wood slow pyrolysis was confirmed at 500 ◦C (Park et al., 2010; Sand & Bel Fdhila, 2011).

3.1.2. Nickel-alumina catalyst

Nickel-alumina was characterized using SEM-EDX to determine the surface morphology and constituent components. SEM-EDX analysis shows that the catalyst consists of five components, Ni, Al, O, Na, and C (**Figure 6a)**. Ni is a metal catalyst, Al and O compose Al_2O_3 structure as catalyst support indicated by its large number. Ni loading in this catalyst is 7.36% (wt.%). Alumina (Al2O3) is a catalyst support with a large area of surface and small to medium pore diameter so as to minimize mass transfer limitations (Goula et al., 2015; Tao et al., 2010).
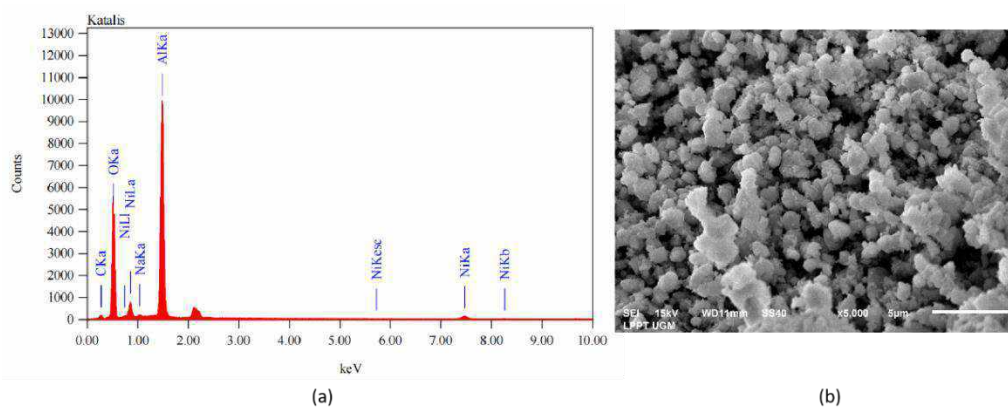

Figure 6. The result of (a) EDX analysis and (b) SEM analysis at a magnificent 5000 times

Figure 6b shows the SEM analysis of the catalyst with a magnification of 5000 times. Based on the figure, the nickel-alumina catalyst appears as fine gray grains. Microscopically these grains form a three-dimensional network with irregular pore sizes and shapes and are structurally and thermally stable (Jamilatun et al., 2019). SEM analysis also showed that morphologically the nickel-alumina catalyst had good porosity as indicated by the abundance of voids on the catalyst's surface.

3.2. Product yield and reaction kinetic modeling

Temperature and catalyst are significant factors related to the pyrolysis product distribution and yields. **Figures 7** and **8** show a comparison between yields of pyrolysis products from the model and experimental data at various times for five experimental temperatures both non-catalytic and catalytic.
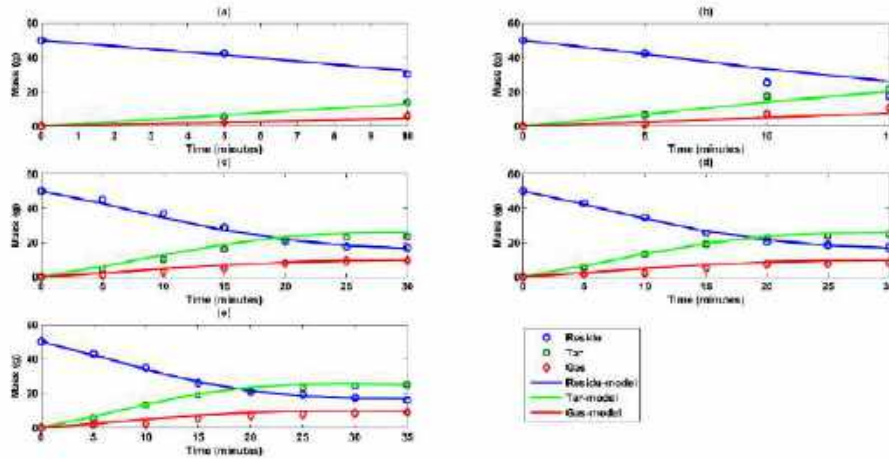

Figure 7. Comparison between yields from model vs experimental data at experimental temperatures of (a) 300 (b) 400 (c) 500 (d) 550 and (e) 600°C for non-catalytic pyrolysis

Figure 8. Comparison between yields from model vs experimental data at experimental temperatures of (a) 300 (b) 400 (c) 500 (d) 550 and (e) 600°C for catalytic pyrolysis

Figures 7 and 8 confirm that the higher the pyrolysis time, the lower the yield of residue (char) and the higher the yield of tar and gas, both non-catalytic and catalytic. Solid decomposition continues as the pyrolysis time increases for five experimental temperatures with a residue yield of 31.68% for the non-catalytic pyrolysis and 30.52% for the catalytic pyrolysis. This value indicates that the solid can further decompose until a fixed carbon composition (19.7%) is obtained. It can be seen also from the figure that the optimum yield of tar is obtained at a pyrolysis time of 25-30 minutes after the first drop of the tar which is equivalent to the temperature of 474-500°C and 456-500°C, with tar yield of 41.52-42.84% for the non-catalytic

pyrolysis and 36.36-37.39% for the catalytic pyrolysis. The optimum temperature and yield of this non-catalytic pyrolysis agree with Abnisa et al (Abnisa et al., 2011). Meanwhile, gas formation continues as the pyrolysis time increases for five experimental temperatures with a

gas yield of 18.05% for the non-catalytic pyrolysis and 28.49% for the catalytic pyrolysis. This reveals that the use of a nickel-alumina catalyst reduces the tar product and increases the gas product. This result agrees with Domlarpyos et al. (Han-U-Domlarpyos et al., 2015).

Figure 9. The product distribution at the final experimental temperatures of (a) non-catalytic and (b) catalytic pyrolysis

Figure 9 shows product distribution at the final of five experimental temperatures. The higher the experimental temperatures, the lower the yield of residue (char) and the higher the yield of tar and gas, both non-catalytic and catalytic. The using of a catalyst increased the yield of gas and decreased the yield of tar and residue. This reveals that the use of a catalyst promotes the secondary tar decomposition reaction.

Figure 7 and 8 above also shows that the model-data fitting was sufficiently good, especially for non-catalytic pyrolysis. Root mean square error (RMSE) was used to evaluate the errors of the predicted model for all experimental temperatures. The coefficient of determination (R^2) was used to evaluate the errors of each pyrolysis product (residue, tar, and gas) at each experimental temperature. The kinetic parameters of the model are presented in **Table 2**.

Table 2. The kinetic parameters

Pyrolysis	Parameters	Value
Non-catalytic	A_1 (s^{-1})	0.002260
	A_2 (s^{-1})	0.004866
	A_3 (s^{-1})	0.029746
	A_4 (s^{-1})	0.000686
	A_5 (s^{-1})	0.000401
	E_1 (kJ.mol^{-1})	11.87
	E_2 (kJ.mol^{-1})	10.56
	E_3 (kJ.mol^{-1})	27.38
	E_4 (kJ.mol^{-1})	51.22
	E_5 (kJ.mol^{-1})	57.36
	RMSE	1.85
	A_1 (s^{-1})	0.029187
	A_2 (s^{-1})	0.026533
	A_3 (s^{-1})	0.014227
	A_4 (s^{-1})	0.000152
	A_5 (s^{-1})	0.000050
	E_1 (kJ.mol^{-1})	22.51
	E_2 (kJ.mol^{-1})	18.25
	E_3 (kJ.mol^{-1})	16.59
	E_4 (kJ.mol^{-1})	19.64
	E_5 (kJ.mol^{-1})	123.02
	RMSE	2.59

The subscripts 1,2,3,4, and 5 in the table are the kinetic parameters of the reactions solid to gas (R_1), solid to tar (R_2), solid to char (R_3), tar to gas (R_4), and tar to char (R_5) respectively. **Table 2** shows that the primary reactions (R_1, R_2, and R_3) are more dominant than the secondary tar reaction (R_4 and R_5) which is indicated by the lower value of the activation energy and the higher value of the pre-exponential factor that result in higher value reaction rate constant (k), both non-catalytic and catalytic pyrolysis.

Table 3. Coefficient of determination of the model

Type of pyrolysis	Experimental temperatures (°C)	Coefficient of determination		
		R^2_{Mr}	R^2_{Mt}	R^2_{Mg}
Non-catalytic	300	0.971	0.986	0.906
	400	0.798	0.953	0.793
	500	0.986	0.936	0.903
	550	0.997	0.990	0.687
	600	0.997	0.984	0.746
Catalytic	300	0.814	0.769	0.890
	400	0.735	0.969	0.980
	500	0.992	0.894	0.683
	550	0.985	0.968	0.893
	600	0.989	0.867	0.844

Table 3 shows the coefficient of determination of each pyrolysis product (residue, tar, and gas) at each experimental temperature. Based on the table, the model provides good fitting data for predicting the yields of pyrolysis product and lack accuracy for predicting the yield of gas product at the experimental temperatures of 550 and 500° C for non-catalytic and catalytic respectively.
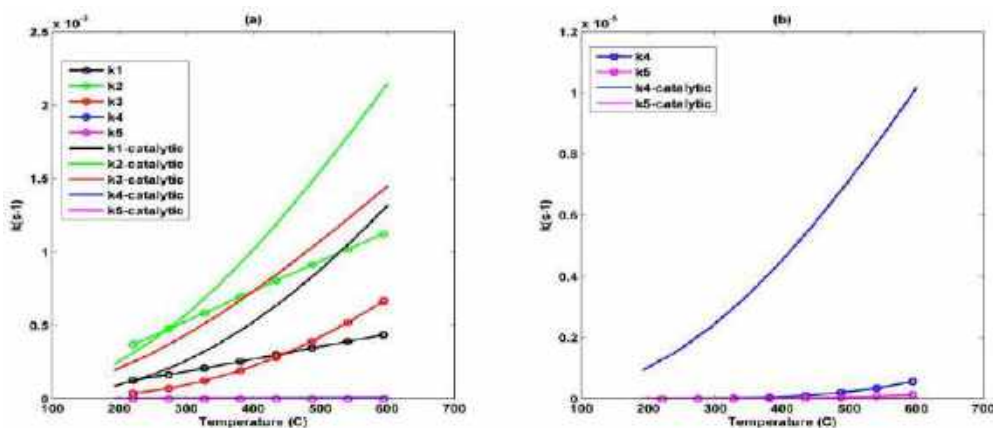

Figure 10. The reaction rate constant vs temperature for (a) overall reactions (b) secondary tar reactions

Figure 10 presented the plot of the reaction rate constants (k) over different temperature ranges both non-catalytic and catalytic. **Figure 10a** confirmed that the use of a catalyst increased the reaction rate constant of R_1, R_2, and R_3. The result showed that the reaction rate constant of R_2 (k_2) was higher than those of R_1, R_3, R_4, and R_5 for all experimental temperatures. This indicates that reactions solid to tar (R_2) had priority in oil palm shells pyrolysis, according to the result has been revealed

by Jinsoo et al. (Vo et al., 2021). **Figure 10a** also confirmed that the secondary tar reaction rate constant (k_4 and k_5) has a small value compared to the primary reaction rate constant (k_1, k_2, and k_3). From **Figure 10b** can be seen that the value of k4 (tar to gas reaction rate constant) in catalytic pyrolysis much greater than in non-catalytic, this may be the reason for the higher gas product in the catalytic compared to the non-catalytic. Based on this result, it can be concluded that at these experimental temperatures of 300-600° C, the decomposition reaction in non-catalytic pyrolysis is completely reliant upon the primary reaction and the secondary tar reaction can be neglected. This conclusion agrees with Park et al. and Sand et al. (Park et al., 2010; Sand & Bel Fdhila, 2011).

The value of T0 (initial decomposition temperature) and β (heating rate) from Equations [13] are determined by evaluating the model at various values of T0 and β based on the experimental data. **Figure 11** shows RMSE at different values of initial decomposition temperature (T0) and heating rate (β).
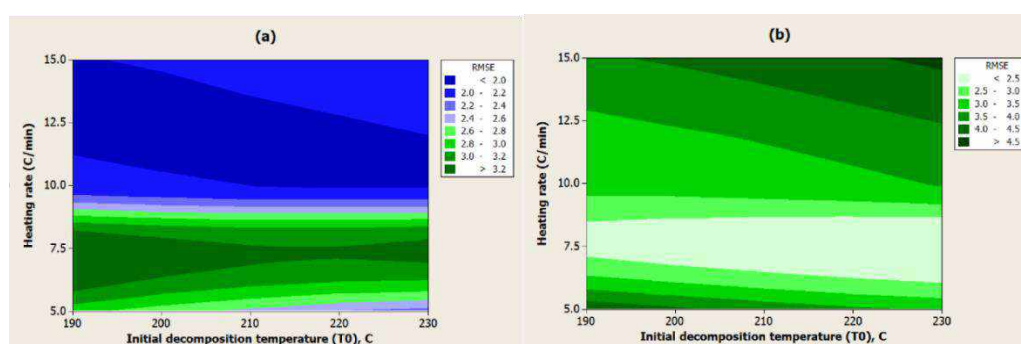

Figure 11. The RMSE value at different T0 and β for (a) non-catalytic pyrolysis and (b) catalytic pyrolysis

The assessment of the RMSE value is determined by comparing its value to zero. The closer the value of RMSE to zero the more accurate the result of the developed model. The figure reveals that for the non-catalytic pyrolysis, a heating rate of about 12-15° C/min gives the minimum value of RMSE for all initial decomposition temperatures. Meanwhile, for catalytic pyrolysis using nickel-alumina catalyst the minimum, RMSE was achieved at a heating rate of about 6.5-10° C/min for all initial decomposition temperatures. Its shows that the selection of the appropriate heating rate is more important rather than the initial decomposition temperature. **Figure 11** also shows that a high heating rate was preferred for non-catalytic pyrolysis, whereas a low heating rate (7.5° C/min) was preferred for catalytic pyrolysis.

By setting the heating rate at 15° C/min for the non-catalytic and 7.5° C/min for the catalytic (the optimum heating rate), taking the value of T0 was equal to 210° C (because the initial decomposition temperature varies depending on the initial conditions of the feedstock), and assuming the secondary tar reactions are neglected because the values of k4 and k5 are very small compared to the value of k1, k2, and k3 both non-catalytic and catalytic, a kinetic model in the form of M=f(T), can be developed to predict the weight of the pyrolysis products. Equation [15-19] can be simplified to:

$$Ms = Ms0 \, exp\left[-\left\{A_1\exp\left(\frac{-E_1}{RT}\right) + A_2\exp\left(\frac{-E_2}{RT}\right) + A_3\exp\left(\frac{-E_3}{RT}\right)\right\}\left(\frac{(T-483)}{\beta}\right)\right] \qquad (24)$$

$$Mg = \frac{Ms0 \, A_1\exp\left(\frac{-E_1}{RT}\right)}{\left(A_1\exp\left(\frac{-E_1}{RT}\right) + A_2\exp\left(\frac{-E_2}{RT}\right) + A_3\exp\left(\frac{-E_3}{RT}\right)\right)}\left[1 - \exp\left[-\left\{A_1\exp\left(\frac{-E_1}{RT}\right) + A_2\exp\left(\frac{-E_2}{RT}\right) + \right.\right.\right.$$
$$\left.\left.\left. A_3\exp\left(\frac{-E_3}{RT}\right)\right\}\left(\frac{(T-483)}{\beta}\right)\right]\right] \qquad (25)$$

$$Mt = \frac{Ms0 \, A_2\exp\left(\frac{-E_2}{RT}\right)}{\left(A_1\exp\left(\frac{-E_1}{RT}\right) + A_2\exp\left(\frac{-E_2}{RT}\right) + A_3\exp\left(\frac{-E_3}{RT}\right)\right)}\left[1 - \exp\left[-\left\{A_1\exp\left(\frac{-E_1}{RT}\right) + A_2\exp\left(\frac{-E_2}{RT}\right) + \right.\right.\right.$$
$$\left.\left.\left. A_3\exp\left(\frac{-E_3}{RT}\right)\right\}\left(\frac{(T-483)}{\beta}\right)\right]\right] \qquad (26)$$

$$Mc = \frac{Ms0 \, A_3\exp\left(\frac{-E_3}{RT}\right)}{\left(A_1\exp\left(\frac{-E_1}{RT}\right) + A_2\exp\left(\frac{-E_2}{RT}\right) + A_3\exp\left(\frac{-E_3}{RT}\right)\right)}\left[1 - \exp\left[-\left\{A_1\exp\left(\frac{-E_1}{RT}\right) + A_2\exp\left(\frac{-E_2}{RT}\right) + \right.\right.\right.$$
$$\left.\left.\left. A_3\exp\left(\frac{-E_3}{RT}\right)\right\}\left(\frac{(T-483)}{\beta}\right)\right]\right] \qquad (27)$$

$$Mr = Ms + Mc \qquad (28)$$

Where the heating rate (β)=15 for non-catalytic and 7.5 for catalytic pyrolysis.

3.3. Model validation

Model validation is important to evaluate whether the developed model is accurate or not and to evaluate the robustness of the model. In this study, model validation methods using residual diagnostics methods (RMSE) are utilized to validate the model on the test dataset that is different from the experimental data (trainee data). **Table 4** shows the series value of RMSE generated from data fitting between the developed model and test dataset around the suggested heating rate ($15°$C/min for the non-catalytic and $7.5°$C/min for the catalytic).

Table 4. The RMSE data at the suggested heating rate for different initial decomposition temperature

Type of pyrolysis	Heating rate (°C/min)	Initial decomposition temperature (°C)				
		190	200	210	220	230
Non-catalytic	12	3.35	3.01	2.72	2.49	2.37
	15	2.02	1.87	1.82	1.92	2.15
Catalytic	7.5	2.10	1.80	1.67	1.78	2.14
	10	1.40	1.30	1.41	1.71	2.15

Table 4 shows that the model validation at the suggested heating rate for the non-catalytic pyrolysis of $15°$C/min and catalytic pyrolysis of $7.5°$C/min were fairly good, with the RMSE value of 1.82 and 1.67 for non-catalytic and catalytic pyrolysis respectively. **Table 4** also shows that setting the value of T0 in the Equation [25-28] at a temperature of $210°$C (483 K) gives an accurate data-model fitting.

4. CONCLUSION

The application of the semi-global kinetic model for predicting the yield distribution in palm shell pyrolysis in FB-TGA was conducted and the developed model has been proposed. The use of FB-TGA makes it possible to evaluate the yield of pyrolysis products (tar, gas, and char) at one cycle of the process for various experimental temperatures. Based on the reaction kinetics

analysis from this study, pyrolysis at a temperature range of 300-600°C only involves primary decomposition reactions especially for non-catalytic pyrolysis, because the value of k4 and k5 (secondary reaction rate constant) was infinitely small. The model validation confirms that the developed model is sufficiently good for predicting the yield of pyrolysis products at the suggested heating rate. The development of a kinetic model based on evolution in mass over time cannot clearly explain the secondary tar reactions due to the small value of k4 and k5, therefore it is suggested to use the basis of evolution in mass with respect to final experimental temperature to explain the secondary tar reactions.

5. ACKNOWLEDGMENT

6. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. The authors confirmed that the paper was free of plagiarism.

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HASIL CEK_IJOST_kinetika - JOKO PITOYO

by Joko Pitoyo Mahasiswa Uad

Semi-Global Kinetic Model for Predicting Yields of Palm Shell Catalytic Pyrolysis using Fixed Bed Analysis Thermal Gravimetric (FB-TGA)

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ABSTRACTS

Pyrolysis is an eco-friendly and sustainable thermochemical method to convert biomass into biofuel. So far, there is no accepted model for predicting the yield of pyrolysis products (tar, char, and gas) over a variety of pyrolysis conditions. This paper investigated the accuracy of the two-stage semi-global kinetic model using multi-component model-fitting techniques in predicting the product yields from palm shell pyrolysis and then develop the model based on obtained kinetic parameters. Palm shell pyrolysis was performed in a fixed-bed thermal gravimetric analysis (FB-TGA) reactor at different experimental temperatures (300, 400, 500, 550, and 600° C) in the range of heating rate of 8-12° C/min. The developed model agreed well with the experimental data both non-catalytic and catalytic. The model validation confirmed that the developed model is sufficiently good to predict the yield of pyrolysis products (tar, char, and gas) at the suggested heating rate, with the RMSE value of 1.82 and 1.67 for non-catalytic and catalytic pyrolysis respectively.

ARTICLE INFO

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1. INTRODUCTION

High population growth coupled with increased industrial and commercial activity results in reduced fossil fuels, increased environmental pollution, global warming, and worsening health effects (Ali et al., 2017). In order to meet global energy needs in the face of this energy crisis, alternative energy sources must be explored (Ighalo & Adeniyi, 2020). Biomass is thought to be the most significant sustainable and renewable resources for the production of biofuels. It provides 14% of the world's annual energy consumption. (Dai et al., 2019).

The two significant processes for converting biomass into biofuel are biochemical and thermochemical (Van de Velden et al., 2010). The biochemical processes can convert biomass into bio-fuels, including extraction, hydrolysis, fermentation (Damartzis & Zabaniotou, 2011), and anaerobic digestion (Tyagi et al., 2018). Thermochemical processes include combustion, gasification, and pyrolysis that produce energy (Tomić et al., 2017).

Pyrolysis is the thermal decomposition in the absence of oxygen. Pyrolysis is more promising than other thermochemical conversions because it is more flexible in the selection of feedstocks, can be applied under atmospheric pressure and a wide range of temperatures, and produces three types of products (char, liquid (tar), and gas) (Terry et al., 2021). Pyrolysis gas, char, and liquid (tar) can be utilized for various purposes. Char can be used as an adsorbent, while tar and gas can be utilized as biofuel (Jamilatun et al., 2022).

Biomass pyrolysis occurs in two reaction steps, primary decomposition reactions and secondary tar decomposition reactions (**Figure 1**). Condensable gas and solid char compose the initial pyrolysis byproduct. The condensable gas further

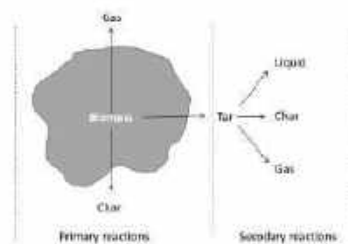decomposed into char, liquid (tar), and non-condensable gas. (Basu, 2010).

Figure 1. Thermal decomposition of biomass

As pyrolysis is an important process in the thermochemical conversion method. Comprehending the kinetics of pyrolysis is crucial for the improvement of the process, optimization, and efficient design of the reactor (Sand & Bel Fdhila, 2011). There are two basic mathematical methods to determine the kinetic parameters of biomass pyrolysis based on experimental data: iso-conventional methods and model-fitting methods (Vo et al., 2021). Model-fitting methods can be classified into one-component or multi-component mechanisms and into lumped or detailed reaction mechanisms (Di Blasi, 2008). The lumped-kinetic models for pyrolysis can be divided into two categories: global-decomposition models and multi-component decomposition models. The multi-component decomposition models were developed based on the constituents of biomass namely hemicellulose, cellulose, and lignin. Generally, these models use first-order reactions to describe the decomposition of biomass (Vo et al., 2021). A lumped model is sufficient to ascertain the kinetic parameters of pyrolysis reactions (Ranzi et al., 2001).

Semi-global decomposition models are used to explain primary and secondary tar decomposition reactions of biomass through the measurement of the rates of weight loss experimentally. The semi-global models seem to be more suitable for

reactor design and process optimization. These models describe competitive reaction schemes which allow predicting the product distribution on the dependence of reaction conditions (Di Blasi, 2008).

Numerous research have focused in the kinetics of the palm shell pyrolysis. Vo et al. (Vo et al., 2021) conducted thermogravimetry analysis (TGA) palm shell and determine the kinetic parameters using isoconventional (FWO and KAS) methods at various heating rates (10, 20, 30 and 40° C min⁻¹). Hernowo et al. (Hernowo et al., 2022) performed pyrolysis on palm shell using a volatile state model and determine the kinetic parameters using the modified Kissinger–Akahira–Sunose (KAS) method. Safavi et al. (Safavi & Richter, 2022) carried out pyrolysis on a walnut shell and determine kinetic parameters using a competitive reaction scheme with three reactions and suggest the use of a competitive reaction scheme including secondary reaction to accurately predict the yields.

To our best knowledge, so far no kinetic study has been conducted on palm shell using semi-global reaction models which include secondary reaction mechanisms. Besides, the use of fixed bed thermal gravimetric analysis (FB-TGA) has its novelty value. FB-TGA is a fixed bed modification based on the TGA concept. The principle of the FB-TGA is a measurement of the mass loss of solid, based on the tar and gas formation. Pyrolysis using fixed bed modification based on the TGA concept in different methods has been conducted by a few researchers (Hernowo et al., 2022; Meng et al., 2015; Sand & Bel Fdhila, 2011). Therefore, this work aimed to perform the semi-global kinetic model developed by several authors (Di Blasi, 2008) to precisely calculate the kinetic parameters of palm shell pyrolysis. The purpose of this study

were as follows: (1) perform pyrolysis experiments on palm shell using fixed bed thermal gravimetric analysis, (2) determine the kinetic parameters of the palm shell pyrolysis, (3) develop a kinetic model to predict tar, residue (char and remaining solid), and gas yields throughout the experimental temperatures of 300 to 600 °C.

2. METHODS

2.1. Experimental Materials
2.1.1. Palm shell

Palm shell was gathered from PT Perkebunan Nusantara V (PTPN V), Riau. The palm shell was washed using clean water to remove impurities, then dried in the sun for 2 days. The dried palm shell was then oven-dried for 24 hours to get a moisture content of less than 10%. The oven-dried palm shell was then grounded with a hammer mill and then sieved to obtain a grain size of 0.425-2.00 mm. The raw materials' elemental composition was ascertained through ultimate analysis. Before ultimate analysis, the palm shell was grounded to obtain a grain size of less than or equal to 60 mesh. CHN analyzer (Perkin Elmer 2400) was used to perform the ultimate analysis in accordance with ASTM D5291-96, while the oxygen content was determined by difference.

2.1.2. Nickel-alumina catalyst

The catalyst was obtained from PT Pupuk Kujang Cikampek in the pellets form, with a dimensions of 33 mm in diameter and 15 mm in height. The catalyst was crushed using a hammer mill. The refined catalyst was sieved to get a grain size of 0.425-2.00 mm. Catalyst analysis was performed using a Scanning Electron Microscope-Energy Disperse X-Ray (SEM-EDX) to determine the morphology (pore, rough, and shape) and element composition of the catalyst. SEM analysis

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was performed using the JSM-6510 instrument which was operated at an accelerating voltage of 15kV, a working distance (WD) of 11 mm, and a spot size (SS) of 40.

2.2. Experimental setup

2.2.1. Fixed Bed Thermal Gravimetric Analysis (FB-TGA)

The study was performed using a fixed bed thermal gravimetric analysis (FB-TGA) reactor in the form of a vertical stainless steel cylinder with an inner diameter of 40 cm, an outer diameter of 4.4 cm, and a height of 60 cm. A nickel wire-based electric heater was equipped on the reactor, and it was looped spirally around the outer of the reactor. The heating temperature was measured using a thermocouple and the heating rate was regulated using a TGDC regulator of 0.5 kva. The reactor is equipped with two vertical cylinders. The palm shell was placed in the first cylinder (R_1), and the second (R2) was for nickel-alumina catalysts. The pyrolysis gas product from R_1 flowed upward through R_2, containing the catalysts (Jamilatun, 2022).
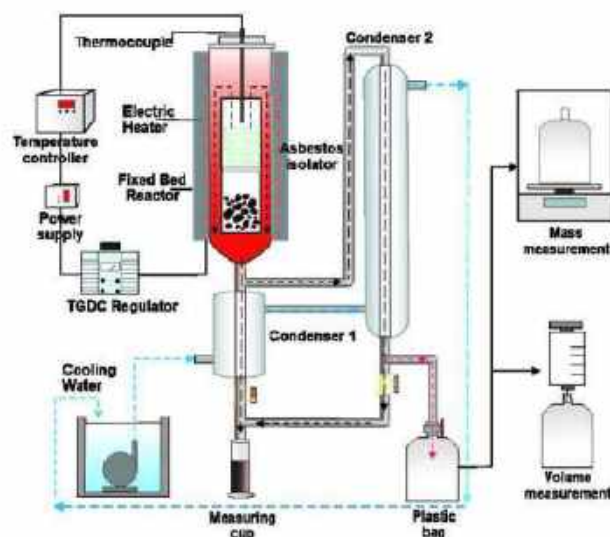

Figure 2. Fixed bed thermal gravimetric analysis (FB-TGA) equipment

2.2.2. Procedure

Pyrolysis was carried out by placing 50 grams of palm shell into reactor R_1 for non-catalytic pyrolysis and adding 40% w/w nickel-alumina catalyst into reactor R_2 for catalytic pyrolysis. The reactor was heated at a heating rate of 10-12° C/min to the desired temperature (300, 400, 500, and 600° C). Data collection starts after the first drop of tar appears. The result of pyrolysis in the form of condensable gas (tar) was collected in a measuring cup and then weighed. Non-condensable gas flowed into a plastic bag, then the weight and volume were measured. Weighing and measurement of tar and non-condensable gas were carried out every 5 minutes after the appearance of the first drop. Residue (char and remaining solid) yields were determined by the difference. The principle of gas weighing was explained using the air buoyancy concept. Air buoyancy is the upward force applied to an

object which causes the object to weigh less. This force is equivalent to the mass of air displaced by the object. So that the weight of the gas is the sum of the weight of the air displaced by the plastic bag and the weight measured on the scale. The yields of the pyrolysis product were calculated using Equations [1-5].

$$Yt = \frac{Mt}{Ms} \times 100\% \qquad (1)$$

$$Yg = \frac{Mg}{Ms} \times 100\% \qquad (2)$$

$$Mg = Msc + Fa \qquad (3)$$

$$Fa = Vg \times \rho u \qquad (4)$$

$$Yr = 100 - Yt - Yg \qquad (5)$$

Where Yt, Yg, and Yr are the yield of tar, gas, and residue respectively. Mt, Mg, and Ms are masses of tar, gas, and solid. Msc, Fa, Vg, and ρu are mass measured on a scale, air buoyancy force, the volume of gas (plastic bag), and density of air.

2.2.3. Reaction kinetic modeling

To investigate the kinetics parameters of palm-shell pyrolysis in the fixed bed thermal gravimetric analysis (FB-TGA), a semi-global kinetic model was hypothesized. Accordingly, the raw material (palm shell) and products were classified into four lumps, namely solid, char, tar, and gas. The kinetic scheme as shown in **Figure 3** illustrates the process of pyrolysis (primary and secondary) which includes the breakdown of biomass into gas, tar, and char, and the tar continues to break down into char and gases.
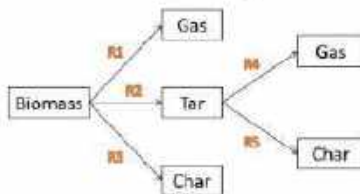

Figure 3. The kinetic scheme of the semi-global model

The mass change of the components with time was modeled in the form of ordinary differential equations as shown in Equations [6-10].

$$\frac{dMs}{dt} = -(k1 + k2 + k3)Ms \qquad (6)$$

$$\frac{dMt}{dt} = k2Ms - (k4 + k5)Mt \qquad (7)$$

$$\frac{dMc}{dt} = k3Ms + k5Mt \qquad (8)$$

$$\frac{dMg}{dt} = k1Ms + k4Mt \qquad (9)$$

$$\frac{dMr}{dt} = \frac{dMs}{dt} + \frac{dMc}{dt} \qquad (10)$$

where Ms, Mt, Mc, Mg, and Mr are the mass (gr) of solid, tar, char, gas, and residue (remaining solid and char), respectively; $k1$, $k2$, $k3$, $k4$, and $k5$ are reaction rate constants of reactions (R1), (R2), (R3), (R4), and (R5), respectively. The initial conditions for the kinetic equations are:

$$t = 0, \ Ms = Mr = Ms0, \ Mt = Mc = Mg = 0$$

The reaction rate constant is formulated by Equation [11].

$$ki = Ai \exp\left(\frac{-Ei}{RT}\right) \qquad i=1\text{-}5 \qquad (11)$$

Where A is the pre-exponential factor (s^{-1}), E is the activation energy (kJ·mol^{-1}), R is the universal gas constant (kJ·K^{-1}·mol^{-1}), and T is the absolute temperature (K).

For non-isothermal conditions, the heating rate (β) is determined using Equation [12], where dT is the change of temperature (K) and dt is the change of time (s).

$$\frac{dT}{dt} = \beta \qquad (12)$$

On solving Equation [12], with the initial conditions t=0, T=T0 we achieve,

$$T = T0 + \beta t \qquad (13)$$

The system of ordinary differential equations in Equations [6-10] can be

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solved analytically or numerically. The analytical solutions of the kinetic equation give Equation [14-18].

$$Ms = Ms0\,exp\{-(k1 + k2 + k3)t\} \tag{14}$$

$$Mt = \frac{Ms0\,k2}{\{(k4+k5)-(k1+k2+k3)\}}[exp\{-(k1 + k2 + k3)t\} - exp\{-(k4 + k5)t\}] \tag{15}$$

$$Mc = \frac{Ms0\,k3}{(k1+k2+k3)}[exp\{-(k1 + k2 + k3)t\}] - \frac{Ms0\,k2\,k5}{\{(k4+k5)-(k1+k2+k3)\}}\left[\frac{1}{(k1+k2+k3)}[1 - exp\{-(k1 + k2 + k3)t\}] + \frac{1}{(k4+k5)}[1 - exp\{-(k4 + k5)t\}]\right] \tag{16}$$

$$Mg = \frac{Ms0\,k1}{(k1+k2+k3)}[exp\{-(k1 + k2 + k3)t\}] - \frac{Ms0\,k2\,k4}{\{(k4+k5)-(k1+k2+k3)\}}\left[\frac{1}{(k1+k2+k3)}[1 - exp\{-(k1 + k2 + k3)t\}] + \frac{1}{(k4+k5)}[1 - exp\{-(k4 + k5)t\}]\right] \tag{17}$$

$$Mr = Ms + Mc \tag{18}$$

$$F = \min_{p} \sum_{i=1}^{n1} \sum_{T=1}^{n2} \sum_{t} \left[Mi^{exp(T,t)} - Mi^{model}(T,t)\right]^2 \tag{19}$$

$$TSS_{Mi} = \sum_{j=1}^{n3}(Mij - \overline{M_{ij}})^2 \tag{20}$$

$$RSS_{Mi} = \sum_{j=1}^{n3}(Mij - \widehat{M_{i,j}})^2 \tag{21}$$

$$R^2{}_{Mi} = 1 - \frac{TSS_{Mi}}{RSS_{Mi}} \tag{22}$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n1}\sum_{T=1}^{n2}\sum_{t}\left[Mi^{exp(T,t)} - Mi^{model}(T,t)\right]^2}{(n1\,n2\,n3)}} \tag{23}$$

An optimization tool in the Matlab software package i.e. *fminsearch* function was used to solve the Equations [14-18] simultaneously related to the change of product yields with time across overall the experimental temperatures. The objective of this optimization was to search the set of coefficients p = (A1, A2, A3, A4, A5, E1, E2, E3, E4, and E5) that minimizes the Equations [19]. Where F is the objective function, TSS_{Mi} is the total sum of squares of Mi, n1, n2, and n3 are the number of observations of product phase, temperature, and time, respectively. Mij is the jth value of Mi from the experiment ($j \leq n3$), $\overline{M_{ij}}$ is the mean value of Mi from the experiment, RSS_{Mi} is the residue sum of squares of Mi, $\widehat{M_{i,j}}$ is the jth predicted value of Mi from modeling, $R^2{}_{Mi}$ is the coefficient of determination of Mi. $RMSE$ is the root mean square error of the predicted model.
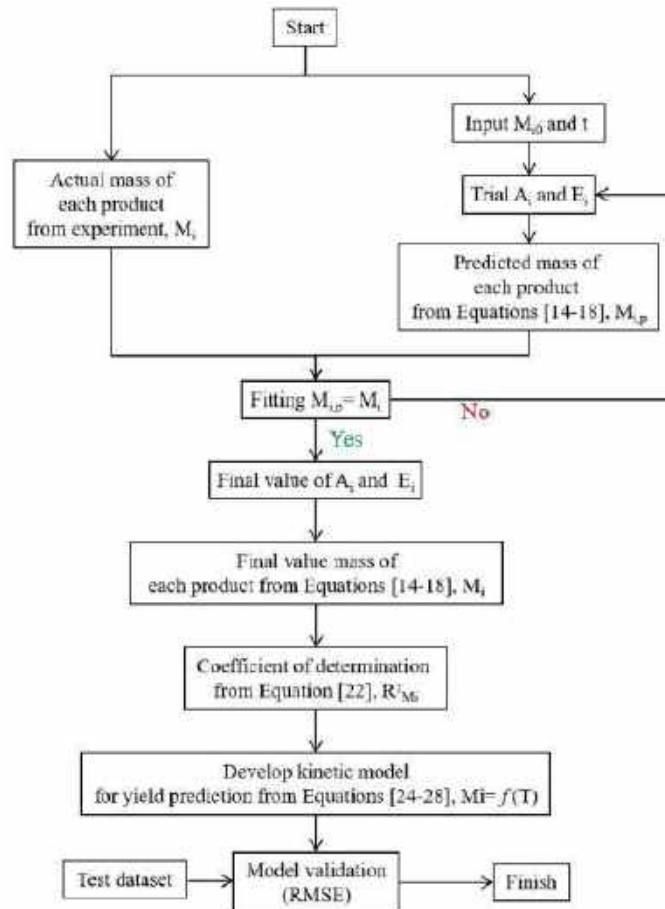
Figure 4. The flowchart to predict yields and to develop a reaction kinetic model

3. RESULTS AND DISCUSSION

3.1. Characteristics of the materials and FB-TGA

3.1.1. Palm shell

Composition, proximate and ultimate analysis of the palm shell was important to estimate the energy content in the palm shell. The result of the analysis of palm shell was shown in **Table 1** and the results of the analysis agree with other literature (Abnisa et al., 2011)(Han-U-Domlarpyos et al., 2015).

Proximate analysis of palm shell shows a high content of volatile materials in palm shell. High volatile matter content will increase the yield of bio-oil produced because high volatile matter content gives high volatility and reactivity to raw materials (Ferreira et al., 2020). The ash content (minerals) in the sample is formed by the presence of alkali metals such as K, Ca, Mg, P, and Si. Ash content has an impact on the yield of bio-oil. The high content of ash will reduce the bio-oil produced and increase the yield of char and gas produced (Pitoyo et al., 2022). High ash content can also reduce the HHV value of biomass (Ferreira et al., 2020).

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Table 1. The result of composition and elemental analysis of palm shell

Proximate analysis (wt.%)	
Moisture	11
Volatile matter	67.2
Fixed Carbon	19.7
Ash	2.1
Composition analysis (wt.%)	
Cellulose	27.7
Hemicellulose	21.6
Lignin	44
Ultimate analysis (wt.%)	
C	48.99
H	6.6
N	0.37
S	0.076
O*	43.96
H/C	1.62
O/C	0.67
HHV (MJ/Kg)	24.27

Ultimate analysis of palm shell was performed to determine the chemical composition of palm shell, namely C, H, N, S, and O. The low content of nitrogen (N) and sulphur (S) in palm shell can make palm shell an eco-friendly fuel. The high index of aromatization and carbonization is indicated by the high content of hydrogen

(H) and carbon (C) compared to the content of oxygen (O). A low O/C ratio gives a high higher heating value (HHV) (Braza & Crnkovic, 2014). **Table 1** shows that the oil palm shell has H/C, O/C, and HHV of 1.62, 0.67, and 24.27 respectively. The HHV in this study was higher compared to the HHV in other works (Vo et al., 2021)(Han-U-Domlarpyos et al., 2015).

Figure 5 shows the mass evolution and the derivative mass loss of palm shell pyrolysis at a heating rate of 8-12° C/min. According to the figure, palm shell pyrolysis showed a similar mass loss pattern, especially at 400, 500, 550, and 600° C, and little difference related to the value caused by the difference in heating rate, which means the equipment has good performance and more precise heating rate control is recommended. From the figure, it can be seen also that palm shell initial mass loss under five experimental temperatures starts at a range of 190-220° C. This was because the data collection starts after the appearance of the first drop of tar. There was a delay between the actual decomposition temperature and the appearance of the first drop. So the actual decomposition time was less than 190° C.
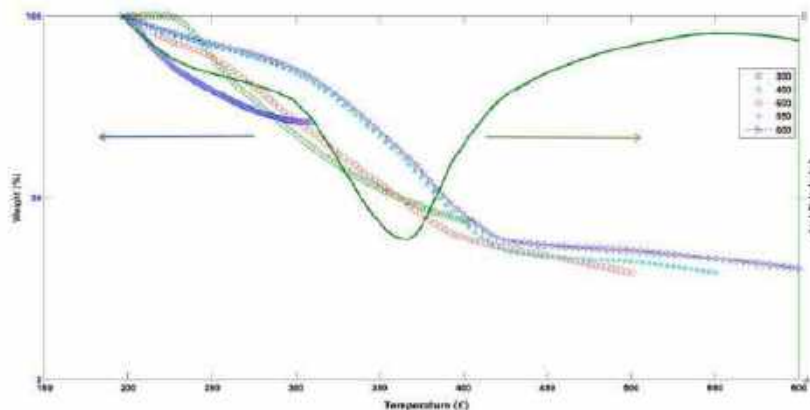

Figure 5. Mass loss evolution and derivative mass loss of palm shell pyrolysis

Palm shell is consist of complex components (cellulose, hemicellulose, and lignin), thus it can be seen that the

thermal decomposition of palm shell occurs over wide temperature range (~190-600° C). The primary temperature

range of palm shell decomposition was from 300 to 420° C with the highest decomposition at 365° C. The simultaneous decomposition of cellulose, hemicellulose, and lignin was responsible for the major decomposition peak, and this was reasonable given because the decomposition temperature of hemicellulose is 250-350 ° C, the decomposition temperature of cellulose is 325-400 " C, and whereas lignin needs a higher decomposition temperature (between 300 and 550 °C) due to its complex structural makeup (K N est al., 2022). At temperatures of 300°C, the decomposition of hemicellulose and the loss of moisture were responsible for the palm shell decomposition. The remaining component of lignin and secondary biochar decomposition might be responsible for the slow decomposition temperatures higher than 420 C. (Aysu et al., 2016; Yang et al., 2007).

The curve of the derivative mass loss in **Figure 5** confirms the presence of one peak and the tendency to form a second peak at the temperature of 600 C. It indicates that the primary reaction occurs at the range temperature of 200-~600 C, and the secondary tar reaction occurs starting at 550 C. It is relevant to Sand et al. and Park et al., who stated that the secondary tar decomposition reaction in the palm shell and wood slow pyrolysis was confirmed at 500 °C (Park et al., 2010; Sand & Bel Fdhila, 2011).

3.1.2. Nickel-alumina catalyst

Nickel-alumina was characterized using SEM-EDX to determine the surface morphology and constituent components. SEM-EDX analysis shows that the catalyst consists of five components, Ni, Al, O, Na, and C (**Figure 6a**). Ni is a metal catalyst, Al and O compose Al_2O_3 structure as catalyst support indicated by its large number. Ni loading in this catalyst is 7.36% (wt.%). Alumina (Al2O3) is a catalyst support with a large area of surface and small to medium pore diameter so as to minimize mass transfer limitations (Goula et al., 2015; Tao et al., 2010).
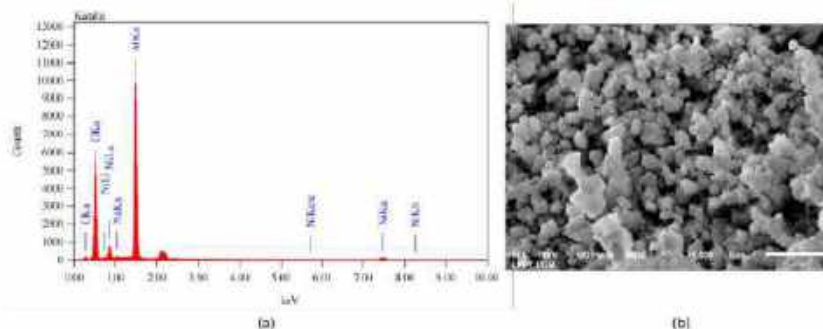

Figure 6. The result of (a) EDX analysis and (b) SEM analysis at a magnificent 5000 times

Figure 6b shows the SEM analysis of the catalyst with a magnification of 5000 times. Based on the figure, the nickel-alumina catalyst appears as fine gray grains. Microscopically these grains form a three-dimensional network with irregular pore sizes and shapes and are structurally and thermally stable (Jamilatun et al., 2019). SEM analysis also showed that morphologically the nickel-alumina catalyst had good porosity as indicated by the abundance of voids on the catalyst's surface.

3.2. Product yield and reaction kinetic modeling

Temperature and catalyst are significant factors related to the pyrolysis product distribution and yields. **Figures 7 and 8** show a comparison between yields of pyrolysis products from the model and experimental data at various times for five experimental temperatures both non-catalytic and catalytic.
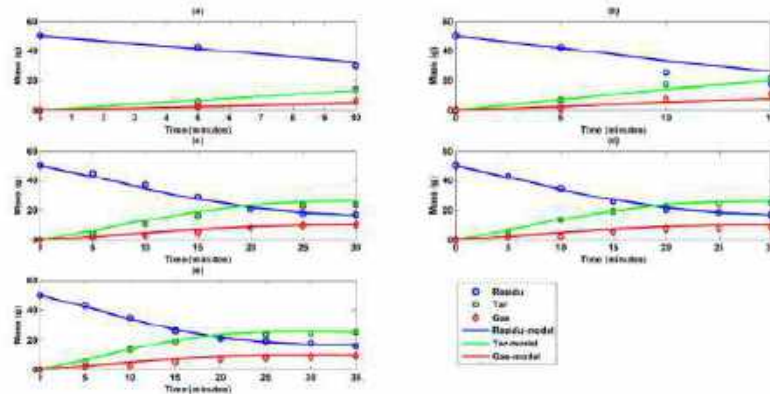

Figure 7. Comparison between yields from model vs experimental data at experimental temperatures of (a) 300 (b) 400 (c) 500 (d) 550 and (e) 600°C for non-catalytic pyrolysis
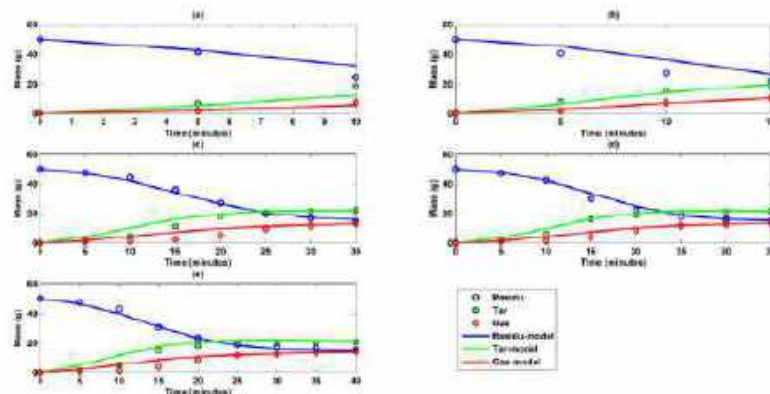

Figure 8. Comparison between yields from model vs experimental data at experimental temperatures of (a) 300 (b) 400 (c) 500 (d) 550 and (e) 600°C for catalytic pyrolysis

Figures 7 and 8 confirm that the higher the pyrolysis time, the lower the yield of residue (char) and the higher the yield of tar and gas, both non-catalytic and catalytic. Solid decomposition continues as the pyrolysis time increases for five experimental temperatures with a residue yield of 31.68% for the non-catalytic pyrolysis and 30.52% for the catalytic

pyrolysis. This value indicates that the solid can further decompose until a fixed carbon composition (19.7%) is obtained. It can be seen also from the figure that the optimum yield of tar is obtained at a pyrolysis time of 25-30 minutes after the first drop of the tar which is equivalent to the temperature of 474-500° C and 456-500° C, with tar yield of 41.52-42.84% for the non-catalytic

pyrolysis and 36.36-37.39% for the catalytic pyrolysis. The optimum temperature and yield of this non-catalytic pyrolysis agree with Abnisa et al (Abnisa et al., 2011). Meanwhile, gas formation continues as the pyrolysis time increases for five experimental temperatures with a gas yield of 18.05% for the non-catalytic pyrolysis and 28.49% for the catalytic pyrolysis. This reveals that the use of a nickel-alumina catalyst reduces the tar product and increases the gas product. This result agrees with Domlarpyos et al. (Han-U-Domlarpyos et al., 2015).
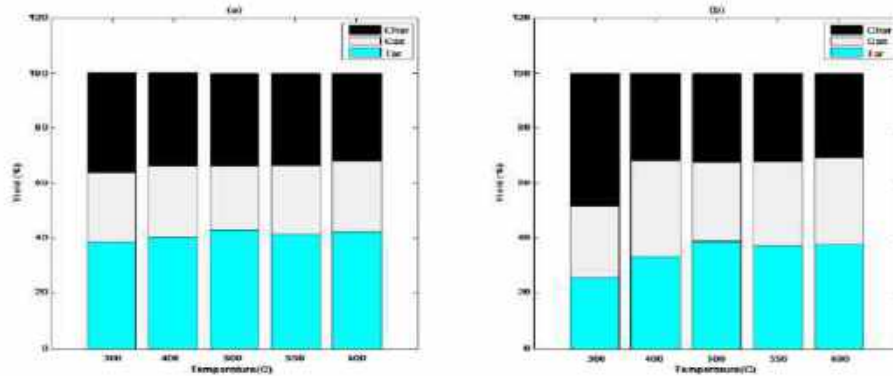

Figure 9. The product distribution at the final experimental temperatures of (a) non-catalytic and (b) catalytic pyrolysis.

Figure 9 shows product distribution at the final of five experimental temperatures. The higher the experimental temperatures, the lower the yield of residue (char) and the higher the yield of tar and gas, both non-catalytic and catalytic. The using of a catalyst increased the yield of gas and decreased the yield of tar and residue. This reveals that the use of a catalyst promotes the secondary tar decomposition reaction.

Figure 7 and 8 above also shows that the model-data fitting was sufficiently good, especially for non-catalytic pyrolysis. Root mean square error (RMSE) was used to evaluate the errors of the predicted model for all experimental temperatures. The coefficient of determination (R^2) was used to evaluate the errors of each pyrolysis product (residue, tar, and gas) at each experimental temperature. The kinetic parameters of the model are presented in **Table 2**.

Table 2. Kinetic parameters obtained from the model

Type of pyrolysis	Parameters	Value
Non-catalytic	A_1 (s^{-1})	0.002260
	A_2 (s^{-1})	0.004866
	A_3 (s^{-1})	0.029746
	A_4 (s^{-1})	0.000686
	A_5 (s^{-1})	0.000401
	E_1 ($kJ.mol^{-1}$)	11.87
	E_2 ($kJ.mol^{-1}$)	10.56
	E_3 ($kJ.mol^{-1}$)	27.38
	E_4 ($kJ.mol^{-1}$)	51.22
	E_5 ($kJ.mol^{-1}$)	57.36
	RMSE	1.85
Catalytic	A_1 (s^{-1})	0.029187
	A_2 (s^{-1})	0.026533
	A_3 (s^{-1})	0.014227
	A_4 (s^{-1})	0.000152
	A_5 (s^{-1})	0.000050
	E_1 ($kJ.mol^{-1}$)	22.51
	E_2 ($kJ.mol^{-1}$)	18.25
	E_3 ($kJ.mol^{-1}$)	16.59
	E_4 ($kJ.mol^{-1}$)	19.64
	E_5 ($kJ.mol^{-1}$)	123.02
	RMSE	2.59

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The subscripts 1,2,3,4, and 5 in the table are the kinetic parameters of the reactions solid to gas (R₁), solid to tar (R₂), solid to char (R₃), tar to gas (R₄), and tar to char (R₅) respectively. **Table 2** shows that the primary reactions (R₁, R₂, and R₃) are more dominant than the secondary tar

reaction (R₄ and R₅) which is indicated by the lower value of the activation energy and the higher value of the pre-exponential factor that result in higher value reaction rate constant (k), both non-catalytic and catalytic pyrolysis.

Table 3. Coefficient of determination of the model

Type of pyrolysis	Experimental temperatures (° C)	Coefficient of determination		
		R^2_{Mr}	R^2_{Mt}	R^2_{Mg}
Non-catalytic	300	0.971	0.986	0.906
	400	0.798	0.953	0.793
	500	0.986	0.936	0.903
	550	0.997	0.990	0.687
	600	0.997	0.984	0.746
Catalytic	300	0.814	0.769	0.890
	400	0.735	0.969	0.980
	500	0.992	0.894	0.683
	550	0.985	0.968	0.893
	600	0.989	0.867	0.844

Table 3 shows the coefficient of determination of each pyrolysis product (residue, tar, and gas) at each experimental temperature. Based on the table, the model provides good fitting data for predicting the

yields of pyrolysis product and lack accuracy for predicting the yield of gas product at the experimental temperatures of 550 and 500° C for non-catalytic and catalytic respectively.
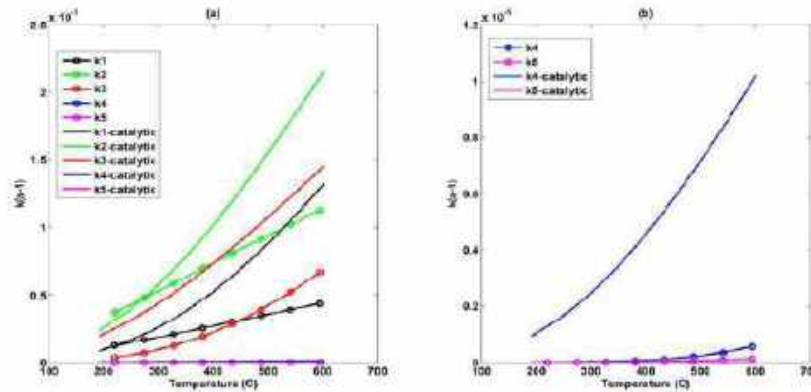

Figure 10. The reaction rate constant vs temperature for (a) overall reactions (b) secondary tar reactions

Figure 10 presented the plot of the reaction rate constants (k) over different temperature ranges both non-catalytic and catalytic. **Figure 10a** confirmed that the use of a catalyst increased the reaction

rate constant of R₁, R₂, and R₃. The result showed that the reaction rate constant of R₂ (k₂) was higher than those of R₁, R₃, R₄, and R₅ for all experimental temperatures. This indicates that reactions solid to tar (R₂)

had priority in oil palm shells pyrolysis, according to the result has been revealed by Jinsoo et al. (Vo et al., 2021). **Figure 10a** also confirmed that the secondary tar reaction rate constant (k_4 and k_5) has a small value compared to the primary reaction rate constant (k_1, k_2, and k_3). From **Figure 10b** can be seen that the value of k4 (tar to gas reaction rate constant) in catalytic pyrolysis much greater than in non-catalytic, this may be the reason for the higher gas product in the catalytic compared to the non-catalytic. Based on this result, it can be concluded that at these experimental temperatures of 300-600° C, the decomposition reaction in non-

catalytic pyrolysis is completely reliant upon the primary reaction and the secondary tar reaction can be neglected. This conclusion agrees with Park et al. and Sand et al. (Park et al., 2010; Sand & Bel Fdhila, 2011).

The value of T0 (initial decomposition temperature) and β (heating rate) from Equations [13] are determined by evaluating the model at various values of T0 and β based on the experimental data. **Figure 11** shows RMSE at different values of initial decomposition temperature (T0) and heating rate (β).
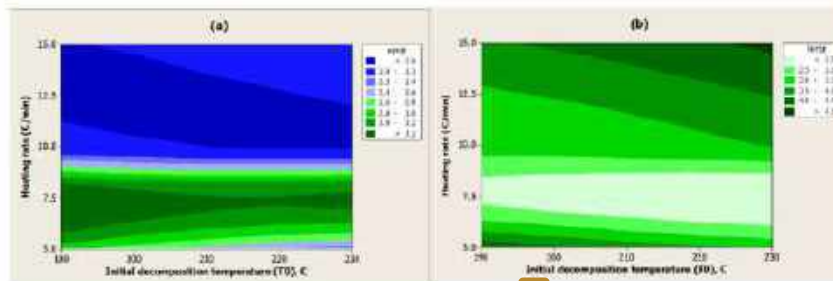

Figure 11. The RMSE value at different T0 and β for (a) non-catalytic pyrolysis and (b) catalytic pyrolysis

The assessment of the RMSE value is determined by comparing its value to zero. The closer the value of RMSE to zero the more accurate the result of the developed model. The figure reveals that for the non-catalytic pyrolysis, a heating rate of about 12-15°C/min gives the minimum value of RMSE for all initial decomposition temperatures. Meanwhile, for catalytic pyrolysis using nickel-alumina catalyst the minimum, RMSE was achieved at a heating rate of about 6.5-10°C/min for all initial decomposition temperatures. Its shows that the selection of the appropriate heating rate is more important rather than the initial decomposition temperature. **Figure 11** also shows that a high heating rate was preferred for non-catalytic

pyrolysis, whereas a low heating rate (7.5°C/min) was preferred for catalytic pyrolysis.

By setting the heating rate at 15°C/min for the non-catalytic and 7.5°C/min for the catalytic (the optimum heating rate), taking the value of T0 was equal to 210°C (because the initial decomposition temperature varies depending on the initial conditions of the feedstock), and assuming the secondary tar reactions are neglected because the values of k4 and k5 are very small compared to the value of k1, k2, and k3 both non-catalytic and catalytic, a kinetic model in the form of M=f(T), can be developed to predict the weight of the pyrolysis products. Equation [15-19] can be simplified to:

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$$Ms = Ms0\,exp\left[-\left\{A_1 \exp\left(\frac{-E_1}{RT}\right) + A_2 \exp\left(\frac{-E_2}{RT}\right) + A_3 \exp\left(\frac{-E_3}{RT}\right)\right\}\left(\frac{(T-483)}{\beta}\right)\right] \quad (24)$$

$$Mg = \frac{Ms0\,k1}{\left(A_1\exp\left(\frac{-E_1}{RT}\right)+A_2\exp\left(\frac{-E_2}{RT}\right)+A_3\exp\left(\frac{-E_3}{RT}\right)\right)}\left[1 - \exp\left[-\left\{A_1\exp\left(\frac{-E_1}{RT}\right) + A_2\exp\left(\frac{-E_2}{RT}\right) + A_3\exp\left(\frac{-E_3}{RT}\right)\right\}\left(\frac{(T-483)}{\beta}\right)\right]\right] \quad (25)$$

$$Mt = \frac{Ms0\,k2}{\left(A_1\exp\left(\frac{-E_1}{RT}\right)+A_2\exp\left(\frac{-E_2}{RT}\right)+A_3\exp\left(\frac{-E_3}{RT}\right)\right)}\left[1 - \exp\left[-\left\{A_1\exp\left(\frac{-E_1}{RT}\right) + A_2\exp\left(\frac{-E_2}{RT}\right) + A_3\exp\left(\frac{-E_3}{RT}\right)\right\}\left(\frac{(T-483)}{\beta}\right)\right]\right] \quad (26)$$

$$Mc = \frac{Ms0\,k3}{\left(A_1\exp\left(\frac{-E_1}{RT}\right)+A_2\exp\left(\frac{-E_2}{RT}\right)+A_3\exp\left(\frac{-E_3}{RT}\right)\right)}\left[1 - \exp\left[-\left\{A_1\exp\left(\frac{-E_1}{RT}\right) + A_2\exp\left(\frac{-E_2}{RT}\right) + A_3\exp\left(\frac{-E_3}{RT}\right)\right\}\left(\frac{(T-483)}{\beta}\right)\right]\right] \quad (27)$$

$$Mr = Ms + Mc \quad (28)$$

Where the heating rate (β)=15 for non-catalytic and 7.5 for catalytic pyrolysis.

3.3. Model validation

Model validation is important to evaluate whether the developed model is accurate or not and to evaluate the robustness of the model. In this study, model validation methods using residual diagnostics methods (RMSE) are utilized to validate the model on the test dataset that is different from the experimental data (trainee data). **Table 4** shows the series value of RMSE generated from data fitting between the developed model and test dataset around the suggested heating rate (15°C/min for the non-catalytic and 7.5°C/min for the catalytic).

Table 4. The RMSE data at the suggested heating rate for different initial decomposition temperature

Type of pyrolysis	Heating rate (°C/min)	Initial decomposition temperature (°C)				
		190	200	210	220	230
Non-catalytic	12	3.35	3.01	2.72	2.49	2.37
	15	2.02	1.87	1.82	1.92	2.15
Catalytic	7.5	2.10	1.80	1.67	1.78	2.14
	10	1.40	1.30	1.41	1.71	2.15

Table 4 shows that the model validation at the suggested heating rate for the non-catalytic pyrolysis of 15°C/min and catalytic pyrolysis of 7.5°C/min were fairly good, with the RMSE value of 1.82 and 1.67 for non-catalytic and catalytic pyrolysis respectively. Table 4 also shows that setting the value of T0 in the Equation [25-28] at a temperature of 210°C (483 K) gives an accurate data-model fitting.

4. CONCLUSION

The application of the semi-global kinetic model for predicting the yield distribution in palm shell pyrolysis in FB-TGA was conducted and the developed model has been proposed. The use of FB-TGA makes it possible to evaluate the yield of pyrolysis products (tar, gas, and char) at one cycle of the process for various experimental temperatures. Based on the reaction kinetics analysis from this study, pyrolysis at a

temperature range of 300-600°C only involves primary decomposition reactions especially for non-catalytic pyrolysis, because the value of k4 and k5 (secondary reaction rate constant) was infinitely small. The model validation confirms that the developed model is sufficiently good for predicting the yield of pyrolysis products (tar, char, and gas) at the suggested heating rate. The development of a kinetic model based on evolution in mass over time cannot clearly explain the secondary tar reactions due to the small value of k4 and k5, therefore it is suggested to use the basis of evolution in mass with respect to final experimental temperature to explain the occurrence of the secondary tar reactions.

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6. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. The authors confirmed that the paper was free of plagiarism.

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Slow Pyrolysis Without Lignocellullose Catalyst (Sugar Cane Bagasse, Palm Kernel Shell and Empty Palm Oil Bunch) in Batch Reactor: Yield and Liquid Product Characteristics

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Abstract-Waste from the processing of plantation crops can still be utilized by burning directly as boiler fuel and industrial needs, but if it is further processed with the latest technology it can produce energy, high-value chemicals, fertilizers and adsorbents. Conversion technologies used with thermochemistry, biochemistry and chemistry. One of the conversion of biomass waste that is low cost and without the addition of additives with thermochemistry is pyrolysis. Pyrolysis of empty fruit bunches and palm shells

produces chemicals including phenol, while sugarcane bagasse produces levoglucosan. The highest content of phenol and eugenol was obtained at 500 C with yields of 35.89 and 1.83 wt.%. The highest xylenol content was obtained at 600°C with a yield of 0.21 wt.%.

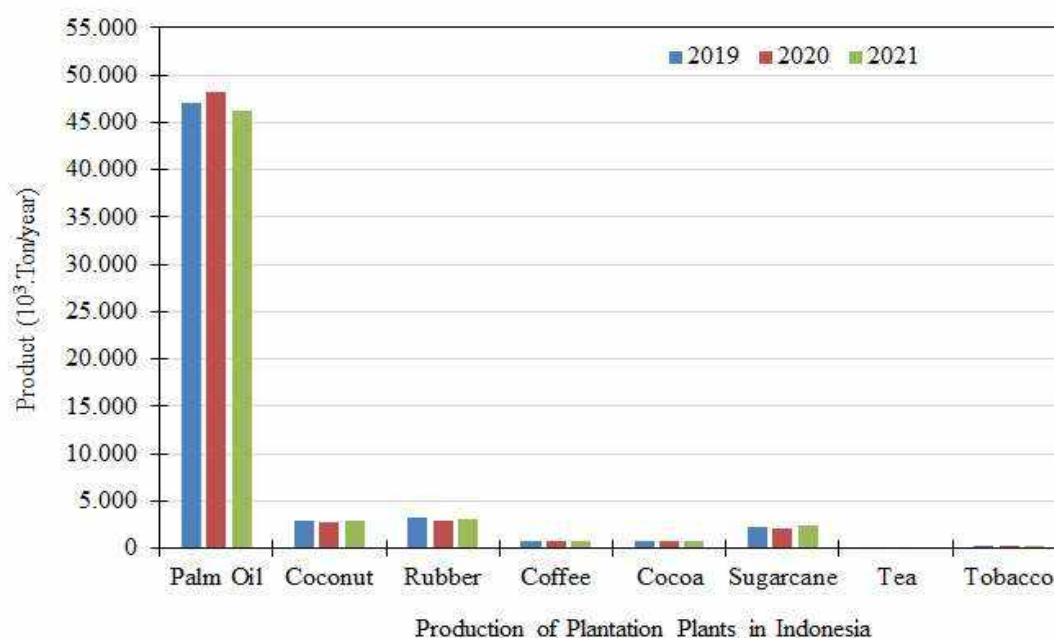**Keywords-**Plantation waste; pyrolysis; phenols; levoglucosan; chemicals

1. Introduction

The potential for plantation crops in Indonesia is diverse and their availability is very abundant in the last 3 years (2019-2021), such as coconut plants (2835.03.103 tons/year), oil palm (47213.47.103 million tons/year), rubber (3102.5103 tons /year), tobacco (256.03.103 tons/year), tea (134.3.103 tons/year), coffee (760.33.103 tons/year), cocoa (718.2.103 tons/year), and sugar cane (2258.7.103 tons/year) [1], plantation crop products in Indonesia can be seen in Figure 1.

Biomass waste from oil palm processing includes empty palm fruit bunches, palm shells, palm sludge, fibers, and liquid waste. Palm shell waste in 2019 is equivalent to 3.14 million tons, Palm Oil Bunch (EFB) waste with a potential of around 2.5 million tons per year. The production of sugarcane (Saccharum officinarum Linn) in Indonesia with a total of 28.9 million tons in 2020 with bagasse of 10.12 million tons (Food & Agriculture, FAO), with bagasse consisting of 40-50% cellulose, 20-30% hemicellulose, 20–25% lignin and 1.5–3% ash.

Waste from the processing of plantation crops can still be utilized by burning directly as boiler fuel and industrial needs, but if it is further processed with the latest technology it can produce energy, high-value chemicals, fertilizers and adsorbents. Conversion technologies used with thermochemistry, biochemistry and chemistry. One of the

conversion of biomass waste that is low cost and without the addition of additives with thermochemistry is pyrolysis. Pyrolysis of empty fruit bunches and palm shells produces phenol, while sugarcane bagasse produces levoglucosan. Levoglucosan 1,6-anhydro-β-D-glucopyranose is an important product resulting from pyrolysis of cellulose with high yields (up to 60%), this compound can be converted into ethanol, it can also function as a precursor for chemicals, surfactants, food,

Production of Plantation Plants in Indonesia

Phenol is an important raw material in many chemical processes and is currently almost entirely obtained from petrochemical sources. Likewise with alcohol which is generally obtained from starch fermentation, it turns out that levoglucosan can be obtained. Phenol from pyrolysis of empty palm oil has been carried out

Terry et. Al., (2021) in his writing said that currently, a number of studies have been carried outn ……..assessed the phenol preparation from PKS pyrolysis. Asadullah et al. (2013) reported a high biooil yield of 57% and a relative phenol content of more than

40% area using a fluidized bed operating at 550 °C in conjunction with a 2 L/min N2 flow rate and a biomass feed rate of 10 g/min. Omoriyekomwan et al. (2016) obtained a maximum relative phenol content of 64.58% area using microwave-assisted pyrolysis associated with activated carbon as a catalyst.

Stirring the reaction mixture with an overhead stirrer increased the phenol yield to 72% area (Salema and Ani, 2012). To the best of knowledge, this value represents the highest relative phenol

The palm oil industry produces the most consumed vegetable oil worldwide. The largest producers of crude palm oil are Indonesia, Malaysia and Thailand in the tropical region of Southeast Asia.4]. Oil palm fruit is processed in palm oil mills, where only about one-fifth of the harvest period is utilized as the main product, palm oil, while the other part of the processed fruit bunches is left as waste biomass. Therefore, by-products are formed in very large quantities, in the amount of millions of tonnes every year [5]. The most important biomass wastes are empty oil palm fruit bunches (EFB), mesocarp fiber (MF), and core shell (KS), which are suitable raw materials for energetic exploitation and thermochemical conversion. Utilization of this type of biomass is promising because it is available at the palm oil mill site; thus, no further transportation is required before further conversion in contrast to grain or forestry harvest residues [6,7].

In this study, we characterize OPEFB, MF, and KS derived from the palm oil production process with the aim of utilizing these materials as potential renewable energy raw materials. The specific objective of this work is to obtain information about the composition and thermal decomposition reaction of this biomass by-product, because the use of palm oil residue can still be optimized in a more energy-efficient system. The thermal decomposition of oil palm residues is described in several publications [12–14];

however, the evolution of volatile liquid products has not been studied by thermogravimetry/mass spectrometry (TG/MS) in detail. This work combines the results of compositional analysis of organic and inorganic constituents with the findings of thermal decomposition experiments using pyrolysis-GC/MS and TG/MS. Therefore,

Pyrolysis is the thermal decomposition of biomass without the presence of oxygen (Sukiran et al., 2011). Pyrolysis is more promising than other thermochemical conversions because it is more flexible in the selection of raw materials (no need to pay attention to the type, shape and physical and chemical properties of raw materials), can be operated over a wide temperature range and at atmospheric pressure, and produces three types of products (solid, liquid, and gas) (Melia et al., 2021).

Palm shells also contain valuable chemicals including phenol and phenolic components derived from lignin decomposition (Ani, nd; Omoriyekomwan et al., 2016). Research to study the composition of phenol and phenolic components in palm shells has been carried out by previous researchers. Yang An et al, carried out catalytic pyrolysis of palm shells to produce phenol and hydrogen (An et al., 2020). Kanit et al. studied phenol and phenolic components resulting from the fast pyrolysis of organosolv lignin (Soongprasit et al., 2020). Phenol production through the pyrolysis process has also been carried out by other researchers.

This research was conducted to study the effect of pyrolysis temperature on biomass waste in the form of empty palm oil peels, palm kernel shells and sugarcane bagasse on yield and components in liquid products. Biomass waste sample analysis was carried out by proximate, ultimate and calorific value tests. The liquid product was analyzed by GC-MS.

2. Research methods

2.1. Ingredients

BThe material used in this research is palm shell. Palm shells are obtained from oil palm plantations in West Borneo. Before use, the oil palm shells are cleaned by washing them with clean water to remove impurities, then dried in the sun for two days, crushed using a hammer mill, and sieved to obtain a particle size of -16+40 mesh. Then it was dried in an oven at 1050C for 24 hours to get a moisture content of about 10% dry weight.

2.2. Tool

The equipment used in this study was a vertical cylindrical fixed bed reactor made of stainless steel with an inner diameter of 40 mm, an outer diameter of 44 mm, and a height of 600 mm. The reactor is equipped with a heater made of nickel wire which is wrapped around the outside of the reactor. Heating temperature and speed are measured and regulated using K-type thermocouples and a PID controller (Jamilatun et al., 2019).

Pyrolysis was carried out under isothermal conditions by inserting 50 grams of palm shells into the reactor, then heating at a heating speed of 10-120C/minute, after the reactor temperature reached the desired temperature (300, 400, 500, and 6000C) heating was continued for 60 minutes continuously. isothermal.

The results of pyrolysis in the form of condensed gas were stored in an accumulator and were measured by weight and analyzed by GC-MS (QP2010-SE, Shimadzu). The non-condensed gas is flowed into the water tank to be absorbed, while the char (charcoal) that is formed is taken after the pyrolysis is complete, then weighed.

3. Research Results and Discussion

3.1. Characteristics of Raw Materials

Table 1.Composition of Oil Palm Bunches, Shells and Bagasse

Element	Sugarcane Bagasse	Palm Shell (Dewanti, 2019)	Palm Oil Field (Shafaghataet al., 2019), Abdullah, Brigwater 2007)
C. %	42.5	48.99	42.6
H. %	6.17	6.60	5.7
N. %	0.23	0.37	1.7
S.%	0.1	0.08	0.3
O*. %	51.0	43.96	49.7
O/C	1.2	0.90	1.68
H/C	0.121	0.14	0.13
FC. %	22.14	16	13.4
volatile matter. %	71.42	71.84	78.8
water. %	3.87	7.92	5.5
Ash. %	2.57	4.28	2.3
Calories MJ/kg	18.79	24.28	39.5
Cellulose. %	45.96	26.6	45.9
Hemicellulose. %	20.64	27.7	18.3
Lignin. %	21.80	29.4	18.3
Extractive	11.60	16.30	17.50

*oxygen was calculated by difference.

Characteristics of Sugarcane Bagasse	
Proximate analysis, %	
moisture	5,4
volatile matter	80,2
Fixed carbon	11,3
Ash content	3,1
Ultimate analysis, %	
Carbon(C)	44,86
Hydrogen (H)	5.87
Nitrogen (N)	0.24
Sulfur (S)	0.06
Oxygen (O)	48.97
O/C molar ratio	0.82
H/C molar ratio	1.57
HHV (MJ/kg)	18.0
Lignocellulosic composition, %	
Cellulose	47,6
Hemicellulose	39
Lignin	11,2
Extractives	2,2

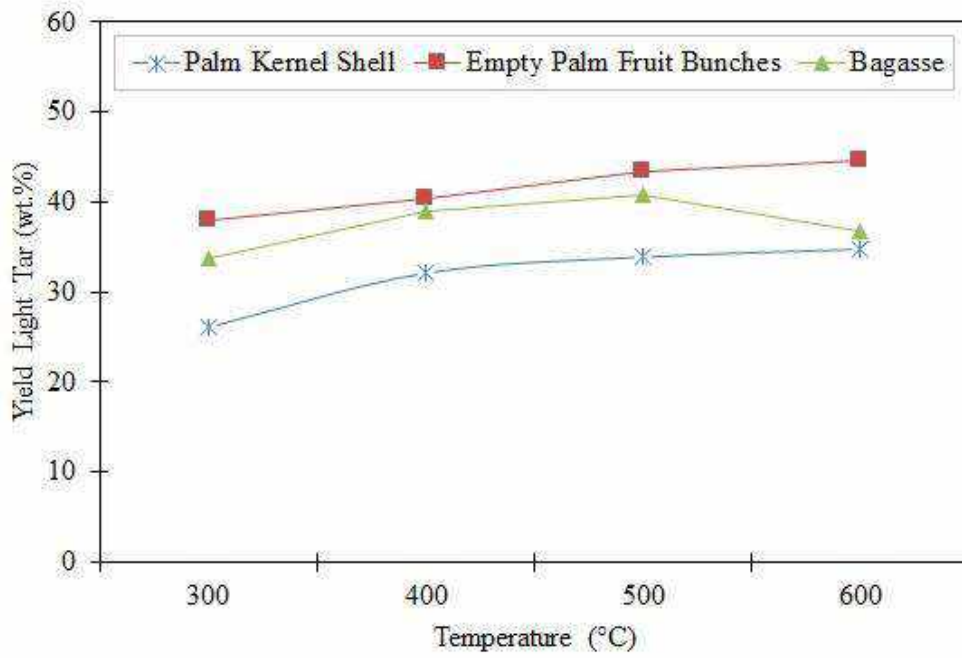## 3.2. Effect of temperature and type of biomass on Product Yield

Figure .

Organic Phase Characterization.
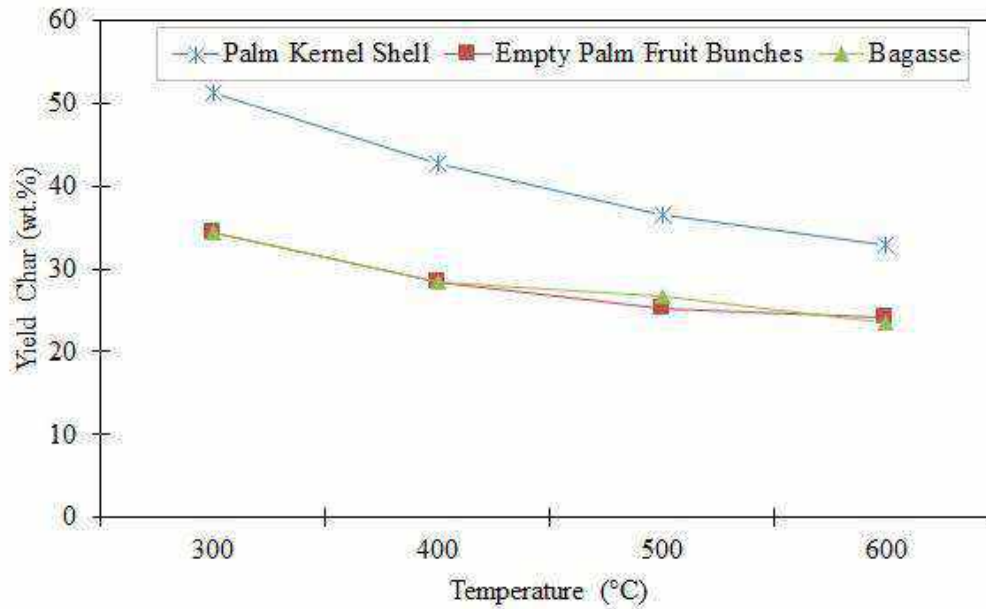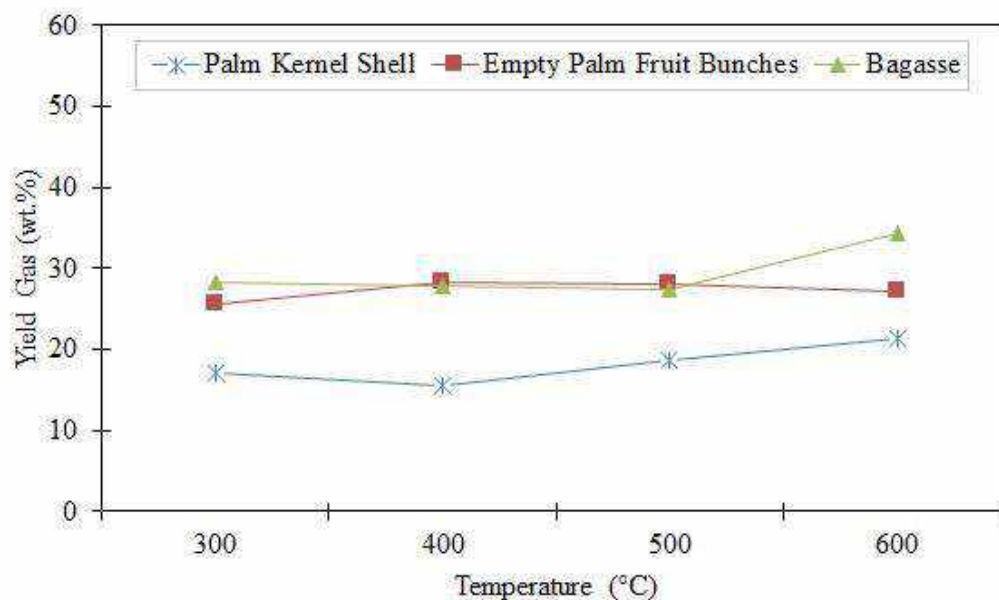
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3.3.3. Effect of temperature and type of biomass on the characteristics of bio-oil

3.3.3.1. Bagasse at pyrolysis temperature 500°C

Component (Heavy phase)	Area %	Components (Light phase)	Area %
Glucose and its derivatives		**Glucose and its derivatives**	
		1.6-Anhydro-Beta-D-Glucopyranose (Levoglucosan)	70.52
		Alpha.-.Beta.-D-Ribopyranose. 1.3-Di-O-Acetyl-	2.18
Acids and their derivatives		**Acids and their derivatives**	
Dodecanoic Acid	3.19	Hexadecanoic Acid (Cas)	2.02
Hexadecanoic Acid (Cas)	5.54	Octadecenoic Acid (Z)-. 2.3-Dihydroxypropyl Esters (Cas)	2.57
1.2-Benzenedicarboxylic Acid	18.47		
Hydrocarbons		**Hydrocarbons**	
Octadecane (Cas)	2.07		
2.3.3-Trimethyloctane	8.29		
Dotriacontane (Cas)	3.58		
Heptacosane (Cas)	2.35		
Octadecane (Cas)	2.65		

Other compounds		Other compounds	
4-(Ethylamino)-6-(4-Morpholinyl)-1.3.5-Triazine-2-Carboxamide	3.27	2-Cyclopenten-1-One. 2-Hydroxy-3-Methyl- (Cas)	1.82
2.5-Dimethoxy-2-Methyl-Tetrahydrofuran	2.49	Heptyl Formate (Probably 2-Ethylpentyl Formate)	8.27
1-Heptanol. 2-Propyl- (Cas)	16.14	Benzene. 1.2.3-Trimethoxy- (Cas)	4.04
Tetradecane. 1-Chloro- (Cas)	8.87	Benzene. 1.2.3-Trimethoxy-5-Methyl- (Cas)	1.21
Oxacyclotridecan-2-One (Cas)	3.84		
2-Cyclobuten-1-One. 4.4-Dimethyl-3-(1-Piperidinyl)-(Cas)	7.71		

3.3.3.2. Palm Kernel Shell

Component (Heavy phase)	Area %	Components (Light phase)	Area %
Phenols and their derivatives		**Phenols and their derivatives**	
Phenol	35.11	Phenol	65.31
Phenol. 2.6-Dimethoxy-	3.88		
Phenol. 4-Ethyl-2-Methoxy-	3.08		
Phenol. 2-Methoxy-	2.27		
Phenol. 2.6-Dimethoxy-4-(2-Propenyl)-	1.52		
2-Methoxy-4-Methylphenol	2.8		
Acids and their derivatives		**Acids and their derivatives**	
2.4-Hexadienedioic Acid	2.6	3-Oxo-2.6.6-trimethyl-2-cyclohexen-1-carboxylic acid	0.94
Dodecanoic Acid	13.9	2.4-Hexadienedioic acid	0.76
Hexadecanoic Acid	5.78		
Octadec-9-Enoic Acid	5.4		
Tetradecanoic Acid	5.22		
Octadecanoic Acid	1.22		
Hexadecanoic acid. methyl esters	0.57		
Benzene and its derivatives		**Benzene and its derivatives**	
Benzene. 1.2.3-Trimethoxy-5-Methyl-	2.88	1.2.4-Trimethoxybenzene	3.79
Benzofuran. 2-Methyl-	1.22		
1.2.4-Trimethoxybenzene	4.41		

Other compounds		Other compounds	
		2-Furancarboxaldehyde	1.85
		[15N]-Aniline	22.52
		2-Cyclopenten-1-One. 3-(Acetyloxy)-	2.14

3.3.3.3. Oil Palm Empty Bunches

Component (Heavy phase)	Area %	Components (Light phase)	Area %
Phenols and their derivatives		**Phenols and their derivatives**	
Phenol (CAS)	11.21	Phenol	18.43
Phenol. 2-Methoxy-	1.06	Phenol. 2-Methoxy-	3.38
Phenol. 2.6-Dimethoxy- (CAS)	5.65	Phenol. 2.6-Dimethoxy- (CAS)	8.79
Phenol. 3.4-Dimethoxy- (CAS)	1.50	Phenol. 2.6-Dimethoxy-4-(2-Propenyl)- (CAS)	1.10
2.4-Dimethoxyphenol	1.46	Phenol. 2.6-Dimethoxy-4-(2-Propenyl)- (CAS)	1.07
Phenol. 2.6-Dimethoxy-4-(2-Propenyl)- (CAS)	1.39		
Acids and their derivatives			
2.4-Hexadienedioic Acid. 3-Methyl-4-Propyl-. Dimethyl Esters. (EE)- (CAS)	1.43	Hexadecanoic Acid (CAS)	3.61
Heptadecene-(8)-Carbonic Acid-(1)	1.18	9-Octadecenoic Acid. (E)-	13.58
2-Propenoic Acid. 2-Methyl-. Ethyl Esters (CAS)	4.99	Octadecanoic Acid (CAS)	2.13
		9-Octadecenoic Acid (Z)-. 2.3-Dihydroxypropyl Esters	1.71
		Butanoic Acid. 2-Propenyl Esters (CAS)	1.57
Benzene and its derivatives		**Benzene and its derivatives**	
1.2.4-Trimethoxybenzene	3.07	1.2.4-Trimethoxybenzene	1.86

		Benzene. 1.2.3-Trimethoxy-5-Methyl- (CAS)	3.41
Other compounds		**Other compounds**	
2-Furanmethanol. Tetrahydro-	8.22	1.2-Epoxy-3-Propyl Acetate	2.13
2-Cyclopenten-1-One. 2-Hydroxy-3-Methyl- (CAS)	7.68	2-Cyclopenten-1-One. 2-Methyl- (CAS)	1.27
Ethanone. 1-(1H-Pyrrol-2-Yl)- (CAS)	11.71	3-Pentanone. 2-Methyl- (CAS)	1.36
Glycine. N-(Trifluoroacetyl)-. 1-Methylpentyl Esters (CAS)	6.81	2-Furanmethanol. Tetrahydro-	6.41
Pentane. 3-Bromo- (CAS)	3.28	2-Cyclopenten-1-One. 2-Hydroxy-3-Methyl- (CAS)	14.84
Pentanal (CAS)	1.61	3.5-DimethylCyclopentenolone	1.31
Disulfide. Ethyl(1-Methylpropyl) (CAS)	1.35	Pentanal (CAS)	1.95
3-Ethyl-2-Hydroxy-2-Cyclopenten-1-One	6.53	3-Ethyl-2-Hydroxy-2-Cyclopenten-1-One	4.82
2-Isononenal (CAS)	2.61	1.5-Dioxonane. 2-Ethoxy-9-Methyl- (CAS)	2.70
Crotonaldehyde. 2-Methyl-. Diethylhydrazone (CAS)	2.94		
Dl-Ribitol. 1.4-Anhydro-. Cyclic 2.3-(Ethylboronate)	4.94		
Hydrazine. (2-Methyl-1-Propenyl)- (CAS)	1.23		
Ethanone. 1-(2.6-Dihydroxy-4-Methoxyphenyl)- (CAS)	6.25		

The composition of the bio-oil produced by pyrolysis of palm shells at a temperature range of 300 – 6000C is shown in table 1. The GC-MS results also show that

the pyrolysis of palm shells produces a variety of valuable chemicals such as phenol. guaiacol. syringol. creosol. p-ethylguaiacol. eugenol. o-cresol. and xylenol.

Table 1. GC-MS analysis of the organic phase

Pyrolysis of palm shells at 3000C produces the main components phenol and guaiacol. Pyrolysis at 4000C produces the main components of phenol. syringol. p-ethylguaiacol. creosol. guaiacol. and eugenol. Pyrolysis at 5000C produces the main component phenol. syringol. p-ethylguaiacol. creosol. guaiacol. and eugenol. While pyrolysis at 6000C produces the main component phenol. syringol. p-ethylguaiacol. creosol. guaiacol. and eugenol.

Phenol is the main raw material for various chemical processes and has various applications (Ani. nd; Chang et al. 2018). Phenols together with acids and carbonyls can work as antimicrobials so they can inhibit the decomposition of preserved products (Stołyhwo & Sikorski. 2005). Phenol is also the main raw material for the manufacture of bio-plastics. phenolic resin or epoxy resin or polyurethane (Omoriyekomwan et al.. 2016). Phenol is also used in the manufacture of automotive spare parts. household appliances. electronic components. adhesive. paint. plywood and insulating material (Ani. nd).

Guaiacol is a natural organic component that acts as an aromatic oil. Guaiacol is derived from guaiacum and is present in a variety of essential oils and is a useful precursor

for the production of green fuels because it is produced from biomass. Guaiacol and syringol are the main products of the pyrolysis of hardwood lignin (KN et al. 2022).

Eugenol(2-Methoxy-4-prop-2-enylphenol) is a phenolic compound from the phenylpropanoid group and is the main component of clove oil. Eugenol has various pharmacological activities such as antioxidants. anti-inflammatory. anti-microbial. analgesia and local anesthesia (Yu et al. 2022).

The results of pyrolysis besides having broad applications both in the pharmaceutical field. food. cosmetics. as well as industry. also has a high selling price (table 2) which makes the refinery valuable chemicals process from the organic phase of pyrolysis of palm oil shells very promising.

Table 2.

Component	Application	Price (IDR)
Phenol	Anti microbial. phenolic resins. plywood. pharmaceutical products(Ani. nd; Chang et al. 2018)	1.831.661.72/100 gr
Guaiacol (Phenol. 2-methoxy-)	Anti cancer(Widiyarti et al. 2014). anti-microbial(N. Li et al. 2021). vanillin production(Soongprasit et al. 2020)	205.400.22/100 gr
p-Ethylguaiacol (Phenol. 4-ethyl-2-methoxy-)	Fragrance ingredients. antioxidants(H. Li et al. 2018)	2.530.445.96/100 g
Creosol (2-Methoxy-4-methylphenol)	Flavoring agent. bio-fuels(Aliu et al. 2021)	1.132.877.48/ml
Syringol (Phenol. 2.6-dimethoxy-)	Flavoring agent. fragrance ingredients(Api et al. 2022)	1.614.615.10/100 gr
1,6-Anhydro-beta-d-glucose	It can be converted into ethanol for fuel production, as a chemical precursor for surfactants, food and pharmaceutical additives.	

Eugenol (Phenol. 2.6-dimethoxy-4-(2-propenyl)-)	Campylobacter activity inhibitor(Irem & Korkmaz. 2022). [35]. Inhibits inflammatory response and reduces fungus(Yu et al. 2022)	364.638.32/100 mg
o-Cresol (Phenol. 2-methyl-)	Fragrance ingredients(Api et al.. 2021). epoxy resins(Zeng et al. 2020)	109.687.95/100 mg
Xylenol (Phenol. 2.4-dimethyl-)	Synthetic material. medicinal intermediates. and insecticide(Tsukatani et al. 2010)	223.399.20/100g

Effect of Temperature on Organic Phase Yield

Palm oil shell pyrolysis produces an organic phase. water phase. gas. and char. The effect of temperature on the yield of pyrolysis products is shown in Figure 4. Figure 4 shows that the higher the temperature, the higher the yield of the organic phase. water phase. and gas. while the char is decreasing. The highest organic phase yield was obtained at 600 ℃ with an organic phase yield of 11.03%.

Increasing the temperature from 300 ℃ to 500 ℃ causes an increase in bio-oil yield from 5.67% to 11.03%. The increase in bio-oil in this temperature range was due to increased biomass decomposition (Melia et al. 2021) because hemicellulose decomposition occurs in the temperature range of 250-350 ℃. cellulose decomposition in the range of 325 -400 ℃. and lignin decomposition at 300-550 ℃ (KN et al. 2022).

Figure 4. Yield of pyrolysis products at a temperature range of 300-600 C

The Effect of Temperature on the Yield of Phenolic Components as Valuble Chemicals

Palm shell pyrolysis produces valuable chemicals in the form of phenolic components resulting from lignin decomposition. The type and content of valuable chemicals in the form of phenolic components depend on the lignin content and structural characteristics of the phenolic components of the biomass. Lignin is a polymer with three-dimensional cross-linking which has a complex structure consisting of three phenolpropanoid units. namely H-phenol. G-phenol. and S-phenol. H-phenol is a product with p-hydroxyphenyl units derived from p-coumaryl alcohol. G-phenol is a product with guaiacyl units which is a derivative of coniferyl alcohol. S-phenol is a product with a syringil unit which is a derivative of sinapyl alcohol. Most of these units are joined together by ether bonds (C—C) and C—C bonds (Lyu et al. 2015; Soongprasit et al. . 2020).

Figure 5 shows the distribution of H-phenol. G-phenol. and S-phenol at 300-600°C. The figure shows that the higher the temperature, the lower the yield of G-phenol and S-phenol. Meanwhile, the higher the temperature, the higher the yield of H-phenol, the greater the yield up to 500°C. then decreased at 600°C. This happens because of the deoxygenation of oxygenate components including phenolic components through demethylation. demethoxylation and dehydroxylation (KN et al. 2022) into aliphatic and aromatic hydrocarbons by releasing CO gas. CO_2. and others (Jamilatun et al.. 2019).

Figure 6. Phenol composition at various temperatures

The phenol content in bio-oil from palm shells in this study was relatively high compared to other phenolic components. The high content of phenol in bio-oil from palm shells is also reported in some literature (Kim et al.. 2010). The high content of phenol in bio-oil in palm shells is due to the high lignin content (Chang et al. 2016). Lignin is decomposed through dehydration of carboxyl groups on alkyl chains followed by breaking of inter-aromatic bonds (Misson et al. 2009) and hydrolysis of ether bonds in lignin (Toor et al. 2011) to produce phenol and its derivatives. benzene. xylene. pyridine and furan derivatives. The phenol content in the bio-oil in this study was in the range of 21.40-35.89 wt.% (figure 6). The highest phenol content was 35.89 wt.% at 500°C . The phenol content at temperatures below 300°C is quite high whereas lignin decomposition occurs at temperatures of 300-550 °C (KN et al.. 2022). The formation of phenol at temperatures below 300°C is due to the termination of the ferulic acid ester branch chain in xylan and also the polymerization of unsaturated light components (Evans & Milne, 1987).

The formation of phenol increased from 21.40 at 300°C to 35.89 wt.% at 500°C. this is due to the increased lignin decomposition that occurs in the temperature range of 300 to 500°C (Yang et al. 2007). and also due to the termination of the methoxy and alkyl chains on groups substituted for phenols such as methoxy phenol. alkyl phenol. alkyl methoxy phenol. and oxygenated alkyl methoxy phenol (Soongprasit et al.. 2020). At temperatures above 500°C. The phenol content decreases with increasing temperature which is caused by the deoxygenation of phenol into aromatic hydrocarbons by releasing CO gas. CO_2. and others (Jamilatun. Budhijanto. et al.. 2020) or due to electrophilic aromatic substitution through alkylation and acylation reactions (Roswanda et al.. 2018).

Figure 7. Yield valuable chemicals (G-phenol and S-phenol) at 300-600 C

Figure 7 shows the yield of valuable chemicals in the form of G-phenol (guaiacol. creosol. p-ethylguaiacol) and S-phenol (syringol. and eugenol) at temperatures of 300-600° C. Guaiacol and syringol are included in the methoxy phenol category. phenol component with a methoxy group. While creosol and p-ethylguaiacol are included in the category of alkyl-methoxy phenol. phenolic components with alkyl groups and methoxy groups. The picture shows that guaiacol and syringol are the highest components. The high content of guaiacol and syringol indicates that the product originates from the pyrolysis of hardwood lignin.

At 400°C the product is dominated by guaiacol and syringol. At temperatures of 400 to 600°C there is a decrease in the amount of both components and an increase in the amount of phenol. this is caused by radical induced rearrangement (ipso-substitution) reactions to produce cresol and xylenol. then these two aromatic compounds undergo further decomposition by producing phenol through a demethylation reaction (Stefanidis et al.. 2014).

Increasing pyrolysis temperature causes guaiacol content. creosol. p-ethylguaiacol. and syringol tends to decrease. Guaiacol content. creosol. p-ethylguaiacol. and the highest syringol was obtained at 400°C with a yield of 2.88 respectively. 3.62. 3.86. and 5.03 wt.%. The highest eugenol content was obtained at 500°C with a yield of 1.83 wt.%.

Figure 8. Yield valuable chemicals (H-phenol) at a temperature of 300-600 C

Figure 8 shows the yield of H-phenol (o-cresol and xylenol) at 300-400°C. Cresol and xylenol are included in the category of alkyl phenols. phenolic components with alkyl groups. Both components are included in the simple phenol. Simple phenols are formed from the decomposition of cellulose and hemicellulose (Evans & Milne. 1987). These two components are also formed due to radical induced rearrangement (ipso-substitution) reactions to guaiacol and syringol and demethoxylation to alkyl methoxi phenols. Further reactions of the two components through demethylation reactions produce phenol. At 300°C the contents of these two components were not detected. Whereas at temperatures above 300°C the amount of o-cresol slightly decreased while the amount of xylenol tended to be stable.

Increasing temperature causes the o-cresol content to decrease slightly and the xylenol content to remain constant. The highest content of o-cresol and xylenol was obtained at 400°C with yields of 0.41 and 0.21 wt.%.

4. CONCLUSION

Palm shell pyrolysis produces an organic phase. water phase. gas. and char. The organic phase resulting from pyrolysis contains valuable chemicals such as phenol. guaiacol. syringol. creosol. p-ethylguaiacol. eugenol. o-cresol. and xylenol. These components have applications in the pharmaceutical field. food. cosmetics. and industry and has a high selling price. Increasing the temperature of pyrolysis causes a decrease in the content of G-phenol and S-phenol such as guaiacol. creosol. p-ethylguaiacol. and syringol. and increase the content of H-phenols such as phenol. Guaiacol content. creosol. p-ethylguaiacol. The highest o-cresol and syringol were obtained at 400°C with a yield of

2.88 respectively. 3.62. 3.86. 0.41. and 5.03 wt.%. The highest content of phenol and eugenol was obtained at 500 C with yields of 35.89 and 1.83 wt.%.

Acknowledgments

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Bio-oil from Oil Palm Shell Pyrolysis as Renewable Energy: A Review

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ABSTRACT

Oil palm shell (OPS) is biomass with high carbon and hydrogen content, so it has the potential to produce renewable energy through the thermochemical method. Pyrolysis is a relatively inexpensive thermochemical method that continuously converts biomass into valuable gas, bio-oil, and char products. Bio-oil is used directly to fuel boilers and furnaces or to produce fuel oil. This article reviews the pyrolysis process of biomass from oil palm shells, discussing the operating parameters that influence the pyrolysis process and the method of upgrading bio-oil. This review shows a relationship between biomass composition (cellulose, hemicellulose, and lignin) and bio-oil yield. The water content in the raw material needs to be controlled at around 10%. The optimum particle size is closely related to the biomass's natural structure and reactor type. The higher the ash and fixed carbon content, the lower the bio-oil yield. The optimum temperature for pyrolysis is between 450-550 °C. A high heating rate will increase the decomposition of biomass into bio-oil. Particle size and reactor type strongly influence feed rate, residence time, and reaction time. A fluidized bed reactor gives the highest bio-oil yield. Using plastic in co-pyrolysis and catalyst increases the heating value and decreases the oxygenated content.

1. Introduction

The reduced production of fossil energy, especially oil, and the global commitment to reducing greenhouse gas emissions, has prompted the government to continuously increase the role of renewable energy to maintain energy security and independence [1]. The Indonesian government is committed to climate change adaptation in the Paris Agreement by accelerating the energy transition from fossil fuels to renewable energy or energi baru dan terbarukan (EBT). The government targets the EBT mix of 23% by 2025, equivalent to 92.2 Million Tonnes of Oil Equivalent (MTOE), a quarter of which is planned from biofuels or bahan bakar nabati (BBN). The impact of the COVID-19 pandemic has caused the supply of EBT to decline with a nominal value of around 23.6 - 36.6 million Barrels of Oil Equivalent (BOE). EBT development needs serious attention related to the target of the EBT mix of 23% by 2025 [2]. Researchers have identified biomass as a sustainable, renewable, and environmentally friendly energy source [3].

Biomass is a term used for all organic materials from a plant produced through photosynthesis using sunlight [4]. Biomass is a carbon-neutral material with lower greenhouse gas (GHG) emissions due to its lower nitrogen and sulfur content than petroleum and coal [5]. Biomass is considered the largest renewable and sustainable source of carbon for the production of biofuels as a source of abundant and inexpensive energy. It accounts for 14% of world energy consumption [6].

Biomass can be converted into fuel through several processes, including combustion, digestion, gasification, pyrolysis, fermentation, and catalytic reactions [4]. Pyrolysis is a relatively inexpensive process that continuously converts biomass into valuable gas, liquid, and char [7].
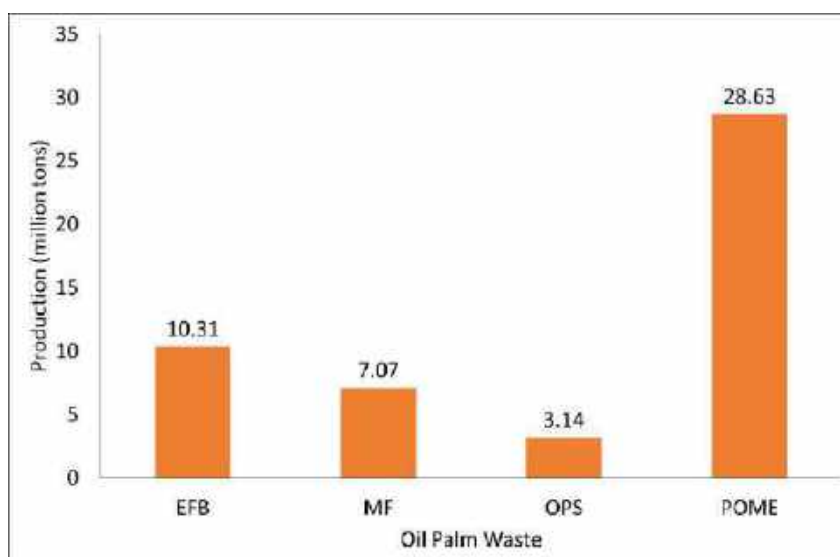

Fig. 1. Oil palm waste production in Indonesia in 2021 [8]

The production of EBT in biofuels relies heavily on crude palm oil (CPO) processing. The increase in crude palm oil (CPO) production in Indonesia has led to the rise of biomass waste from oil palm, including oil palm shells (OPS), empty fruit bunches (EFB), mesocarp fibers (MF), and palm oil mills effluent (POME) [9]. It is estimated that palm oil production in 2021 will be 49 million tons [10], with palm shell waste of 3.14 million tons (Fig. 1). This article contains a review of the pyrolysis process of biomass from oil palm shells, focusing on discussing the operating parameters that influence the pyrolysis process and the method of upgrading bio-oil.

2. Oil Palm Shell Biomass

Biomass is classified into four generations of biomass (Table 1). First-generation biomass refers to biomass from food crops such as sugarcane, starch, vegetable oils, and animal fats. The second generation is biomass from non-food and lignocellulosic plant residues such as wood, grass, and municipal solid waste. Meanwhile, the third generation biomass is the biomass from microalgae [11]. First-generation biomass as an energy source is limited because it competes with food demands [12].

Table 1. Biomass Classification by generation [11]

	1st	2nd	3th	4th
Feedstock	Sugarcane, grains, soybeans, corn, flours, vegetable oils, animal fats	*Wood, agricultural waste, municipal solid waste, animal waste, grass, pulp sludge*	Microalgae	Genetically modified crop
Product	Biodiesel, alcohol, corn ethanol	Hydrotreating oil, bio-oil, FT-oil	Algae oil	Biofuel
Advantages	Environmentally friendly, economical, and socially secure	We are not competing with food; environmentally friendly	High protein and residual nutrient algae can be used for jet fuel and animal feed.	Easily capture CO_2 and convert it into carbon-neutral fuel.
Disadvantages	Limited, mixed with conventional fuel	Acidic, viscous, high oxygenated content	Slow growth, complicated and expensive algae extraction	-

Oil palm shell is second-generation biomass rich in carbon and hydrogen and similar to hardwood [13], thus making palm shells a superior raw material for producing biofuels, valuable chemical products, or energy through thermochemical methods [14]. The oil palm shell is one of the lignocellulosic biomass, containing three main components: cellulose, hemicellulose, and lignin [15]. Cellulose is the essential component in biomass because it has the most significant percentage and contains a long linear chain of -(1,4)-glycoside composed of D-glucose monomers [16]. Hemicellulose is a polysaccharide complex in the cell wall and cellulose, which acts as a connecting element between cellulose and lignin [17]. Lignin is a non-carbohydrate component of wood with a polyphenol structure that plays a role in building cell walls and combining all cells into one [15].

Oil palm shells contain about 24% hemicellulose, 50% lignin, and 30% cellulose. Compared to fossil fuels, oil palm shells have lower nitrogen content (<1%), lower sulfur content (<0.2%), and higher oxygen content (40-50%). The low nitrogen and sulfur content will reduce the content of NO_x and SO_x, a greenhouse gas. The high carbon content is suitable for manufacturing high-density briquettes [18]. The proximate and ultimate analysis of oil palm shells is shown in table 2.

Table 2. Palm shell proximate dan ultimate analysis

Proximate Analysis	Value (wt%)					Ultimate Analysis	Value (wt%)				
Moisture Content	5.69	7.96	12.69	9.4	11	*Carbon*	46.92	50.01	51.56	44.56	50.7
Volatile	69.10	72.47	75.14	82.5	67.2	*Hydrogen*	8.95	6.85	6.31	5.22	6.0
Fixed Carbon	23.49	18.7	22.05	1.4	19.7	*Nitrogen*	1.15	1.90	0.7	0.4	0.4
Ash	1.72	1.1	2.81	6.7	2.1	*Sulfur*	2.35	-	0.1	0.05	0.1
						Oxygen	40.63	41.15	41.33	49.77	42.8
Ref.	[19]	[20]	[21]	[22]	[23]		[19]	[20]	[21]	[22]	[24]

Biochemical and thermochemical can convert biomass into solid, liquid, and gaseous fuels, including extraction, hydrolysis, and fermentation [25]. It takes a long time and has a low yield. Thermochemical conversion includes combustion, gasification, and pyrolysis process that produces heat. Gasification is the thermochemical conversion of raw materials into syngas through chemical reactions at high temperatures under controlled oxygen conditions [26].

3. Oil Palm Shell Biomass Pyrolysis

Thermochemical conversion has advantages over other technologies, one of which is pyrolysis. Pyrolysis is the thermal decomposition of biomass in the absence of oxygen. This process is more promising because it is more flexible in selecting raw materials (no need to pay attention to the type, shape, and physical and chemical properties). It can be operated over a wide temperature range and at atmospheric pressure, producing three products (solid, liquid, and gas) [27]. Pyrolysis is a complex reaction [28]; pyrolysis is carried out for three primary purposes: (1) to produce smokeless fuel (clean in combustion), (2) to have energy with a higher heating value than the raw material, and (3) to make more reactive power [4]. The schematic of biomass pyrolysis is shown in Fig. 2.
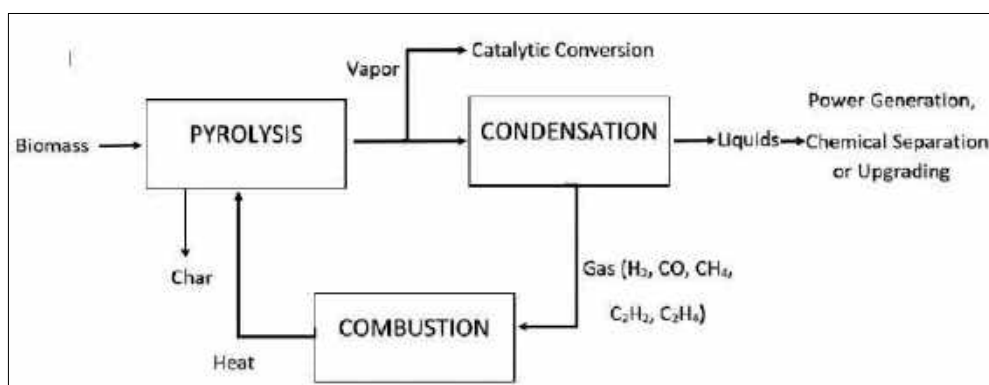

Fig. 2. Pyrolysis process schematic

3.1. Lignocellulose Pyrolysis Mechanism

The reaction mechanism of lignocellulose pyrolysis is based on the pyrolysis of three main components: cellulose, hemicellulose, and lignin. Several reactions occur during the pyrolysis process of lignocellulose, including dehydration, depolymerization, decarboxylation, isomerization, dehydrogenation, and fragmentation [29].

1) *Cellulose Pyrolysis*
   Cellulose decomposition occurs at a temperature of 250-350 ℃. Cellulose pyrolysis products are anhydrosugar (levoglucosan) as the main product, hydroxy acetaldehyde, acid, alcohol, char, and gas. Pyrolysis of cellulose produces a lot of CO gas due to the high carbonyl content and the carboxyl and carbonyl groups [29].

2) *Hemicellulose Pyrolysis*
   Hemicellulose decomposition occurs at a temperature of 250-350 ℃. The main product of hemicellulose pyrolysis is xylan; other products are furfural, ketone, phenol, acetic acid, and aldehyde. Hemicellulose pyrolysis produces much CO_2 gas due to the high carboxyl content [30].

3) *Lignin Pyrolysis*
   Lignin decomposition occurs at a temperature of 300-550 ℃ [31]. The main products of lignin pyrolysis are phenol complexes (guaiacol, catechols, phenol) [32]. Chang et al. carried out the pyrolysis of various biomass. They stated that phenol is the main component in bio-oil from palm kernel shells produced from the decomposition of p-coumaryl alcohol in lignin [33]. Pyrolysis of lignin produces much H_2 gas due to the cracking of aromatic rings and CH_4 gas caused by methoxyl cracking [30].

3.2. Type of Pyrolysis

The distribution of solid, liquid, and gaseous products highly depends on the operating conditions during the pyrolysis process [27]. This indicates three types of pyrolysis: slow pyrolysis, fast pyrolysis, and flash pyrolysis [34]. All three differ in heating rate, temperature, residence time, and particle size [35].

1) *Slow Pyrolysis*
   Slow pyrolysis is carried out at low temperature (< 500 ℃), long residence time (can be hours or days), relatively large particle size (5-50 mm), and low heating rate (0.1-2 ℃/seconds) with the main product in the form of biochar [29]. Lee et. al. [36] performed slow pyrolysis of oil palm shells at a heating rate of 18.9-20 ℃/min, a temperature of 500-500.4 ℃, and produced 27.5% biochar.

2) *Fast Pyrolysis*
   This type is carried out with a high heating rate (10-20 ℃/sec), relatively fast residence time (< 2 seconds) with a bio-oil yield of 50-70% [29]. Kim et. al. carried out pyrolysis at a temperature of 490 ℃, the heating rate of 10-20 ℃/min, and the residence time of about 0.5 seconds, and yielded 48.7% bio-oil [22]. Asadullah et. al. [13] conducted fast pyrolysis of oil palm shells at a temperature of 550 ℃ with a 56% bio-oil yield.

3) *Flash Pyrolysis*
   This type of pyrolysis is carried out with a heating rate of 10^3-10^4 ℃/sec, residence time <0.5 seconds, with a bio-oil yield of 75-80% [29]. Matamba et. al. [37] carried out flash pyrolysis of oil palm shells at a temperature of 600-900 ℃ and a pressure of 0.1-4.0 MPa, indicating that this process can be an effective method to increase the formation of H_2 gas and PAHs.

3.3. Process Parameter

Many factors affect the pyrolysis process, the product's amount, and the product's characteristics. These factors include the type and composition of biomass (lignocellulose, water content, ash, volatile, fixed carbon), pretreatment (physical, chemical, and biological), temperature, heating rate, residence time, atmospheric reaction, co-reactants, and reactor type [29, 34].

1) *Biomass type and composition*
   Biomass with a high cellulose content will produce a lot of bio-oil because the decomposition of cellulose will have a higher volatile material which will be condensed during the pyrolysis

process [34]. However, Liu et. al. [38] studied the pyrolysis of a mixture of cellulose and lignin. They showed that the increase in bio-oil yield with increasing cellulose content was not proven, indicating that lignin inhibited cellulose pyrolysis to bio-oil. Wang et. al. [39] showed a weak interaction between cellulose, hemicellulose, and lignin.

2) Pretreatment

Biomass pretreatment includes thermal pretreatment (drying, torrefaction, hot water treatment), physics (crushing and grinding), chemical (acid/base treatment), biology (with fungi, enzymes, microbes), and a combination of the above methods [40, 41]. Various literature shows that before the pyrolysis process, oil palm shells undergo several treatments such as drying in the sun, refining, sifting, and drying in an oven for 24 hours at 105 ℃. Then a proximate analysis was carried out to determine the volatile, fixed carbon, and water content using TGA. Ultimate analysis was conducted to determine the value of C, H, N, S, O, and ash/mineral content [42].

The high water content will inhibit the temperature rise because some of the heat is used to evaporate water [27]. Based on the literature, the water content in the biomass feedstock is controlled at around 10% [43, 44]. Palm shells have a water content of about 10%. High water content in raw materials causes high water content in bio-oil products, reducing the calorific value of bio-oil [34] and phase separation in liquid yield [45, 46].

Biomass has a low thermal conductivity; therefore, reducing the biomass particle size can increase heat transfer efficiency to increase biomass decomposition [34]. The microscopic size will reduce the bio-oil produced because biomass decomposition occurs quickly. It gives enough time for the secondary reaction to happen to the pyrolysis vapor. As a result, it will increase the gas yield and reduce the liquid and char yield. The optimum particle size is closely related to the natural structure of the biomass and the reactor design [27].

The ash (mineral) content affects the yield of bio-oil. High ash content will reduce bio-oil yield and increase char and gas production. Abnisa et. al. [48] showed an increased biomass bio-oil output with lower ash content. The high content of NaCl and KCl will increase the formation of glycolaldehyde and decrease the formation of levoglucosan. While $MgCl_2$ and $CaCl_2$ will increase the formation of levoglucosan and furan [49]. The presence of sodium and potassium will reduce the yield of bio-oil. In contrast, the presence of sulfur and phosphorus with ammonium salt content significantly affects bio-oil yield and increases char formation [34].

Fixed carbon is carbon that is not evaporated during the heating process. The content of fixed carbon negatively correlates with the bio-oil yield; the higher fixed carbon content, the lower the bio-oil yield [34]. The high carbon content is suitable for manufacturing high-density briquettes [18].

Elemental analysis shows the biomass's chemical composition (C, H, N, S, O), and oxygen is obtained from the calculations. One of the characteristics of biomass is that it has low nitrogen and sulfur content compared to fossil fuels. The high aromatic and carbonation index is indicated by the high range of H and C compared to the oxygen content. A low O/C ratio characterizes the high heating value (HHV) because the chemical energy of the C-C bond is higher than that of the O-C bond [50].

3) Temperature

The efficiency of biomass conversion increases with increasing pyrolysis temperature until it reaches the peak temperature, producing maximum bio-oil [27]. The literature shows the optimum pyrolysis temperature is between 450-550 ℃, but this value changes depending on the type of biomass and process variables [34]. Very high temperatures (above the optimum temperature) will reduce the amount of bio-oil produced due to a secondary reaction that converts volatile components (acid, alcohol, levoglucosan, furan) into non-condensable gas (CH_4, CO_2, CO) [51]. Abnisa et. al. [14] carried out the pyrolysis of oil palm shells in a fluidized bed reactor at temperatures between 400-800 ℃ and showed the highest bio-oil yields at a temperature of 500 ℃.

4) Heating Rate

A high heating rate will increase the decomposition of biomass into bio-oil [34]. The process with a high heating rate and temperature will reduce mass and heat transfer limitations, thus producing more bio-oil [47]. For fast pyrolysis, increased heating and cooling rates can

minimize secondary reactions. The high heating rate will inhibit the dehydration reaction, reducing the bio-oil water content [34]. The oxygen content also decreases with the increasing heating rate; this proves that the formation of oxygen-containing gases such as CO_2 or CO increases with increasing heating rate [47].

5) *Feed Rate*

Feed rate is an important parameter in the continuous pyrolysis process [34]. According to Wu et. al. [53], increasing the feed rate will increase the production of condensed vapor, reduce the residence time of vapor in the reactor, and prevent secondary cracking reactions, thereby increasing bio-oil yield. Kim et. al. [22] carried out the pyrolysis of palm shells in a fluidized bed at a temperature of 490 ℃ with a feed rate of 10 g/min and 5 g/min and showed that at a feed rate of 10 g/min produced the most bio-oil by 50%. Asadullah et. al. [13], in a fluidized bed at a temperature of 550 ℃ with a feed rate of 3-10 g/min showed the highest bio-oil yield at a feed rate of 10 g/min.

6) *Vapor Residence Time (Inert Gas Flow rate)*

Pyrolysis vapor can undergo secondary reactions from thermal cracking, depolymerization, and recondensation, which causes a decrease in bio-oil yield [29]. Therefore, taking vapor quickly from the reaction zone is necessary to minimize secondary reactions. The higher the gas flow rate, the shorter the residence time of the moisture in the pyrolysis reaction zone. Gas flow velocity that is too high can reduce bio-oil yield due to incomplete condensation of vapor and carry some of the biomass out of the reactor before the pyrolysis process is completed [53]. Qureshi et. al. carried out the pyrolysis of oil palm shells in a fixed bed reactor at a temperature of 500 ℃ with a residence time of 0.25-15 seconds. The highest yield was at 0.25 seconds [40].

7) *Reaction Time*

Reaction time is when the biomass is maintained at a specific pyrolysis temperature. An extended reaction time can cause secondary reactions to pyrolysis vapor, such as carbonization, gasification, and thermal cracking, which decrease bio-oil yield [54]. Qureshi et. al. in a fixed bed reactor at a temperature of 500 ℃ with a reaction time of 20-60 minutes, the highest yield was at 30 minutes [40]. Abnisa et. al. [14] in a fluidized bed at a temperature of 500 ℃ with a reaction time of 30-150 minutes, the highest yield was at 60 minutes.

8) *Reactor Type*

Several types of reactors have been investigated to obtain high bio-oil yields. Drum, rotary, and screw feed reactors are usually used for slow pyrolysis. Fast pyrolysis uses a microwave, tandem micro, fixed bed, ablative, and fluidized bed. Other reactors used in the pyrolysis process include circulating fluidized bed, rotating cone, vacuum, and solar reactor. Several types of reactors are widely used in the oil palm shell pyrolysis process based on the literature, for example, fluidized bed reactor [14], fixed-bed reactor [19], tandem micro-reactor [55], and microwave [56]. Fig. 3 shows that the fluidized bed reactor gives an average bio-oil yield of 59.16 wt.%, while the fixed bed reactor gives an average bio-oil yield of 44.00 wt.%.
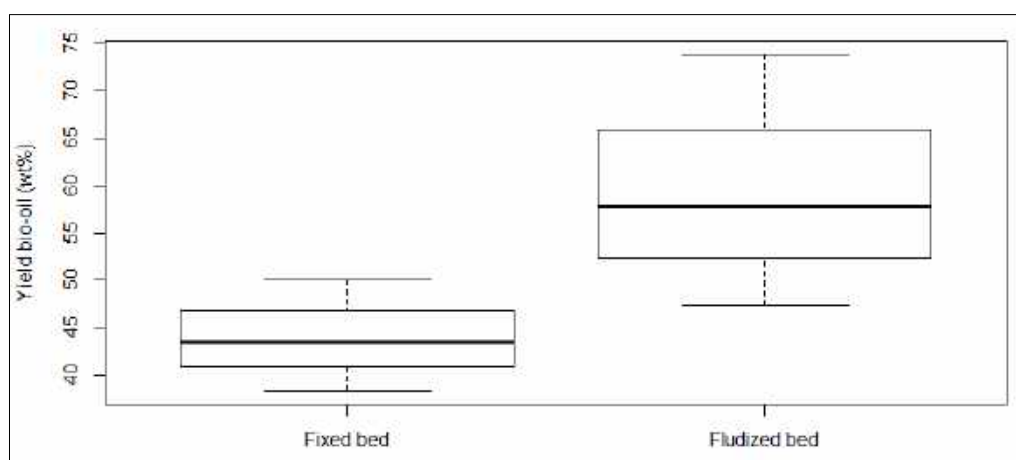

Fig. 3. Bio-oil yield in the most widely used reactor for oil palm pyrolysis

4. Bio-oil

Bio-oil is a liquid product of the pyrolysis process and has several applications. Bio-oil is used directly to fuel boilers and furnaces or to produce fuel oil and chemical products [44]. Bio-oil produced from palm shells has high oxygen content (56-72 wt%), high moisture content (25-53), low pH (2.5-3.5), and low calorific value (6-19 MJ/kg), which are not commercially attractive (Table 3). The high oxygen content is due to the presence of oxygenated compounds. Oil palm shells have a high lignin content, which results in phenol complexes (oxygenate compounds) as the most significant component in the bio-oil produced. The calorific value of oil palm shells is the highest compared to other palm oil wastes due to the high lignin content. However, a high lignin content will produce biochar, thereby reducing bio-oil yield [27]. Therefore, it is necessary to continue upgrading by co-pyrolysis or adding a catalyst or a combination of both [24]. Table 3 shows the characteristic of upgraded bio-oil oil palm shell/polystyrene co-pyrolysis and catalytic pyrolysis using alumina, zeolite socony mobile-5 (ZSM-5), equilibrium catalyst (E-cat), activated carbon (AC), lignite char (LC), and NiMoS/γ-Al$_2$O$_3$.

Table 3. Characteristics of pyrolysis bio-oil and the effect of the upgrading process

Characteristic	OPS	OPS/PS	Alumina	ZSM-5	E-cat	AC	LC	NiMoS/ γ-Al$_2$O$_3$
Temperature, ºC	500	600	485	485	485	500	500	550
Calorific Value, MJ/kg	6.58	40.34	23.2	28.9	31.3	18.79	31.13	29.3
Moisture Content, %	53	1.9	32.1	42.9	33.5	-	-	-
Viscosity, cP	3.2	8.28						
pH	2.5	2.8	-	-	-	-	-	-
Density, kg/m^3	1051	1058	1200	1200	1170			
Carbon, wt%	19.48	81.34	51.59	64.42	69.2	50.94	66.68	-
Hydrogen, wt%	8.92	7.79	6.98	7.28	9.04	4.72	6.41	-
Oxygen, wt%	71.40	10.50	34.60	19.92	14.5	43.91	25.78	-
Nitrogen, wt%	0.2	-	6.65	7.93	6.79	0.68	1.02	-
Sulfur, wt%	0.04	-	0.18	0.45	0.47	-	-	-
O/C		0.1	0.5	0.23	0.16	0.65	0.3	0.12
H/C		1.5	1.62	1.36	1.57	1.11	1.12	-
TAN, mgKOH/g	207		207	201	171	-	-	51.9
Ref.	[14]	[57]	[58]	[58]	[58]	[56]	[56]	[59]

5. Upgrading

The pyrolysis process upgrades include reducing the oxygenate content in bio-oil through deoxygenation reactions. It includes dehydration, decarboxylation, and decarbonylation by adding a catalyst or plastic in the pyrolysis process (Table 3). Plastic is added in co-pyrolysis because it has a high carbon and hydrogen content (H/C value close to 2), thus providing a sufficient hydrocarbon pool to react with the oxygen in the bio-oil [14]. Polypropylene (PP), Low-Density Polyethylene (LDPE), and High-Density Polyethylene (HDPE) plastics are suitable for use in co-pyrolysis with biomass from palm oil because they have a high hydrogen content (about 14%) [27]. Using plastic in co-pyrolysis will improve the bio-oil quality by increasing carbon content, heating value, and decreasing oxygen content [27]. Abnisa et. al. [57] showed an increase in carbon content from 19.48 to 81.34 wt%, an increase in calorific value from 6.58 to 40.34 MJ/kg, and a decrease in oxygen from 71.40 to 10.50 wt%., while hydrogen is constant.

Deoxygenation can also be done with a catalyst to increase the selectivity of the desired component in the resulting bio-oil. Catalysts are grouped into acidic, basic, and neutral catalysts (Table 4). Acid catalysts such as HZSM-5/ZSM-5 with high acidity show superior performance for aromatization. Lewis and Bronsted acid sites in HZSM-5 promote cracking and cleavage of C-O and C-C bonds in oxygenating components. Through acid catalysis, deoxygenation, oligomerization, dehydrogenation, and dealkylation [27].

Table 4. Type of Catalyst

Group	Catalyst	Ref.
Acid	Micropores (HZSM-5, Fluid catalytic cracking (FCC), ZSM-5 Macropores (MesoMFI, Al-SBA-15, Al-MSU-F)	[58][60][61][62]
Alkali	Alkali & alkali earth metal (CaO, MgO, ZnO, K_2CO_3, $Ca(OH)_2$ Bentonite, Dolomite, Olivine	[62][63][64]
Neutral	Graphite nanofiber	[61]

The bio-oil quality can be evaluated from O/C, H/C, and HHV values. The low value of O/C and high value of H/V and HHV indicate the high quality of bio-oil [5, 65]. Likewise, bio-oil quality can be evaluated based on the functional groups in bio-oil and the content of oxygenated and aromatic compounds before and after the pyrolysis process. The lower the range of oxygenate compounds and the higher the content of aromatic compounds, the better the quality of the bio-oil [66]. Compared to commercial fuels (diesel and gasoline), oil palm shell bio-oil has a higher O/C content. The addition of plastic and catalyst can increase the calorific value but is still low compared to commercial fuels [66].

The problem with catalytic pyrolysis is coke's formation and the catalyst's deactivation [57]. The coke's formation can accelerate the catalyst's deactivation, close the catalyst pores, and poison the catalyst [67]. The formation of coke is caused by too small pore size as in the micropores of the catalyst (HZSM-5, ZSM-5), which inhibits the mass transfer of significant components [27]. This problem can be solved by using mesoporous catalysts with a high acidity level and a larger pore size (0.52-0.59 nm) [68]. The modification of the zeolite catalyst (HZSM-5/ZSM-5) through metal doping (such as Ga, Mo, Co, Ni, Zn, Fe, Z, Pd, and Pt) can increase aromatic production [69, 70]. Adding plastics with a high hydrogen content can increase conversion efficiency and reduce coke formation [57].

6. Knowledge Gap

This review discusses the operating parameters that influence the pyrolysis process and the methods of upgrading bio-oil. However, bio-oil quality does not meet the quality standards of commercial fuels. So it is necessary to study an upgrading process that can produce high-quality fuel or valuable chemical products such as hydrotreatment to reduce oxygen content, supercritical water method to increase heating value, supercritical fluids, and esterification of bio-oils. Likewise, economic feasibility studies, resource conservation systems, and heat integration techniques on the pyrolysis process of oil palm shells are still limited; this indicates the potential for future research.

7. Conclusion

This review discusses the operating parameters that influence the pyrolysis process and the methods of upgrading bio-oil in the pyrolysis process, namely co-pyrolysis and catalytic cracking. The result shows a relationship between biomass composition (cellulose, hemicellulose, and lignin) and bio-oil yield. The water content in the raw material needs to be controlled at around 10%. The optimum particle size is closely related to the biomass's natural structure and reactor type. The higher the ash and the fixed carbon content, the lower the bio-oil yield. The optimum temperature for pyrolysis is between 450-550 ℃. A high heating rate will increase the decomposition of biomass into bio-oil. Particle size and reactor type strongly influence feed rate, residence time, and reaction time. The fluidized bed reactor type gives the highest average bio-oil yield of 59.16 wt.%. The use of plastics in co-pyrolysis and catalyst increases the heating value and decreases the oxygen content. The use of polystyrene (PS) in oil palm shells co-pyrolysis increases the heating value from 6.58 to 40.34 MJ/kg and decreases the oxygen content from 71.40 to 10.50 wt.%. Using a catalyst (ZSM-5) increases the heating value from 6.58 to 28.9 MJ/kg and decreases the oxygen content from 71.40 to 19.92 wt.%.

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BIOFUELS DARI CANGKANG KELAPA SAWIT: PENGARUH SUHU DAN KATALIS TERHADAP YIELD DAN KONVERSI

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Abstrak

Cangkang kelapa sawit merupakan biomassa dengan kandungan karbon dan hidrogen yang tinggi sehingga potensial untuk memproduksi biofuels baik dalam bentuk bio-oil, syngas, maupun bio-char . Penelitian ini dilakukan untuk mempelajari pengaruh suhu dan katalis nikel-alumina 40% b/b terhadap yield dan konversi dari proses pirolisis. Pirolisis dilakukan dengan tanpa katalis (non-katalitik) dan dengan menggunakan katalis (katalitik) di dalam reaktor fixed bed pada kisaran suhu 300 – 600ᵒC. Hasil penelitian menunjukkan bahwa suhu berpengaruh terhadap yield dan konversi. Semakin tinggi suhu maka semakin tinggi yield bio-oil dan water phase sampai suhu optimum tertentu, semakin tinggi yield gas untuk pirolisis katalitik adapun untuk non-katalitik bernilai konstan, dan semakin rendah yield char. Terkait dengan konversi maka semakin tinggi suhu konversi semakin besar. Penggunaan katalis nikel-alumina 40% b/b mampu meningkatkan konversi dan yield gas dan menurunkan yield bio-oil dan yield char dibandingkan pirolisis tanpa katalis. Yield bio-oil tertinggi didapatkan pada pirolisis non-katalitik pada suhu 500ᵒC dengan yield bio-oil sebesar 13.02% b/b, yield gas tertinggi didapatkan pada pirolisis katalitik pada suhu 600ᵒC dengan yield gas sebesar 28.49% b/b, yield char optimum didapatkan pada suhu pirolisis katalitik pada suhu 600ᵒC dengan yield char sebesar 30.52% dan konversi tertinggi didapatkan pada pirolisis katalitik pada suhu 600ᵒ C dengan konversi sebesar 69.48%.

Kata kunci: biofuels; cangkang sawit; pirolisis; suhu; nikel-alumina

Pendahuluan

Ketergantungan pada energi fosil di Indonesia khususnya minyak bumi masih tinggi mencapai 96% dari total konsumsi (Tim Sekretaris Jenderal Dewan Energi Nasional, 2019). Demikian juga komunitas global pada abad 21 menghadapi tantangan dikarenakan ledakan populasi yang tinggi yang dibarengi dengan meningkatnya aktivitas industri dan komersial yang berakibat pada berkurangnya bahan bakar fosil, meningkatnya polusi lingkungan, pemanasan global dan memburuknya efek kesehatan (Ali et al., 2017). Krisis energi ini menuntut pencarian sumber energi alternatif untuk menjamin tercukupinya kebutuhan energi dunia (Ighalo & Adeniyi, 2020). Para peneliti telah mengindentifikasi biomassa sebagai sumber energi yang berkelanjutan, dapat diperbaharui, dan ramah lingkungan (Rajendra et al., 2019).

Biomassa adalah material dengan karbon netral dan mempunyai emisi GHG (greenhouse gas) yang rendah disebabkan sedikitnya kandungan nitrogen dan sulfur berbeda dengan minyak bumi dan batubara (Gholizadeh et al., 2019). Sumber biomassa yang bisa dijadikan energi alternatif meliputi kayu, sisa hasil pengolahan kayu, tanaman pertanian, sisa hasil pengolahan tanaman pertanian, dan *municipal solid waste* (Azeta et al., 2021).
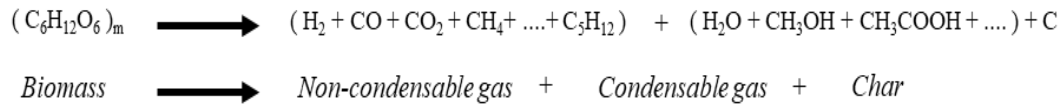
Badan Pusat Statistik (BPS) mencatat produksi perkebunan kelapa sawit Indonesia melonjak selama lima tahun terakhir. Pada 2019, produksinya mencapai 48,42 juta ton atau meningkat 12,92% dari tahun sebelumnya yakni 42,88 juta ton (Direktorat Jendral Perkebunan, 2019). Meningkatnya produksi perkebunan kelapa sawit di Indonesia menyebabkan meningkatnya produksi limbah biomassa dari kelapa sawit, diantaranya adalah tandan kosong sawit, cangkang kelapa sawit, lumpur sawit, serabut, dan limbah cair (Subiyanto et al., 2007).

Cangkang kelapa sawit adalah biomassa generasi kedua yang kaya dengan kandungan karbon dan hidrogen dan setara dengan kayu keras (Asadullah et al., 2013) sehingga menjadikan cangkang kelapa sawit sebagai bahan baku yang potensial untuk memproduksi *biofuels*, produk kimia berharga, atau energi melalui metode termokimia (Abnisa et al., 2011) (Asadullah et al., 2013). Cangkang kelapa sawit mempunyai kandungan nitrogen yang lebih rendah (<1%), kandungan sulfur (<0.2%) dan kandungan oksigen yang lebih tinggi (40-50%) dibandingkan dengan bahan bakar dari fosil. Rendahnya kandungan nitrogen dan sulfur akan mengurangi kandungan NOx dan SOx yang merupakan *green house gas* (GHG). Kandungan karbon yang tinggi cocok untuk pembuatan briket dengan densitas

tinggi (Chang et al., 2020). Cangkang kelapa sawit dapat diubah menjadi sumber energi terbarukan melalui proses pirolisis menghasilkan bio-oil atau syngas tergantung pada suhu dan waktu reaksi [9].

Pirolisis adalah dekomposisi termal biomassa tanpa kehadiran oksigen (Sukiran et al., 2011). Pirolisis lebih menjanjikan dibandingkan konversi termokimia yang lain karena lebih fleksibel di dalam pemilihan bahan baku (tidak perlu memperhatikan tipe, bentuk dan sifat fisik dan kimia bahan baku), dapat dioperasikan pada kisaran suhu yang luas dan pada tekanan atmosfer, dan menghasilkan tiga jenis produk (padat, cair, dan gas) (Melia et al., 2021). Pirolisis cangkang sawit telah banyak dilakukan oleh para peneliti sebelumnya (Abnisa et al., 2011; Kim et al., 2010; Matamba et al., 2020; Qureshi et al., 2021).

Reaksi kimia yang terjadi pada proses pirolisis adalah sebagai berikut:

$$(C_6H_{12}O_6)_m \longrightarrow (H_2 + CO + CO_2 + CH_4 + ... + C_5H_{12}) + (H_2O + CH_3OH + CH_3COOH + ...) + C$$

$$Biomass \longrightarrow Non\text{-}condensable\ gas + Condensable\ gas + Char$$

Gambar 1. Reaksi kimia pada pirolisis biomassa (Basu, 2010)

Katalis berpengaruh terhadap jalannya reaksi pirolisis. Penggunaan katalis dalam proses pirolisis mempunyai beberapa pengaruh diantaranya menurunkan suhu dekomposisi, meningkatkan kualitas bio-oil dengan adanya proses deoksigenasi dan meningkatkan kestabilan dengan berkurangnya reaksi polimerisasi (Mohanty, 2014). Beberapa literature telah menyebutkan penggunaan katalis dalam pirolisis cangkang kelapa sawit (Niu et al., 2020; Omoriyekomwan et al., 2016; Won et al., 2014). Katalis Nikel alumina merupakan *metal catalyst. Metal catalyst* menyediakan permukaan aktif untuk meningkatkan terjadinya pemutusan rantai ikatan C-C pada proses reforming dan ikatan C-O pada proses methanasi dan hidrogenasi (Davda et al., 2005).

Penelitian ini dilakukan untuk mempelajari pengaruh suhu dan katalis nikel-alumina 40% b/b terhadap yield dan konversi dari proses pirolisis.

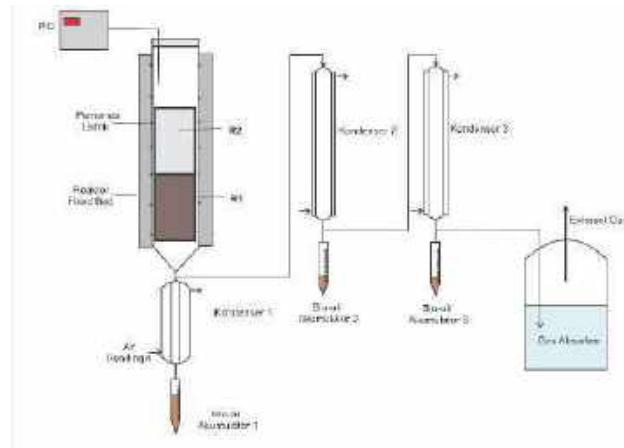## Bahan dan Metode

Cangkang sawit

Cangkang sawit didapatkan dari perkebunan kelapa sawit di Kalimantan Barat. Sebelum digunakan cangkang kelapa sawit dibersihkan dengan dicuci menggunakan air bersih, dikeringkan di bawah sinar matahari selama 2 hari, dihaluskan, dan diayak untuk mendapatkan ukuran partikel -16+40 mesh. Kemudian dilakukan pengeringan di dalam oven pada suhu 105 C selama 24 jam untuk mendapatkan kadar air sekitar 10% berat kering.

Katalis nikel-alumina

Katalis nikel-alumina didapatkan dari PT Pupuk Kujang Cikampek, Jawa Barat dengan merek dagang Reformax. Untuk proses pirolisis katalis perlu dihaluskan dan diayak dengan ukuran -16+40 mesh, kemudian dilakukan analisis SEM-EDX Mapping untuk mengetahui morfologi, komposisi, dan persebaran unsur pada katalis dan Image J Processing untuk mengetahui dispersi void pada permukaan katalis.

Peralatan

Penelitian dilakukan menggunakan reaktor *fixed bed* yang yang berbentuk silinder vertikal yang terbuat dari stainless steel dengan diameter dalam 40 mm, diameter luar 44 mm, dan tinggi 600 mm. Reaktor dilengkapi dengan pemanas yang terbuat dari kawat nikelin yang dililitkan pada bagian luar reaktor. Suhu dan kecepatan pemanasan diukur dan diatur menggunakan thermocouples dan PID controller (Jamilatun et al., 2019).

Gambar 2. Rangkaian alat pirolisis

Pirolisis

Pirolisis dilakukan dengan memasukkan 50 gram cangkang kelapa sawit ke dalam reaktor R1 untuk pirolisis non-katalitik, dan ditambah dengan memasukkan katalis nikel-alumina 40% b/b ke dalam reaktor R2 untuk pirolisis katalitik. Kemudian melakukan pemanasan dengan kecepatan pemanasan 10-12 C/menit, setelah suhu reaktor mencapai suhu yang dinginkan (300, 400, 500, dan 600 ºC) pemanasan dilanjutkan selama 60 menit secara isothermal. Hasil pirolisis berupa gas terkondensasi ditampung dalam akumulator dan ditimbang beratnya. Char yang terbentuk diambil setelah pirolisis selesai, kemudian ditimbang. Gas yang tidak terkondensasi dialirkan ke dalam gas absorber dan dicari beratnya dengan neraca massa.

Perhitungan Yield dan Konversi

Hasil bio-oil, water phase, arang, dan gas dihitung dengan persamaan (1) - (5).

$$Ybo = \frac{Wbo}{Wm} \; x \; 100\% \tag{1}$$

$$Ywp = \frac{Wwp}{Wm} \; x \; 100\% \tag{2}$$

$$Yc = \frac{Wc}{Wm} \; x \; 100\% \tag{3}$$

$$Yg = \frac{(Wm-Wbo-Wwp-Wc)}{Wm} \; x \; 100\% \tag{4}$$

Konversi dihitung dengan persamaan berikut:

$$Yg = \frac{(Wbo+Wwp+Wg)}{Wm} \; x \; 100\% \tag{5}$$

Dengan Y_{bo}, Y_{wp}, Y_c, dan Y_g adalah hasil dari bio-oil (wt%), water phase (wt%), char (wt%), dan gas (wt%). W_m, W_{bo}, W_{wp}, dan W_c adalah berat dari sampel cangkang kelapa sawit (gram), bio-oil (gram), water phase (gram), dan char (gram).
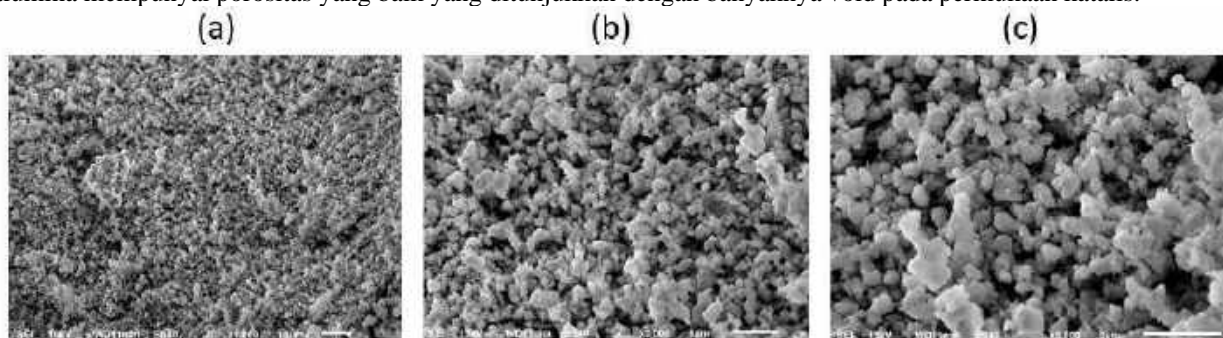
Hasil dan Pembahasan

Karakterisasi katalis nikel-alumina

Karakterisasi katalis nikel-alumina dilakukan dengan analisis SEM-EDX. Hasil dari analisis SEM-EDX ditunjukkan dalam tabel 1 dan gambar 3. Tabel 1 menunjukkan hasil analisis EDX terhadap katalis. Dari tabel 1 dapat dilihat bahwa nikel-alumina terdiri atas 5 komponen yaitu Ni (7.36%), Al (36.90%), O (49.75%), Na (0.35%), dan C (5.65%). Tabel tersebut menunjukkan bahwa alumina merupakan penyangga (*support*) bagi katalis Ni. Penyangga katalis dengan luas permukaan yang besar dan diameter pori yang kecil atau medium seperti alumina bisa meminimalkan batasan transfer massa sehingga meningkatkan transfer massa reaktan (Goula et al., 2015; Tao et al., 2010).

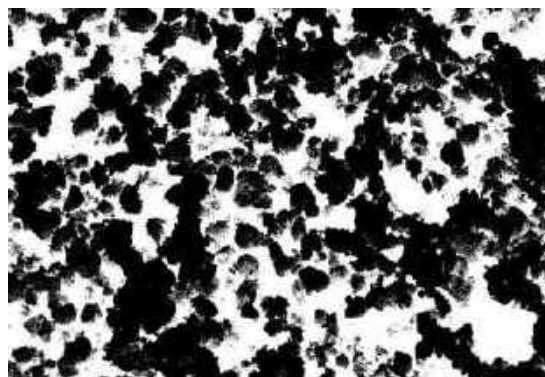Tabel 1. Komposisi elemen pada analisis EDX

Elemen	% massa
Ni	7.36
Al	36.90
O	49.75
Na	0.35
C	5.65

Gambar 3 menunjukkan analisis SEM dari katalis dengan perbesaran 1000, 3000, dan 5000 kali. Berdasarkan gambar 3(c) katalis nikel-alumina terlihat berupa butiran halus berwarna abu-abu. Secara mikroskopik butiran tersebut membentuk jaringan tiga dimensi dengan ukuran dan bentuk pori yang tidak teratur dan stabil secara struktur dan thermal (Jamilatun et al., 2020). Analisis SEM juga menunjukkan bahwa secara morfologi katalis nikel-alumina mempunyai porositas yang baik yang ditunjukkan dengan banyaknya void pada permukaan katalis.

Gambar 3. Foto analisis SEM dengan perbesaran a) 1000 kali b) 3000 kali c) 5000 kali
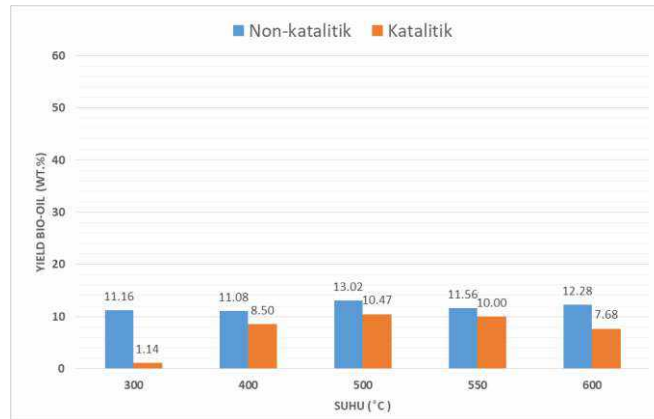
Gambar 4 menunjukkan analisis Image J terhadap hasil foto SEM pada perbesaran 5000 kali. Analisis image J menggunakan type image 8 bit, size 0-infinity, dan circularity 0.00-1.00. Area void ditunjukkan oleh nodul berwarna putih. Hasil analisis Image J menunjukkan permukaan katalis mempunyai persen luas area void yang cukup besar yaitu 58.87%. Luas permukaan yang besar akan meningkatkan terjadinya adsorbsi reaktan pada site aktif katalis sehingga meningkatkan terjadinya reaksi permukaan pada katalis.

Gambar 4. Analisis Image J hasil SEM dengan perbesaran 5000 kali

Pengaruh suhu dan katalis terhadap yield bio-oil

Pengaruh suhu dan katalis terhadap yield bio-oil ditunjukkan oleh gambar 5. Gambar 5 menunjukkan yield bio-oil tertinggi didapatkan pada suhu 500 ºC dengan yield bio-oil sebesar 13.02% untuk pirolisis non-katalitik dan 10.47% untuk pirolisis katalitik. Meningkatnya suhu dari 300 ºC menjadi 500 ºC menyebabkan kenaikan yield bio-oil dari 11.16% menjadi 13.02% pada pirolisis non-katalitik dan menyebabkan kenaikan dari 1.14% menjadi 10.47% pada pirolisis katalitik. Kenaikan bio-oil pada kisaran suhu tersebut disebabkan oleh meningkatnya dekomposisi biomassa (Melia et al., 2021) karena dekomposisi hemiselulosa dari biomassa terjadi pada kisaran suhu 250 -350 ºC C, dekomposisi selulosa terjadi pada kisaran 325-400 ºC, dan dekomposisi lignin terjadi pada suhu 300-550 ºC (K N et al., 2022).
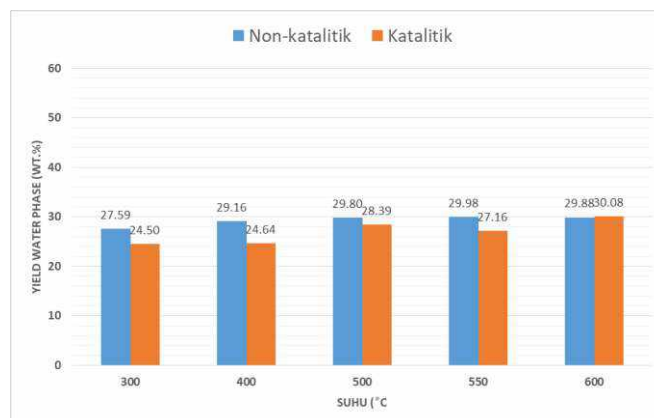
Gambar 5. Pengaruh suhu dan katalis terhadap yield bio-oil

Gambar 3 juga menunjukkan bahwa pemanasan pada suhu diatas 500 ⁰C menyebabkan penurunan yield bio-oil baik pada pirolisis katalitik maupun non-katalitik. Hal ini terjadi karena pemanasa diatas 500 ⁰C menyebabkan adanya reaksi sekunder yang mengubah komponen volatile (asam, alcohol, levoglukosan, furan) menjadi *non-condensable gas* (CH_4, CO_2, CO) (Isahak et al., 2012; Sukiran et al., 2009) atau karena adanya pemutusan rantai panjang pada komponen organic dan hidrokarbon menjadi rantai pendek sehingga tidak bisa diembunkan (Jamilatun, Yuliestyan, et al., 2019).

Gambar 3 menunjukkan bahwa penggunaan katalis nikel-alumina menyebabkan penurunan yield bio-oil dibandingkan dengan tanpa katalis. Hal ini terjadi karena penggunaan katalis akan menyebabkan terjadinya dekomposisi molekul dengan berat molekul yang besar dan komponen organic rantai panjang yang ada dalam bentuk *condensable gas* menjadi molekul dengan berat molekul yang kecil melalui pemutusan ikatan C-C, transfer hidrogen, isomerisasi, pemutusan rantai aromatik, dan deoksigenasi menghasilkan hidrokarbon rantai pendek (C1-C4), H_2O, CO_2, dan CO (Hu et al., 2018) sehingga akan mengurangi yield bio-oil. Penggunaan katalis menurunkan yield bio-oil rata-rata sebesar 2.82%.

Pengaruh suhu dan katalis terhadap yield water phase

Gambar 4 menunjukkan pengaruh suhu terhadap yield water phase. Gambar 4 menunjukkan semakin tinggi suhu maka yield water phase semakin meningkat. Pada piirolisis non-katalitik yield water phase meningkat dari 27.59% pada suhu $300°C$ menjadi 29.88% pada suhu $600°C$. Sedangkan pada pirolisis katalitik yield water phase meningkat dari 24.50% pada suhu $300°C$ menjadi 30.08% pada suhu $600°C$. Water phase pada bio-oil berasal dari biomassa (10%) dan reaksi dehidrasi selama proses pirolisis (Tsai et al., 2007). Semakin tinggi suhu maka reaksi dehidrasi semakin meningkat sehingga akan menaikkan yield water phase.

Gambar 6. Pengaruh suhu dan katalis terhadap yield water phase

Kenaikan yield water phase pada pirolisis katalitik lebih besar dibandingkan pada pirolisis non-katalitik. Hal ini terjadi karena katalis nikel-alumina menyediakan permukaan aktif yang bisa meningkatkan pemutusan rantai C-O melalui proses methanasi, hidrogenasi, dan dehidrasi menghasilkan H_2O (Davda et al., 2005). Kandungan air yang tinggi akan menyebabkan pemisahan fase pada produk bio-oil yang dihasilkan (Kan et al., 2016)(Onarheim et
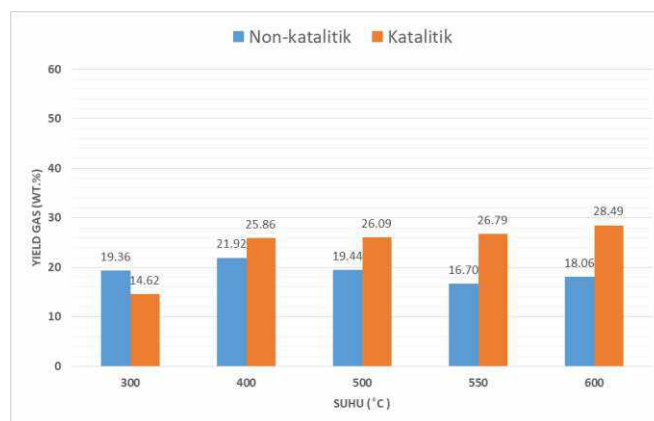
al., 2015)(Cheng et al., 2016), mengurangi nilai kalor dan menurunkan viskositas (Guedes et al., 2018; Omulo et al., 2019).

Pirolisis katalitik menghasilkan yield water phase yang lebih rendah dibandingkan tanpa katalis. Hal ini terjadi karena penggunaan katalis akan meningkatkan terjadinya *water-gas shift reaction* yang menghasilkan CO_2 dan H_2 dan proses reforming yang mengubah H_2O menjadi gas H_2 (Davda et al., 2005; Han-u-domlarpyos et al., 2015).

Pengaruh suhu dan katalis terhadap yield gas

Gambar 5 menunjukkan pengaruh suhu dan katalis terhadap yield gas. Pada pirolisis non-katalitik yield gas yang dihasilkan cencerung konstan bahkan sedikit mengalami penurunan seiring dengan kenaikan suhu. Hal ini kemungkinan terjadi karena tidak adanya reaksi sekunder yang mengubah komponen volatile menjadi non-condensable gas sehingga berpengaruh terhadap rendahnya yield gas dan tingginya yield tar (bio-oil dan water phase). Pada pirolisis katalitik semakin tinggi suhu maka semakin meningkat yield gas yang dihasilkan dari 14.62 % pada suhu 300°C menjadi 28.49% pada suhu 600°C. Hal ini disebabkan karena semakin tinggi suhu maka semakin meningkat terjadinya reaksi sekunder yang mengubah komponen volatile menjadi non-condensable gas (Guedes et al., 2018) melalui proses cracking atau melalui *water-gas shift reaction* (Velden et al., 2010).
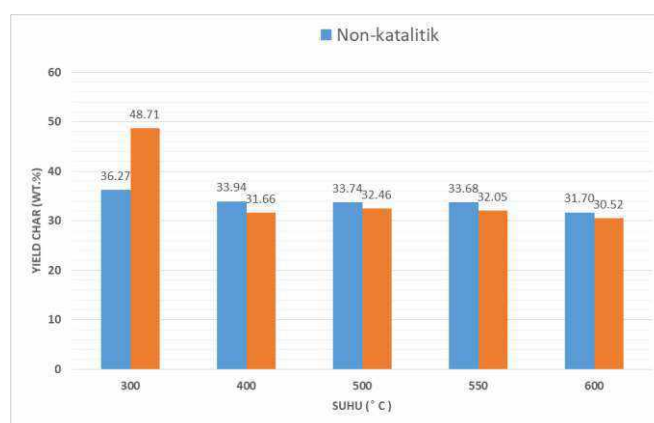
Gambar 5 juga menunjukkan bahwa penggunaan katalis mampu meningkatkan yield gas dengan rata-rata sebesar 7.78% dibandingkan pirolisis non-katalitik. Hal ini terjadi karena adanya aktivasi molekul bio-oil pada permukaan katalis yang kemudian mengalami proses *cracking* menjadi gas dan *coke*, dan *coke* kemudian berubah menjadi gas melalui proses gasifikasi (Hu et al., 2018) dan adanya *water-gas shift reaction* yang menghasilkan CO_2 dan H_2.

Gambar 7. Pengaruh suhu dan katalis terhadap yield gas

Pengaruh suhu dan katalis terhadap yield char

Gambar 6 menunjukkan bahwa semakin meningkatnya suhu maka yield char yang didapatkan semakin rendah baik untuk pirolisis katalitik maupun non-katalitik.. Literatur menyebutkan pirolisis pada suhu rendah kurang dari 400°C akan lebih banyak menghasilkan yield char (Dickerson & Soria, 2013), sementara pirolisis pada suhu tinggi akan lebih sedikit menghasilkan char (Ahmad et al., 2020). Hal ini terjadi karena semakin meningkatnya suhu maka semakin meningkat dekomposisi biomassa sehingga semakin tinggi komponen volatile yang dilepaskan (Jamilatun et al., 2020).
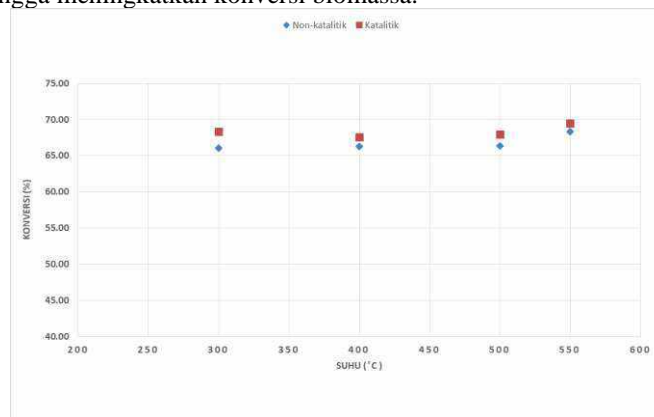

Gambar 8. Pengaruh suhu dan katalis terhadap yield char

Gambar 6 juga menunjukkan bahwa pirolisis katalitik menghasilkan yield char yang lebih rendah dibandingkan pirolisis non-katalitik. Hal ini kemungkinan terjadi karena penggunaan katalis akan meningkatkan kecepatan *cracking* komponen volatile menjadi *non-condensable gas*, sehingga menurunkan konsentrasi komponen volatile pada badan gas dan meningkatkan transfer massa komponen volatile dari permukaan biomassa yang mempunyai konsentrasitinggi ke badan gas yang mempunyai konsentrasi rendah. Hal ini akan berpengaruh pada meningkatnya dekomposisi biomassa sehingga menurunkan yield char.

Pengaruh suhu dan katalis terhadap konversi

Gambar 7 menunjukkan pengaruh suhu dan katalis terhadap konversi biomassa dalam proses pirolisis baik katalitik maupun non-katalitik. Semakin tinggi suhu maka semakin tinggi konversi dari 63.78% pada suhu $300\,^{\circ}C$ menjadi 68.31% pada suhu $600\,^{\circ}C$ untuk pirolisis non-katalitik dan dari 51.29% pada suhu $300\,^{\circ}C$ menjadi 69.48% pada suhu $600\,^{\circ}C$ untuk pirolisis katalitik. Suhu yang tinggi akan meningkatkan keseragaman suhu pada partikel biomassa sehingga lebih meningkatkan dekomposisi biomassa menjadi bio-oil, water phase, dan gas. Dengan demikian semakin tinggi suhu maka konversi biomassa semakin meningkat.

Gambar 7 juga menunjukkan bahwa penggunaan katalis mampu meningkatkan konversi biomassa dengan rata-rata sebesar 1.58% dibandingkan dengan tanpa katalis. Hal ini terjadi karena adanya katalis akan meningkatkan reaksi sekunder yang mengubah komponen volatile menjadi gas yang menyebabkan gradien konsentrasi komponen volatile yang tinggi antara badan gas dan permukaan biomassa. Gradien konsentrasi ini akan meningkatkan transfer massa komponen volatile sehingga meningkatkan konversi biomassa.

Gambar 9. Pengaruh suhu dan katalis terhadap konversi

Pada pirolisis non-katalitik, kenaikan suhu dari $300\,^{\circ}C$ menjadi $600\,^{\circ}C$ meningkatkan konversi sebesar 4.53%. Pada suhu pirolisis tertentu penggunaan katalis meningkatkan konversi rata-rata sebesar 1.58%. Pada pirolisis katalitik dengan kenaikan suhu dari $300\,^{\circ}C$ menjadi $600\,^{\circ}C$ meningkatkan konversi sebesar 18.19%. Meningkatnya suhu dan penggunaan katalis mampu meningkatkan konversi secara signifikan.

Kesimpulan

Cangkang kelapa sawit dapat dijadikan sebagai bahan bakar alternative biofuels dalam bentuk bio-oil, syngas, dan bio-char melalui proses pirolisis. Suhu dan katalis mempunyai pengaruh terhadap yield dan konversi pada proses pirolisis. Hasil penelitian menunjukkan bahwa suhu berpengaruh terhadap yield dan konversi. Semakin tinggi suhu maka semakin tinggi yield bio-oil dan water phase sampai suhu optimum tertentu, semakin tinggi yield gas untuk pirolisis katalitik adapun untuk non-katalitik bernilai konstan, dan semakin rendah yield char. Terkait dengan konversi maka semakin tinggi suhu konversi semakin besar. Penggunaan katalis nikel-alumina 40% b/b mampu meningkatkan konversi dan yield gas dan menurunkan yield bio-oil dan yield char dibandingkan pirolisis tanpa katalis. Yield bio-oil tertinggi didapatkan pada pirolisis non-katalitik pada suhu $500\,^{\circ}C$ dengan yield bio-oil sebesar 13.02% b/b, yield gas tertinggi didapatkan pada pirolisis katalitik pada suhu $600\,^{\circ}C$ dengan yield gas sebesar 28.49% b/b, yield char optimum didapatkan pada suhu pirolisis katalitik pada suhu $600\,^{\circ}C$ dengan yield char sebesar 30.52% dan konversi tertinggi didapatkan pada pirolisis katalitik pada suhu $600\,^{\circ}C$ dengan konversi sebesar 69.48%.

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(Pengaruh Suhu terhadap yield *Valuable chemicals* pada Fase Organik Hasil Pirolisis Cangkang Kelapa Sawit)

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ABSTRAK

Pirolisis cangkang kelapa sawit dengan reaktor fixed bed menghasilkan fase organik, fase air, gas, dan char. Fase organik hasil pirolisis mempunyai kandungan *valuable chemicals* seperti phenol, guaiacol, syringol, creosol, p-ethylguaiacol, eugenol, o-cresol, dan xylenol. Penelitian ini dilakukan untuk mempelajari pengaruh suhu terhadap yield *valuable chemicals* pada fase organik hasil pirolisis cangkang kelapa sawit. Pirolisis dilakukan pada suhu 300, 400, 500, dan 600 ˚C. Komposisi fase organik dianalisis menggunakan Gas Chromatography-Mass Spectrometry (GC-MS). Hasil penelitian menunjukkan bahwa suhu mempunyai peranan penting terhadap yield *valuable chemicals*. Kandungan guaiacol, creosol, p-ethylguaiacol, o-cresol dan syringol tertinggi didapatkan pada suhu 400˚C dengan yield berturut-turut sebesar 2.88, 3.62, 3.86, 0.41, dan 5.03 wt.%. Kandungan phenol dan eugenol tertinggi didapatkan pada suhu 500 ˚C dengan yield sebesar 35.89 dan 1.83 wt.%. Kandungan xylenol tertinggi didapatkan pada suhu 600 ˚C dengan yield sebesar 0.21 wt.%.

Kata kunci: pirolisis, cangkang kelapa sawit, valuable chemicals , fase organik, phenol

ABSTRACT

Pyrolysis of oil palm shells with a fixed bed reactor produces an organic phase, a water phase, a gas, and a char. The organic phase resulting from pyrolysis contains valuable chemicals such as phenol, guaiacol, syringol, creosol, p-ethylguaiacol, eugenol, o-cresol, and xylenol. This research aims to study the effect of temperature on the yield valuable chemicals in the organic phase of the pyrolysis of oil palm shells. Pyrolysis was carried out at temperatures of 300, 400, 500, and 600 ˚C. The composition of the organic phase was analyzed using Gas Chromatography-Mass Spectrometry (GC-MS). The results showed that temperature has an important role in yield valuable chemicals. The highest content of guaiacol, creosol, p-ethylguaiacol, o-cresol and syringol was found at 400 ˚C with yields of 2.88, 3.62, 3.86, 0.41, and 5.03 wt.%, respectively. The highest content of phenol and eugenol was obtained at a temperature of 500 ˚C with yields of 35.89 and 1.83 wt.%. The highest xylenol content was obtained at a temperature of 600 ˚C with a yield of 0.21 wt.%.
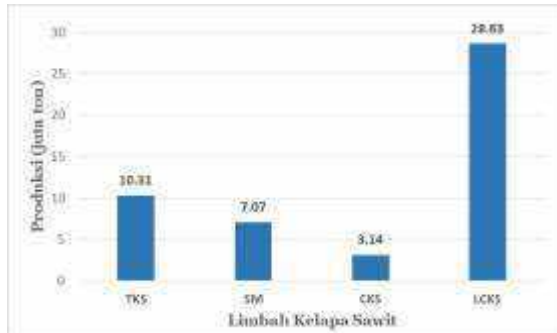
Keywords: pyrolysis, oil palm shell, valuable chemicals , organic phase, phenol

1. PENDAHULUAN

Badan Pusat Statistik (BPS) mencatat bahwa produksi perkebunan kelapa sawit Indonesia meningkat selama lima tahun terakhir. Pada 2019, produksinya mencapai 48,42 juta ton atau meningkat 12,92% dari tahun sebelumnya yakni 42,88 juta ton (Direktorat Jendral Perkebunan, 2021).

Meningkatnya produksi perkebunan kelapa sawit di Indonesia menyebabkan meningkatnya produksi limbah biomassa dari kelapa sawit, diantaranya adalah tandan kosong sawit, cangkang kelapa sawit, lumpur sawit, serabut, dan limbah cair (Subiyanto et al., 2007). Pengolahan tandan segar kelapa sawit menghasilkan

6.5% limbah cangkang sawit (Susanto et al., 2020), sehingga jumlah limbah cangkang sawit pada tahun 2019 setara dengan 3.14 juta ton.

Gambar 1. Produksi limbah pengolahan kelapa sawit di Indonesia tahun 2019 (Direktorat Jendral Perkebunan, 2021)

Cangkang kelapa sawit adalah biomassa generasi kedua yang kaya dengan kandungan karbon dan hidrogen dan setara dengan kayu keras (Asadullah et al., 2013) sehingga menjadikan cangkang kelapa sawit sebagai bahan baku yang potensial untuk memproduksi biofuels, produk kimia berharga, atau energi melalui metode termokimia (Abnisa et al., 2011) (Asadullah et al., 2013). Cangkang kelapa sawit mempunyai kandungan nitrogen yang lebih rendah (<1%), kandungan sulfur (<0.2%) dan kandungan oksigen yang lebih tinggi (40-50%) dibandingkan dengan bahan bakar dari fosil. Rendahnya kandungan nitrogen dan sulfur akan mengurangi kandungan NOx dan SOx yang merupakan green house gas (GHG). Kandungan karbon yang tinggi cocok untuk pembuatan briket dengan densitas tinggi (Chang et al., 2020). Cangkang kelapa sawit dapat diubah menjadi sumber energi terbarukan melalui proses pirolisis menghasilkan bio-oil atau syngas tergantung pada suhu dan waktu reaksi (Jamilatun, Elisthatiana, et al., 2020).

Pirolisis adalah dekomposisi termal biomassa tanpa kehadiran oksigen (Sukiran et al., 2011). Pirolisis lebih menjanjikan dibandingkan konversi termokimia yang lain karena lebih fleksibel di dalam pemilihan bahan baku (tidak perlu memperhatikan tipe, bentuk dan sifat fisik dan kimia bahan baku), dapat dioperasikan pada kisaran suhu yang luas dan pada tekanan atmosfer, dan menghasilkan tiga jenis produk (padat, cair, dan gas) (Melia et al., 2021).

Gambar 2. Skema proses pirolisis

Cangkang sawit juga mengandung *valuable chemicals* diantaranya adalah phenol dan komponen phenolic yang berasal dari dekomposisi lignin (Ani, n.d.; Omoriyekomwan et al., 2016). Penelitian untuk mempelajari komposisi phenol dan komponen phenolic dalam cangkang sawit telah dilakukan oleh para peneliti sebelumnya. Yang An dkk, melakukan pirolisis katalitik cangkang sawit untuk memproduksi phenol dan hydrogen (An et al., 2020). Kanit dkk, mempelajari phenol dan komponen phenolic hasil fast pirolisis organosolv lignin (Soongprasit et al., 2020). Produksi phenol melalui proses pirolisis juga telah dilakukan oleh peneliti yang lain.

Penelitian ini dilakukan untuk mempelajari pengaruh suhu terhadap yield *valuable chemicals* pada fase organik hasil pirolisis cangkang kelapa sawit.
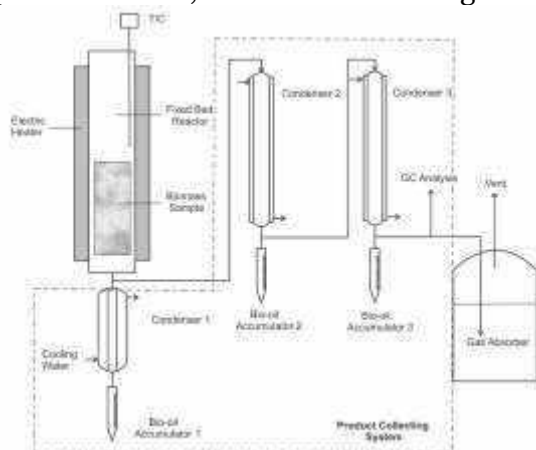
2. METODE PELAKSANAAN

Bahan yang digunakan dalam penelitian ini adalah cangkang sawit. Cangkang sawit didapatkan dari perkebunan kelapa sawit di Borneo Barat. Sebelum digunakan cangkang kelapa sawit dibersihkan dengan dicuci menggunakan air bersih untuk menghilangkan pengotor, kemudian dikeringkan di bawah sinar matahari selama dua hari, dihaluskan menggunakan hammer mill, dan diayak untuk mendapatkan ukuran partikel -16 +40 mesh. Kemudian dilakukan pengeringan di dalam oven pada suhu 105

°C selama 24 jam untuk mendapatkan kadar air sekitar 10% berat kering.

Peralatan yang digunakan dalam penelitian ini adalah reaktor fixed bed yang yang berbentuk silinder vertikal yang terbuat dari stainless steel dengan diameter dalam 40 mm, diameter luar 44 mm, dan tinggi 600 mm. Reaktor dilengkapi dengan pemanas yang terbuat dari kawat nikelin yang dililitkan pada bagian luar reaktor. Suhu dan kecepatan pemanasan diukur dan diatur menggunakan thermocouples tipe K dan PID controller (Jamilatun et al., 2019).

Pirolisis dilakukan dalam kondisi isothermal dengan memasukkan 50 gram cangkang sawit ke dalam reactor, kemudian dilakukan pemanasan dengan kecepatan pemanasan 10-12 °C/menit, setelah suhu reactor mencapai suhu yang dinginkan (300, 400, 500, dan 600 ⁰C) pemanasan dilanjutkan selama 60 menit secara isothermal.

Hasil pirolisis berupa gas terkondensasi ditampung dalam akumulator diukur beratnya dan dianalisis dengan GC-MS (QP2010-SE, Shimadzu). Gas yang tidak terkondensasi dialirkan ke tangki air untuk diserap, sedangkan char (arang) yang terbentuk diambil setelah pirolisis selesai, kemudian ditimbang.

Gambar 3. Rangkaian alat pirolisis dengan reaktor fixed bed

3. HASIL DAN PEMBAHASAN

Karakterisasi Fase Organik.

Komposisi bio-oil hasil pirolisis cangkang sawit pada kisaran suhu 300 – 600 C ditunjukkan pada table 1. Hasil GC-

MS juga menunjukkan bahwa pirolisis cangkang sawit menghasilkan berbagai macam senyawa yang berharga (*valuable chemicals*) seperti phenol, guaiacol, syringol, creosol, p-ethylguaiacol, eugenol, o-cresol, dan xylenol.

Tabel 1. Analisis GC-MS fase organic

Komponen (wt.%)	Suhu			
	300	400	500	600
Phenolics	25.32	52.93	50.7	49.94
Phenol	21.4	35.27	35.89	33.79
Phenol, 2-methoxy- (Guaiacol)	2.03	2.88	2.27	2.72
Phenol, 4-ethyl-2-methoxy- (p-Ethylguaiacol)	0.62	3.86	3.08	3.4
2-Methoxy-4-methylphenol (Creosol)	0.58	3.62	2.96	3.22
Phenol, 2,6-dimethoxy- (Syringol)		5.03	4.17	4.39
Phenol, 2,6-dimethoxy-4-(2-propenyl)- (Eugenol)		1.65	1.83	1.82
Phenol, 2-methyl- (o-Cresol)		0.41	0.33	0.39
Phenol, 2,4-dimethyl- (Xylenol)		0.21	0.17	0.21
4-Methoxy-3-(methoxymethyl)phenol	0.69			

Hasil pirolisis cangkang sawit pada suhu 300 °C menghasilkan komponen utama phenol dan guaiacol. Pirolisis pada suhu 400 °C menghasilkan komponen komponen utama phenol, syringol, p-ethylguaiacol, creosol, guaiacol, dan eugenol. Pirolisis pada suhu 500 °C menghasilkan komponen utama phenol, syringol, p-ethylguaiacol, creosol, guaiacol, dan eugenol. Sedangkan pirolisis pada suhu 600 °C menghasilkan komponen utama phenol, syringol, p-ethylguaiacol, creosol, guaiacol, dan eugenol.

Phenol merupakan bahan baku utama dari berbagai proses kimia dan mempunyai aplikasi yang beragam (Ani, n.d.; Chang et al., 2018). Phenol bersama asam dan karbonil dapat bekerja sebagai antimikrobia sehingga dapat menghambat dekomposisi dari produk-produk awetan (Stołyhwo & Sikorski, 2005). Phenol juga merupakan bahan baku utama untuk pembuatan bio-plastik, resin phenolic atau epoxy resin atau polyurethane (Omoriyekomwan et al., 2016). Phenol juga digunakan dalam pembuatan spare-part automotif, peralatan rumah tangga, komponen elektronik, bahan perekat, cat, kayu lapis dan bahan isolasi (Ani, n.d.).

Guaiacol adalah komponen organic alam yang berperan sebagai minyak aromatik. Guaiacol diturunkan dari guaiacum dan terdapat pada berbagai macam minyak asensial dan merupakan

precursor yang berguna untuk produksi *green fuels* karena dihasilkan dari biomassa. Guaiacol dan syringol adalah produk utama dari pirolisis *hardwood lignin* (K N et al., 2022).

Eugenol (2-Methoxy-4-prop-2-enylphenol) adalah senyawa fenolik dari golongan fenilpropanoid dan merupakan komponen utama pada minyak cengkeh. Eugenol memiliki berbagai aktivitas farmakologis seperti antioksidan, anti-inflamasi, anti-mikroba, analgesia dan anestesi lokal (Yu et al., 2022).

Hasil dari pirolisis selain mempunyai aplikasi yang luas baik di bidang farmasi, makanan, kosmetik, maupun industri, juga memiliki harga jual yang tinggi (tabel 2) yang menjadikan proses refinery *valuable chemicals* dari fase organik hasil pirolisis cangkang kelapa sawit sangat menjanjikan.
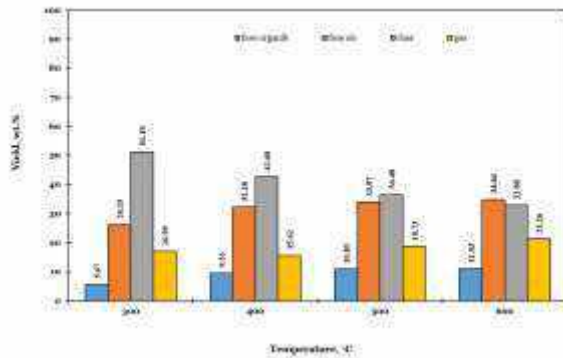
Tabel 2. Aplikasi dan harga jual *valuable chemicals* dari cangkang kelapa sawit

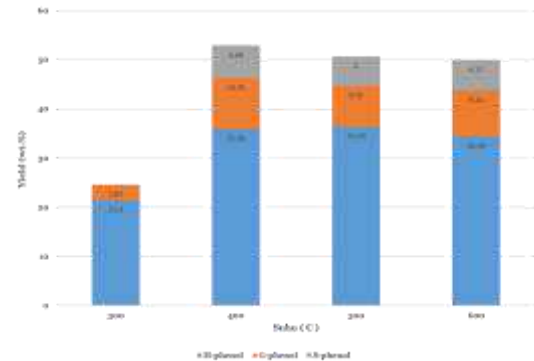| Komponen	Aplikasi	Harga (IDR)
Phenol	Anti mikrobia, resin phenolic, kayu lapis, produk farmasi (Ani, n.d.; Chang et al., 2018)	1.831.661,72/100 g
Guaiacol (Phenol, 2-methoxy-)	Anti kanker (Widiyarti et al., 2014), anti mikroba (N. Li et al., 2021), produksi vanillin (Soongprasit et al., 2020)	205.400,22/100 g
p-Ethylguaiacol (Phenol, 4-ethyl-2-methoxy-)	Bahan pewangi , antioksidan (H. Li et al., 2018)	2.530.445,96/100 g
Creosol (2-Methoxy-4-methylphenol)	Bahan penyedap, bio-fuel (Aliu et al., 2021)	1.132.877,48/ml
Syringol (Phenol, 2,6-dimethoxy-)	Bahan penyedap, bahan pewangi (Api et al., 2022)	1.614.615,10/100 g
Eugenol (Phenol, 2,6-dimethoxy-4-(2-propenyl)-)	Penghambat aktivitas campylobacter (Irem & Korkmaz, 2022), [35], menghambat respon inflamasi dan mengurangi jamur (Yu et al., 2022)	364.638,32/100 mg
o-Cresol (Phenol, 2-methyl-)	Bahan pewangi (Api et al., 2021), resin epoxy (Zeng et al., 2020)	109.687,95/100 mg
Xylenol (Phenol, 2,4-dimethyl-)	Bahan sintetis, *medicinal intermediates*, and insektisida (Tsukatani et al., 2010)	223.399,20/100 g

Pengaruh Suhu terhadap Yield Fase Organik

Pirolisis cangkang kelapa sawit menghasilkan fase organik, fase air, gas, dan char. Pengaruh suhu terhadap yield produk pirolisis ditunjukkan oleh gambar 4. Gambar 4 menunjukkan semakin tinggi suhu semakin tinggi yield fase organik, fase air, dan gas, sedangkan char semakin menurun. Yield fase organik tertinggi didapatkan pada suhu 600 ⁰C dengan yield fase organik sebesar 11.03%.

Meningkatnya suhu dari 300 ⁰C menjadi 500 ⁰C menyebabkan kenaikan yield bio-oil dari 5.67% menjadi 11.03%. Kenaikan bio-oil pada kisaran suhu tersebut disebabkan oleh meningkatnya dekomposisi biomassa (Melia et al., 2021) karena dekomposisi hemiselulosa terjadi pada kisaran suhu 250-350 ⁰C, dekomposisi selulosa pada kisaran 325 - 400 ⁰C, dan dekomposisi lignin pada suhu 300-550 ⁰C (K N et al., 2022).

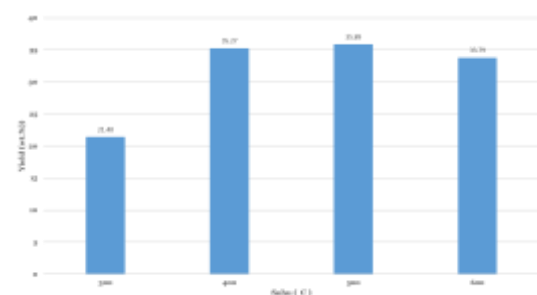Gambar 4. Yield produk pirolisis pada kisaran suhu 300-600 C

Pengaruh Suhu terhadap Yield Komponen Phenolik sebagai *Valuble Chemicals*

Pirolisis cangkang sawit menghasilkan *valuable chemicals* berupa komponen phenolik hasil dekomposisi lignin. Jenis dan kandungan valuable chemicals yang berupa komponen phenolics bergantung kepada kandungan lignin dan karakteristik struktur dari komponen phenolik dari biomassa. Lignin adalah polimer dengan cross-linking tiga dimensi yang mempunyai struktur yang kompleks yang terdiri atas tiga phenolpropanoid unit, yaitu H-phenol, G-phenol, dan S-phenol. H-phenol merupakan produk dengan p-hidroksiphenil unit hasil turunan dari p-coumaryl alcohol. G-phenol adalah produk dengan guaiacyl unit yang merupakan turunan dari coniferyl alcohol. S-phenol adalah produk dengan syringil unit yang merupakan turunan dari sinapyl alcohol. Sebagaian besar unit tersebut digabungkan bersama dengan ikatan ether (C—C) dan ikatan C—C (Lyu et al., 2015; Soongprasit et al., 2020).

Gambar 5. Distribusi H-phenol, G-phenol, dan S-phenol dalam fase organik

Gambar 5 menunjukkan distribusi H-phenol, G-phenol, dan S-phenolpada suhu 300-600 ˚C. Gambar menunjukkan semakin tinggi suhu yield G-phenol dan S-phenol semakin rendah. Sedangkan yield H-phenol semakin tinggi suhu maka yieldnya semakin besar sampai pada suhu 500˚C, kemudian menurun pada suhu 600 ˚C. Hal ini terjadi karena adanya deoksigenasi komponen oksigenat diantaranya komponen phenolic melalui demethylasi, demethoxylasi dan dehidroksilasi (K N et al., 2022) menjadi hidrokarbon alifatik dan hirokarbon aromatic dengan mengeluarkan gas CO, CO_2, dan yang lainnya (Jamilatun et al., 2019).
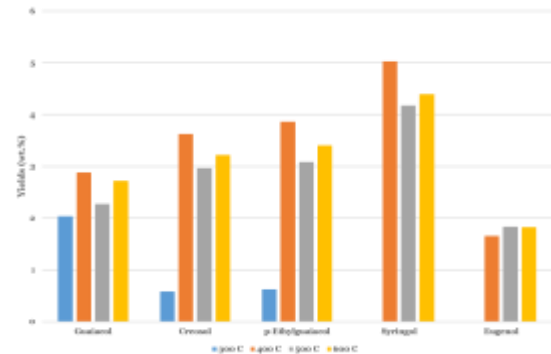

Gambar 6. Komposisi phenol pada berbagai suhu

Kandungan phenol dalam bio-oil dari cangkang sawit pada penelitian ini

relatif tinggi dibandingkan dengan komponen phenolik yang lain. Tingginya kandungan phenol pada bio-oil dari cangkang sawit juga dilaporkan pada beberapa literature (Kim et al., 2010). Tingginya kandungan phenol dalam bio-oil dalam cangkang sawit disebabkan tingginya kandungan lignin (Chang et al., 2016). Lignin terdekomposisi melalui dehidrasi grup carboxyl pada rantai alkyl kemudian diikuti pemutusan ikatan inter-aromatik (Misson et al., 2009) dan hidrolisis ikatan ether pada lignin (Toor et al., 2011) menghasilkan phenol dan turunannya, benzene, xylene, pyridine dan turunan furan. Kandungan phenol dalam bio-oil pada penelitian ini berada pada kisaran 21.40-35.89 wt.% (gambar 6). Kandungan phenol tertinggi 35.89 wt.% pada suhu 500 °C . Kandungan phenol pada suhu dibawah 300 °C cukup tinggi padahal dekomposisi lignin terjadi pada suhu 300-550 ⁰C (K N et al., 2022). Pembentukan phenol pada suhu dibawah 300 °C disebabkan adanya pemutusan rantai cabang ferulic acid ester pada xylan dan juga polimerisasi unsaturated light komponen (Evans & Milne, 1987).

Pembentukan phenol meningkat dari 21.40 pada suhu 300°C menjadi 35.89 wt.% pada suhu 500 °C, hal ini disebabkan oleh meningkatnya dekomposisi lignin yang terjadi pada kisaran suhu 300 sampai 500 °C (Yang et al., 2007), dan juga karena adanya pemutusan rantai methoxy dan alkyl pada gugus-gugus yang tersubstitusi pada phenol seperti methoxy phenol, alkyl phenol, alkyl methoxy phenol, dan oxygenated alkyl methoxy phenol (Soongprasit et al., 2020). Pada suhu di atas 500 °C, kandungan phenol menurun seiring dengan meningkatnya suhu yang mana hal ini disebabkan oleh adanya deoksigenasi phenol menjadi hirokarbon aromatic dengan mengeluarkan gas CO, CO2, dan yang lainnya (Jamilatun, Budhijanto, et al., 2020) atau karena adanya electrophilic aromatic substitution melalui raksi alkilasi dan asilasi (Roswanda et al., 2018).
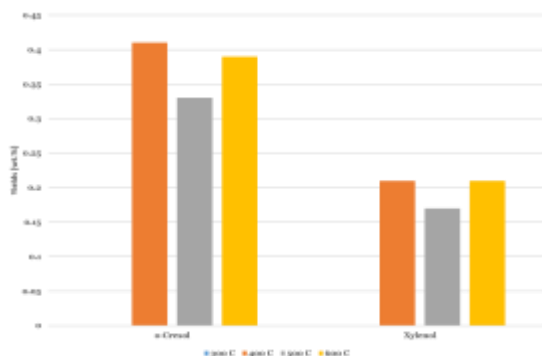

Gambar 7. Yield *valuable chemicals* (G-phenol dan S-phenol) pada suhu 300-600 C

Gambar 7 menunjukkan yield *valuable chemicals* dalambentuk G-phenol (guaiacol, creosol, p-ethylguaiacol) dan S-phenol (syringol, dan eugenol) pada suhu 300-600 ° C. Guaiacol dan syringol termasuk dalam kategori methoxy phenol, komponen phenol dengan grup methoxy. Sedangkan creosol dan p-ethylguaiacol termasuk dalam kategori alkil-methoxy phenol, kompopnen phenol dengan grup alkil dan grup methoxy. Gambar menunjukkan guaiacol dan syringol merupakan komponen yang paling tinggi. Tingginya kandungan guaiacol dan syringol menunjukkan bahwa produk berasal dari pirolisis hardwood lignin.

Pada suhu 400 °C produk didominasi oleh guaiacol dan syringol. Pada suhu 400 sampai 600 °C terjadi penurunan jumlah kedua komponen tersebut dan peningkatan jumlah phenol, hal ini disebabkan oleh adanya radical induced rearrangement (ipso-substitution) reactions dengan menghasilkan cresol dan xylenol, kemudian kedua senyawa aromatic ini mengalami dekomposisi lebih lanjut dengan menghasilkan phenol melalui reaksi demethylasi (Stefanidis et al., 2014).

Meningkatnya suhu pirolisis menyebabkan kandungan guaiacol, creosol, p-ethylguaiacol, dan syringol cenderung menurun. Kandungan guaiacol, creosol, p-ethylguaiacol, dan syringol tertinggi didapatkan pada suhu 400 °C dengan yield berturut-turut sebesar 2.88, 3.62, 3.86, dan 5.03 wt.%. Kandungan eugenol tertinggi didapatkan pada suhu 500 °C dengan yield 1.83 wt.%.

Gambar 8. Yield *valuable chemicals* (H-phenol) pada suhu 300-600 C

Gambar 8 menunjukkan yield H-phenol (o-cresol dan xylenol) pada suhu 300-400 °C. Cresol dan xylenol termasuk dalam kategori alkil phenol, komponen phenol dengan grup alkil. Kedua komponen tersebut termasuk dalam phenol sederhana. Phenol sederhana terbentuk dari hasil dekomposisi selulosa dan hemiselulosa (Evans & Milne, 1987) Kedua komponen tersebut juga terbentuk karena adanya radical induced rearrangement (ipso-substitution) reactions pada guaiacol dan syringol dan demethoxilasi pada alkil methoxi phenol. Reaksi lebih lanjut kedua komponen tersebur melalui reaksi demethilasi menghasilkan phenol. Pada suhu 300 °C kandungan kedua komponen tersebut tidak terdeteksi. Sedangkan pada suhu diatas 300 °C jumlah o-cresol sedikit menurun sedangkan jumlah xylenol cenderung stabil. Hal ini terjadi dimungkinkan karena adanya perbedaan antara kecepatan pembentukan dan dekomposisi kedua komponen tersebut pada suhu tinggi.

Meningkatnya suhu menyebabkan kandungan o-cresol sedikit menurun dan kandungan xylenol bernilai tetap. Kandungan o-cresol dan xylenol tertinggi didapatkan pada suhu 400 °C dengan yield sebesar 0.41 dan 0.21 wt.%.

4. KESIMPULAN

Pirolisis cangkang sawit menghasilkan fase organik, fase air, gas, dan char. Fase organik hasil pirolisis mempunyai kandungan *valuable chemicals* seperti phenol, guaiacol, syringol, creosol, p-ethylguaiacol, eugenol, o-cresol, dan xylenol. Komponen-komponen tersebut memiliki aplikasi dalam bidang farmasi, makanan, kosmetik, dan industri dan mempunyai harga jual yang tinggi. Meningkatnya suhu pirolisis menyebabkan turunnya kandungan G-phenol dan S-phenol seperti guaiacol, creosol, p-ethylguaiacol, dan syringol, dan meningkatkan kandungan H-phenol seperti phenol. Kandungan guaiacol, creosol, p-ethylguaiacol, o-cresol dan syringol tertinggi didapatkan pada suhu 400 C dengan yield berturut-turut sebesar 2.88, 3.62, 3.86, 0.41, dan 5.03 wt.%. Kandungan phenol dan eugenol tertinggi didapatkan pada suhu 500 C dengan yield sebesar 35.89 dan 1.83 wt.%. Kandungan xylenol tertinggi didapatkan pada suhu 600 C dengan yield sebesar 0.21 wt.%.

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TEMPLATE
Seminar Nasional LPPM UMJ 2022

PIROLISIS TANDAN KELAPA SAWIT UNTUK MENGHASILKAN BAHAN BAKAR CAIR, GAS, *WATER FASE* DAN *CHARCOAL*

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ABSTRAK

Pirolisis biomassa mendapatkan perhatian lebih pada dekade terakhir ini. Pirolisis adalah konversi biomassa pada suhu tinggi tanpa kehadiran oksigen untuk mendapatkan produk yang bernilai. Pirolisis bimassa dilakukan untuk mendapatkan 3 hal, yaitu bio-oil, biochar dan gas. Bio-oil adalah produk cair dari proses pirolisis dan mempunyai beberapa aplikasi. Biooil digunakan langsung untuk bahan bakar boiler dan furnace, atau diproses untuk menghasilkan bahan bakar minyak dan produk-produk kimia. Bio-oil tersusun atas campuran kompleks dari substansi- substansi organik seperti hidrokarbon aromatik, fenol, keton, ester, ster, gula, amina, alkohol, furan, dan air yang berasal dari reaksi kimia dan dari biomassa. Kandungan air pada bio-oil relatif tinggi, biasanya pada kisaran 20-25%. (tahapan). Buah sawit mempunyai warna bervariasi dari hitam, ungu, hingga merah tergantung bibit yang digunakan. Buah bergerombol dalam tandan yang muncul dari tiap pelapah. Minyak dihasilkan oleh buah. Kandungan minyak bertambah sesuai kematangan buah. Setelah melewati fase matang, kandungan asam lemak bebas (FFA, free fatty acid) akan meningkat dan buah akan rontok dengan sendirinya.

Kata kunci : Pirolisis, *Bio Oil*, Kelapa Sawit

ABSTRACT

Pyrolysis of biomass has received more attention in the last decade. Pyrolysis is the conversion of biomass at high temperatures in the absence of oxygen to obtain valuable products. Pyrolysis of biomass is carried out to obtain 3 things, namely bio-oil, biochar and gas. Bio-oil is a liquid product of the pyrolysis process and has several applications. Biooil is used directly to fuel boilers and furnaces, or processed to produce fuel oil and chemical products. Bio-oil is composed of a complex mixture of organic substances such as aromatic hydrocarbons, phenols, ketones, esters, sters, sugars, amines, alcohols, furans, and water derived from chemical reactions and from biomass. The water content in bio-oil is relatively high, usually in the range of 20-25%. (stages). Palm fruit has a color that varies from black, purple, to red depending on the seeds used. The fruit is clustered in bunches that emerge from each sheath. The oil is produced by the fruit. The oil content increases as the fruit ripens. After passing through the ripe phase, the content of free fatty acids (FFA) will increase and the fruit will fall off by itself.

Keywords: *Pyrolysis, Bio Oil, Palm Shell*

1. PENDAHULUAN

Tandan kelapa sawit (TKS) merupakan limbah padat yang dihasilkan pabrik/industri pengolahan minyak kelapa sawit. Produksi minyak kelapa sawit kasar Indonesia mencapai 6 juta ton per tahun. Secara bersamaan dihasilkan pula limbah Tandan Kelapa Sawit (TKS) dengan potensi sekitar 2,5 juta ton per tahun. Di pabrik minyak kelapa sawit, TKS hanya dibakar dan sekarang telah dilarang karena adanya kekhawatiran pencemaran lingkungan, atau dibuang sehingga menimbulkan keluhan/masalah karena dapat menurunkan kemampuan tanah menyerap air. Di samping itu, TKS yang membusuk ditempat akan menarik kedatangan jenis kumbang tertentu yang berpotensi merusak pohon kelapa sawit hasil peremajaan di lahan sekitar tempat pembuangan. Salah satu usaha dalam mengatasi hal tersebut adalah memanfaatkan TKS menjadi produk berguna dan bernilai tambah.

Krisis energi ini menuntut pencarian sumber energi alternatif untuk menjamin tercukupinya kebutuhan energi dunia (Ighalo dkk, 2019). Para peneliti telah mengindentifikasi biomassa sebagai sumber energi yang berkelanjutan, dapat diperbaharui, dan ramah linkungan (Ighalo dkk, 2019, Rajendra dkk, 2019, Wang dkk, 2018). Ketergantungan pada energi fosil di Indonesia khususnya minyak bumi masih tinggi mencapai 96% dari total konsumsi (BPPT-OEI, 2019).

Tandan kelapa sawit ini dapat dikembangkan menjadi bahan bakar biomassa dengan cara pirolisis biomassa. Pirolisis adalah konversi biomassa pada suhu tinggi tanpa kehadiran oksigen untuk mendapatkan produk yang bernilai. Pirolisis bimassa dilakukan untuk mendapatkan3 hal, yaitu bio-oil, biochar dan gas (Sharkar dkk, 2020).

Pirolisis merupakan suatu proses devolatilisasi dimana pirolisis itu adalahsuatu proses dekomposisi biomasa secara termal tanpa oksigen sama sekali. Proses dekomposisi pada pirolisis ini juga sering disebut dengan devolatilisasi. Produk utama yang dihasilkan dari pirolisis adalah arang (char), minyak dan gas. Arang yang terbentuk dapat digunakan untuk bahan bakar ataupun digunakan sebagai karbon aktif. Bio oil yang dihasilkan dapat digunakan sebagai zat additif atau campuran dalam bahan bakar. Sedangkan gas yang terbentuk dapat dibakar secara langsung (Sampath,S.S., Babu,B.B., 2005). Pirolisis dari biomasa akan menghasilkan zat baru seperti gas dan arang. Gas dari pirolisis dapat dibedakan menjadi gas yang tidak dapat dikondensasi (CO, CO_2, CH_4, dll) dan gas yang dapat dikondensasi (tar). Minyak akan terjadi pada proses kondensasi dari gas yang terbentuk, disebut juga bio oil.
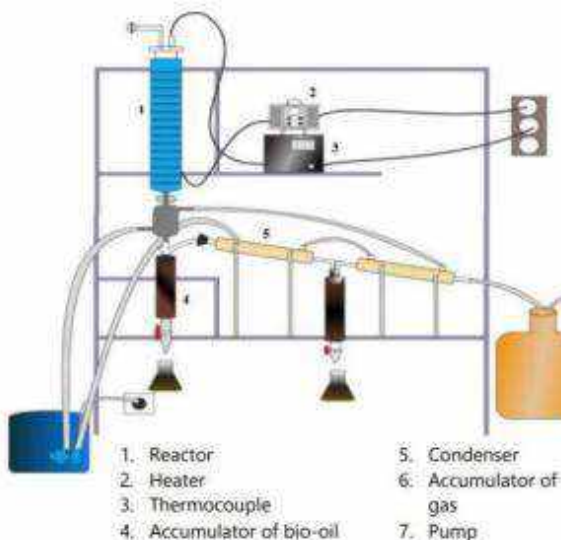
Bio-oil yang dihasilkan dari proses pirolisis dapat dijadikan alternatif bahan bakar setelah melalui proses upgrading (Park dkk, 2008). Noncondensable gas seperti CH_4,H_2,CO_2, dan CO dapat dijadikan sebagai energy recuperation atau dijadikan syngas (Masek dkk, 2013). Sementara itu biochar dapat dijadikan adsorbent atau dijadikan bahan bakar karena mempunyai heating value yang tinggisetara dengan batubara (Fu dkk, 2012).

Bio-oil adalah produk cair dari proses pirolisis dan mempunyai beberapa aplikasi. Bio-oil digunakan langsung untuk bahan bakar boiler dan furnace, atau diproses untuk menghasilkan bahan bakar minyak dan produk-produk kimia (Bridgwater dkk, 2012). Bio-oil tersusun atas campuran kompleks dari substansi - substansi organik seperti hidrokarban

aromatik, fenol, keton, ester, ster, gula,amina, alkohol, furan, dan air yang berasal dari reaksi kimia dan dari biomassa (Alvarez dkk, 2015). Kandungan air pada bio-oil relatif tinggi, biasanya pada kisaran 20-25% (Kharmakar dkk, 2013).

2. METODE PELAKSANAAN

Alat dan bahan : Penelitian dilakukan di dalam fixed bed reaktor yang yang berbentuk silinder vertikal yang terbuat dari stainless steel dengan dimensi diameter dalam 400 mm, diameter luar 44 mm, dan tinggi 600 mm. Reaktor dilengkapi dengan pemanas yang terbuat dari nikel yang dililitkan pada bagian luar reaktor . Reaktor juga dilengkapi instrument penting untuk mempelajari karakteristik reaktor berupa suhu dan kecepatan pemanasan (Jamilatun dkk, 2019). Rangkaian alat secara lengkap ditunjukkan pada Gambar 1. Dan untuk bahan yang digunakan yaitu tandan kelapa sawit.

1. Reactor
2. Heater
3. Thermocouple
4. Accumulator of bio-oil
5. Condenser
6. Accumulator of gas
7. Pump

Gambar 1. Rangkaian Alat Pirolisis

Cara kerja : Pirolisis dimulai dengan memasukkan 15 gram biomassa cangkang kelapa sawit sebagai umpan. Kemudian umpan dimasukkan ke dalam reaktor.

Pemanasan dilakukan dengan arus listrik melalui kawat nikel yang dililitkan pada bagian luar reaktor dengan kecepatan rata-rata antara 5-35 C/menit. Pirolisis dilakukan dengan variasi suhu 300, 400, 500, 550, 600 dan 700 ⁰C dan dimonitor dengan thermocouple. Gas yang mengembun ditampung dalam akumulator bio-oil dan ditimbang beratnya. Gas yang tidak mengembun dialirkan ke dalam tangki air untuk diabsorbsi, sedangkan arang yang terbentuk di dalam reaktor diambil setelah pirolisis selesai dan ditimbang beratnya. Proses pirolisis dihentikan setelah mencapai suhu yang diinginkan dan didiamkan dengan suhu konstan selama 30 menit.
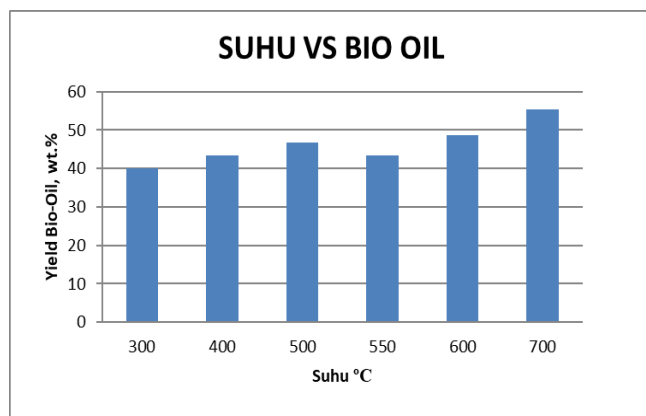
3. HASIL DAN PEMBAHASAN

Serat kelapa sawit memiliki sifat yang keras dan kuat. Pori – pori pada permukaan serat kelapa sawit memiliki rata – rata diameter sebesar 0.07 m. Morfologi permukaan pori ini sangat berguna untuk meningkatkan ikatan mekanik dengan resin matriks jika digunakkan pada pembuatan komposit. Dalam mikrofibril Tandan Kelapa Sawit terdapat selulosa, lignin, dan hemiselulosa sebagai komponen utama. Senyawa yang paling banyak terkandung dalam serat kelapa sawit adalah selulosa, lignin, hemiselulosa, dan holoselulosa. Holoselulosa dan hemiselulosa memiliki struktur kimia yang sama dengan selulosa tetapi memiliki sifat yang sama dengan lignin. Selulosa berfungsi untuk membentuk pori pada komposit. Berikut merupakan komposisi dari Tandan Kelapa Sawit:

Tabel 1. Komposisi Tandan Kelapa Sawit

UNSUR	NILAI
Selulosa (%)	42,7 – 65
Lignin (%)	13,2 – 25,31
Hemiselulosa (%)	17,1 – 33,5

Holoselulosa (%)	68,3 – 86,3
Kadar Abu (%)	1,3 – 6,04
Ekstraktif dalam air panas (%)	2,8 – 14,79
Kelarutan dalam air dingin (%)	8 – 11,46
Alkali larut (%)	14,5 – 31,17
Alfa selulosa (%)	41,9 – 60,6
Kelarutan alcohol-benzene (%)	2,7 – 12
Pentosan (%)	17,8 – 20,3
Glukosa (%)	66,4
Silika (%)	1,8
Cu (g/g)	0,8
Kalsium (g/g)	2,8
Mn (g/g)	7,4
Fe (g/g)	10,0
Sodium (g/g)	11,0

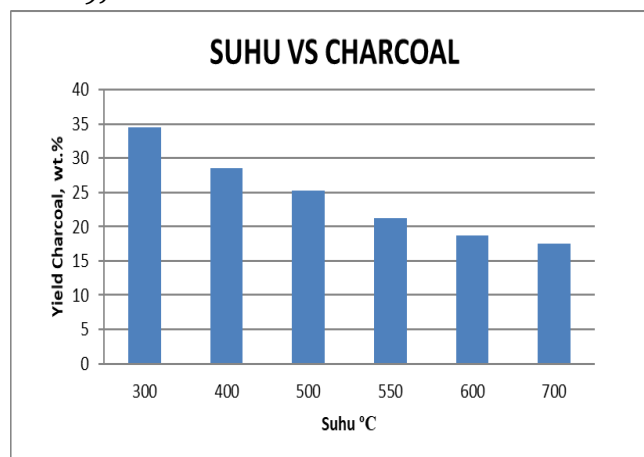(Egi, Muthia Rahmasita dkk, 2017)

Grafik 1. Perbandingan Suhu vs Bio-Oil

Dari Grafik 1, terlihat bahwa rendemen bio-oil maksimum pada suhu optimum 700°C adalah 55,53 wt.%. Eksperimen ini menemukan bahwa rendemen bio-oil meningkat dari 40 wt.% menjadi 46,67 wt.% ketika suhu berkisar antara 300°C hingga 500°C. Sedangkan pada suhu 550 °C, rendemen bio oil mengalami penurunan menjadi 43,33 wt.% dan mengalami kenaikan kembali pada suhu 600°C dan 700 °C. Pada grafik menunjukkan bahwa berdasarkan jumlah

bio-oil tertinggi, suhu 700°C merupakan suhu optimum untuk pirolisis tanpa katalis.

Penurunan rendemen bio-oil dipengaruhi oleh terjadinya secondary cracking pada tar (fase bio-oil dan air). Pada proses pirolisis terjadi reaksi perengkahan, yaitu pemutusan ikatan CC dari rantai karbon panjang (polimer) dan berat molekul masif menjadi rantai karbon pendek (monomer) dengan berat molekul kecil. Hal ini dapat mempengaruhi peningkatan suhu pirolisis; semakin banyak ikatan (rantai hidrokarbon) yang putus, sehingga rendemen meningkat. Temperatur tinggi juga mempengaruhi pengurangan produk cair dan konsisten dengan produk gas teratasnya. Terjadi proses secondary cracking, yaitu memecah rantai panjang senyawa organik dan hidrokarbon menjadi rantai yang lebih pendek sehingga tidak dapat terkondensasi kembali (Jamilatun et al., 2019).

Grafik 2. Perbandingan Suhu vs Charcoal

Grafik 2 menunjukkan pengaruh suhu terhadap hasil arang dari pirolisis Tandan Kelapa Sawit. Rendemen arang diperoleh dari temperatur 300, 400, 500, 550, 600 dan 700 °C dengan presentase 34,37 wt.%, 28,47 wt.%, 25,27 wt.%, 21,2 wt.%, 25,33 wt.%, 24,2 wt.%. Hasil ini
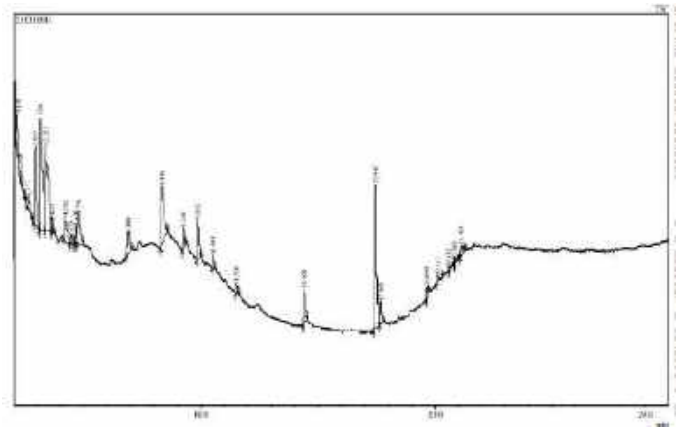
menunjukkan bahwa rendemen arang mengalami naik turun.

Berdasarkan tinjauan literatur (Dickerson T, 2013) menunjukkan bahwa pirolisis pada suhu rendah kurang dari 400 ° C atau pemanasan yang relatif rendah akan menghasilkan produk arang yang relatif tinggi. Laju pemanasan yang lebih rendah dan waktu tinggal yang lebih lama menyebabkan reaksi perengkahan sekunder akan mempengaruhi sifat bio-oil. Semakin tinggi suhu pirolisis yang digunakan maka kandungan arang akan semakin rendah karena kandungan penyusun Tanda Kelapa Sawit akan terdekomposisi, dan kandungan volatile matter akan semakin menurun dengan meningkatnya suhu pirolisis.
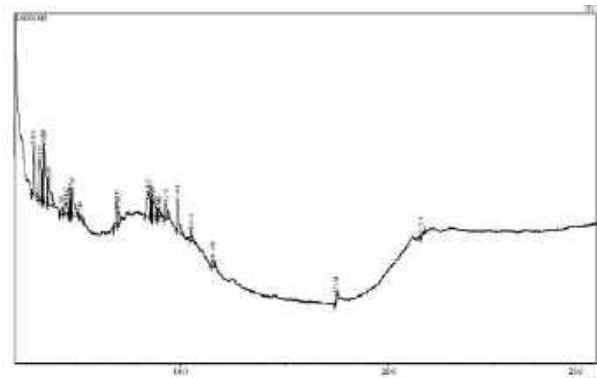
Identifikasi Komponen Produk Cair dengan Metode GC-MS

Pada umumnya, metode optimasi hasil pirolisis dilakukan sesuai dengan tujuan dari proses pirolisis yang dilakukan. Perbedaan temperature reaksi akan menentukan distribusi senyawa produk atau komponen produk cair sehingga juga berpengaruh terhadap reaksi yang terlibat dalam proses. Identifikasi senyawa dilakukan untuk mengetahui kualitas produk cair yang dihasilkan.

Pada penelitian ini, identifikasi produk cair dilakukan dengan metode GC-MS. Identifikasi ini dilakukan untuk mengetahui distribusi komponen senyawa pada produk cair hasil pirolisis. Berikut adalah hasil dari pemecahan spectra pada GC-MS terhadap produk cair pirolisis:

Gambar 2. Identifikasi senyawa produk cair dengan metode GC-MS pada temperature 300°C

Gambar 3. Identifikasi senyawa produk cair dengan metode GC-MS pada temperature 600°C

Puncak-puncak spektra pada gambar diatas menunjukkan jenis-jenis komponen yang dikandung oleh cairan hasil pirolisis. Berdasarkan gambar dapat dilihat bahwa jumlah komponen yang teridentifikasi mencapai 21 jenis komponen yang ditunjukkan dengan terbentuknya 25 *peak*. Hasil identifikasi terhadap komponen tersebut kemudian ditabulasikan pada tabel berikut:

Tabel 2. Karakteristik GC-MS produk cair
pirolisis pada temperature 300°C

Peak	Komponen	Area %
1	1,2-Epoxy-3-propyl acetate	2,13
2	2-Cyclopenten-1-one, 2-methyl- (CAS)	1,27
3	3-Pentanone, 2-methyl- (CAS)	1,36
4	2-FURANMETHANOL, TETRAHYDRO-	6,41
5	Phenol	18,43
6	2-Cyclopenten-1-one, 2-hydroxy-3-methyl- (CAS)	14,84
7	3,5-dimethyl cyclopentenolone	1,31
8	Phenol, 2-methoxy-	3,38
9	Butanoic acid, 2-propenyl ester (CAS)	1,57
10	Pentanal (CAS)	1,95
11	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	4,82
12	1,5-Dioxonane, 2-ethoxy-9-methyl- (CAS)	2,70
13	Phenol, 2,6-dimethoxy- (CAS)	8,79
14	1,2,4-Trimethoxybenzene	1,86
15	Benzene, 1,2,3-trimethoxy-5-methyl- (CAS)	3,41
16	Phenol, 2,6-dimethoxy-4-(2-propenyl)- (CAS)	1,10
17	Phenol, 2,6-dimethoxy-4-(2-propenyl)- (CAS)	1,07
18	Hexadecanoic acid (CAS)	3,61
19	9-Octadecenoic acid, (E)-	13,58
20	Octadecanoic acid (CAS)	2,13
21	9-Octadecenoic acid (Z)-, 2-hydroxyethyl ester (CAS)	0,83
22	Triethylene glycol monododecyl ether	0,48
23	1,4,7,10,13,16-Hexaoxacyclooctadecane (CAS)	0,54
24	1,6-Di-.2-phenylbenzimidazolylmethyl-2,5-piperazindione	0,73
25	9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester	1,71

Tabel 3. Karakteristik GC-MS produk cair
pirolisis pada temperature 600°C

Peak	Komponen	Area %
1	2-furanmethanol, tetrahydro-	8,22
2	Phenol (CAS)	11,21
3	2-Cyclopenten-1-one, 2-hydroxy-3-methyl- (CAS)	7,68
4	Ethanone, 1-(1H-pyrrol-2-yl)- (CAS)	11,71
5	Glycine, N-(trifluoroacetyl)-, 1-methylpentyl ester (CAS)	6,81
6	PHENOL, 2-METHOXY-	1,06
7	Pentane, 3-bromo- (CAS)	3,28
8	Pentanal (CAS)	1,61
9	Disulfide, ethyl(1-methylpropyl) (CAS)	1,35
10	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	6,53
11	2(5H)-Furanone, 5-ethyl- (CAS)	0,97
12	2-Propenoic acid, 2-methyl-, ethyl ester (CAS)	4,99

13	2-Isononenal (CAS)	2,61
14	Phenol, 2,6-dimethoxy- (CAS)	5,65
15	Crotonaldehyde, 2-methyl-, diethylhydrazone (CAS)	2,94
16	2,4-Dimethoxyphenol	1,46
17	Dl-ribitol, 1,4-anhydro-, cyclic 2,3-(ethylboronate)	4,94
18	Hydrazine, (2-methyl-1-propenyl)- (CAS)	1,23
19	Phenol, 3,4-dimethoxy- (CAS)	1,50
20	1,2,4-Trimethoxybenzene	3,07
21	Ethanone, 1-(2,6-dihydroxy-4-methoxyphenyl)-(CAS)	6,25
22	2,4-Hexadienedioic acid, 3-methyl-4-propyl-, dimethyl ester, (E,E)- (CAS)	1,43
23	Phenol, 2,6-dimethoxy-4-(2-propenyl)- (CAS)	1,39
24	Heptadecene-(8)-carbonic acid-(1)	1,18
25	9,12,15-Octadecatrienoic acid, 2-[(trimethylsilyl)oxy]-1-[[(trimethylsilyl)oxy]methyl]ethyl ester, (Z,Z,Z)-(CAS)	0,94

Dari tabel diatas dapat dilihat bahwa komponen utama cairan produk pirolisis adalah fenol. Fenol dan turunannya adalah senyawa dengan komposisi paling besar. Senyawa fenol dapat meningkatkan kemampuan terbakar produk cair, tetapi dikarenakan produk ini masih mengandung air maka pembakaran produk cair ini masih tergolong lama.

4. KESIMPULAN

Berdasarkan hasil penelitian yang telah dilakukan, dapat disimpulkan bahwa:

a. Pada Bio-oil, semakin tinggi suhu maka semakin banyak bio-oil yang dihasilkan dari pirolisis Tandan Kelapa Sawit. Namun pada charcoal, semakin tinggi suhu maka charcoal yang dihasilkan semakin sedikit.

b. Pada hasil menunjukkan bahwa berdasarkan jumlah bio-oil tertinggi, suhu $700°C$ merupakan suhu optimum untuk pirolisis tanpa katalis.

c. Hasil produk cair pada pirolisis Tandan Kelapa Sawit presentase kandungan tertingginya adalah senyawa fenol yang dapat meningkatkan kemampuan terbakar produk cair, tetapi dikarenakan produk ini masih mengandung air maka pembakaran produk cair ini masih tergolong lama.

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SURAT PERNYATAAN TANGGUNG JAWAB BELANJA

Yang bertanda tangan di bawah ini :

Nama : Dr. Ir. Siti Jamilatun, MT
Judul Penelitian : Pengembangan Biofuel dan Chemicals dari Pirolisis Limbah Padat Pengolahan Kelapa Sawit (LPPKS) untuk Penguatan Green Economy dalam mendukung Kemandirian energi dan Penyediaan Bahan Kimia
Nomor Kontrak : PD-072/SP3/LPPM-UAD/VII/2022
Dana penelitian : Rp 12.000.000,-

Dengan ini menyatakan bahwa biaya kegiatan penelitian tersebut di atas digunakan untuk pos-pos pembelajaan sebagai berikut.

No	Uraian Pengeluaran	Jumlah (Rp)
1.	Bahan (ATK, material/bahan penelitian, Dll.)	500.000,-
2.	Pengumpulan Data (Penggandaan angket, FGD, transport responden, dll.)	3.250.000,-
3.	Analisis Data (Biaya uji lab., biaya analisis data, dll.)	2.650.000,-
4.	Pelaporan dan Luaran Penelitian (Penyusunan laporan dan luaran, biaya translate ke bahasa asing, biaya submit, biaya pendaftaran HKI, dll.)	2.400.000,-
5.	Lain-lain (HR tim peneliti dan pembantu lapangan)	2.000.000,-
	Jumlah Pengeluaran (Rp)	10.800.000,-
	Sisa Anggaran (Rp)	0,-

Demikian surat pernyataan ini dibuat dengan sebenarnya.

Yogyakarta, 27 Januari 2023

Dr. Ir. Siti Jamilatun, MT