TUGAS AKHIR TF141581

PENGARUH SUHU DEKOMPOSISI DAN KONSENTRASI KATALIS KALSIUM OKSIDA (CaO) DARI CANGKANG TELUR AYAM TERHADAP SINTESIS BIODIESEL DARI MINYAK JELANTAH

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FINAL PROJECT TF141581

EFFECTS OF DECOMPOSITION TEMPERATURES AND CATALYST CONCENTRATION OF CALCIUM OXIDE (CaO) FROM CHICKEN EGGSHELLS ON BIODIESEL PRODUCTION FROM WASTE COOKING OIL

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PENGARUH SUHU DEKOMPOSISI DAN KONSENTRASI KATALIS KALSIUM OKSIDA (CaO) DARI CANGKANG TELUR AYAM TERHADAP SINTESIS BIODIESEL DARI MINYAK JELANTAH

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TUGAS AKHIR

Diajukan Untuk Memenuhi Salah Satu Syarat
Memperoleh Gelar Sarjana Teknik
pada
Bidang Studi Rekayasa Bahan
Program Studi S-1 Departemen Teknik Fisika
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JULI 2017

PENGARUH SUHU DEKOMPOSISI DAN KONSENTRASI KATALIS KALSIUM OKSIDA (CaO) DARI CANGKANG TELUR AYAM TERHADAP SINTESIS BIODIESEL DARI MINYAK JELANTAH

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Abstrak

Limbah minyak jelantah merupakan alternatif bahan baku untuk menghasilkan biodiesel yang ekonomis dan murah. Limbah ini terlebih dahulu mengalami proses pre-treatment yang bertujuan untuk menghilangkan kadar asam lemak bebas (FFA). Biodiesel diproduksi dengan transesterifikasi antara trigliserida dan alkohol dengan adanya katalis. Katalis oksida padat yang ada paling banyak dikembangkan dalam produksi biodiesel, salah satunya adalah kalsium oksida (CaO). Katalis CaO bersumber dari cangkang telur ayam melalui proses kalsinasi. Cangkang telur ayam kemudian dibersihkan, dan dikeringkan dalam oven dengan suhu 120^oC *selama 24 jam. Kemudian cangkang telur dikalsinasi di dalam tungku dengan variasi suhu 600*^oC*, 700*^oC*, 800*^oC*, dan 900*^oC *selama 6 jam yang kemudian dikarakterisasi melalui uji XRD dan FTIR. Sintesis biodiesel pada penelitian ini dilakukan pada suhu 65°C dengan perbandingan mol minyak-metanol 1:6. Waktu reaksi diberikan selama 2 jam dengan variasi konsentrasi berat katalis yaitu 3wt%, 6wt%, dan 9wt%. Kondisi optimum untuk reaksi adalah CaO yang dikalsinasi pada suhu 900*^oC *dengan konsentrasi katalis 9wt% yang mampu mengkonversi biodiesel dengan sebesar 81,43% dan sisanya adalah gliserol sebagai produk samping. Dapat disimpulkan bahwa suhu* *kalsinasi dan konsentrasi sangat mempengaruhi proses sintesis biodiesel.*

Kata kunci: *minyak jelantah, biodiesel, biodegradable, katalis kalsium oksida, FFA*

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Abstract

Waste cooking oil (WCO) is an alternative raw material to produce economical and cheaper biodiesel. WCO first undergoes a pre-treatment process that aims to remove free fatty acid (FFA). Biodiesel was produced by transesterification between trigliceride and methanol with aided by catalyst. At present, one of the mostly developed solid oxide catalyst in biodiesel production is calcium oxide (CaO). CaO catalyst was obtained from calcined egg shell. Eggshell was cleaned, weighted, and dried in oven at 120^{o}C for 24 hours. Then the eggshell was calcined in a furnace at 600^{o}C, 700^{o}C, 800^{o}C, and 900^{o}C for 6 hours and the results were then characterized by XRD and FTIR. The biodiesel synthesis in this research was conducted at 65ºC with molar ratio of 1: 6 WCO to methanol. Reaction time of 2 hours was used with variation of catalyst weight concentration namely 3wt%, 6wt%, and 9wt%. The optimum condition for the reaction was obtained for CaO calcined at 900^{o}C with a catalyst concentration of 9wt%. This process yields 81.43% conversion and glycerol (by-product). From this research, it can be concluded that the temperature of calcination and concentration catalyst greatly affect the process of biodiesel synthesis.

Keywords: *waste cooking oil, biodiesel, biodegradable, catalyst calcium oxide, free fatty acid*

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Surabaya, Juli 2017

Penulis

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BAB I
PENDAHULUAN

1.1 Latar Belakang

Biodiesel merupakan bahan bakar yang digunakan pada mesin diesel dengan proses sintesis melalui reaksi transesterifikasi dari trigliserida dengan alkohol atau reaksi esterifikasi dari asam lemak bebas dengan alkohol. Sintesis biodiesel sebagian besar berbahan dasar dari minyak nabati, minyak tidak dapat dimakan, lemak, limbah minyak jelantah, dan ganggang. Keuntungan menggunakan minyak nabati sebagai bahan baku untuk produksi biodiesel adalah kandungan asam lemak bebas (FFA) yang rendah (Ullah, dkk., 2009). Karena apabila kandungan FFA yang tinggi dalam sintesis biodiesel dapat memicu terjadinya reaksi saponifikasi atau reaksi penyabunan yang mengakibatkan kualitas hasil pembuatan biodiesel akan menurun (Rhofita, 2015).

Tidak hanya minyak nabati yang dapat disintesis menjadi biodiesel, limbah minyak jelantah hasil penggorengan dapat dijadikan bahan utama sebagai bahan pembuat biodiesel secara efektif. Pembuatan biodiesel dengan bahan baku minyak nabati murni membutuhkan biaya produksi lebih mahal jika dibandingkan dengan menggunakan minyak jelantah hasil penggorengan (Supple, dkk., 2002). Minyak jelantah sangat mudah untuk didapat dan ditemukan karena sifatnya tidak digunakan lagi, itu sebabnya minyak jelantah dapat digunakan sebagai bahan mentah alternatif dalam pembuatan biodiesel (Canakci, 2007).

Sampai saat ini, produksi bahan bakar biodiesel telah meningkat sangat besar dan dapat bersaing dengan bahan bakar fosil (Gnanaprakasam & Sivakumar, 2013). Produksinya yang semakin meningkat inilah yang menunjukkan bahwa bahan bakar biodiesel memiliki kelebihan yaitu: *biodegradable, renewable,* ramah lingkungan, biaya produksi yang murah, tidak mengemisikan karbon ke atmosfer dan bahan dasarnya yang mudah didapatkan (Martinez,dkk., 2010).

Dalam reaksi pembuatan biodiesel diperlukan katalis karena reaksi cenderung berjalan lambat. Katalis biosiesel berfungsi untuk menurunkan energi aktifasi reaksi sehingga reaksi dapat berlangsung lebih cepat (Kirk & Othmer, 1980). Katalis yang digunakan dapat berupa katalis basa homogen atau katalis heterogen. Katalis homogen seperti NaOH dan KOH karena memiliki kemampuan katalisator yang lebih tinggi dibandingkan dengan katatalis lainnya tetapi memiliki kelemahan sulit dipisahkan dari campuran reaksi sehingga tidak dapat digunakan kembali. Tetapi jika menggunakan katalis heterogen yang meskipun memiliki kemampuan katalisator yang sedikit lebih rendah dibandingkan dengan katalis basa homogen, katalis basa heterogen dapat dengan mudah dipisahkan dari campuran reaksi sehingga dapat digunakan kembali (Santoso, dkk., 2013).

Katalis kalsium oksida (CaO) merupakan suatu katalis basa heterogen yang dapat dijadikan sebagai pemercepat reaksi sintesis biodiesel. Katalis CaO salah satunya dapat disintesis melalui proses pemanasan atau kalsinasi dari bahan $CaCO_3$. Di kehidupan sehari-hari sebenarnya banyak sekali dijumpai bahan-bahan yang memiliki kandungan $CaCO_3$ seperti, limbah cangkang kerang, limbah cangkang telur ayam, dan sebagainya. Salah satu limbah yang banyak mengandung $CaCO_3$ adalah cangkang telur ayam. Cangkang telur memiliki kelebihan, yaitu *biodegradable*, dapat didaur ulang, dan biokompatibel (Soleymani, dkk., 2009). Cangkang telur terdiri dari 94% kandungan $CaCO_3$, 1% kandungan $MgCO_3$, 1% kandungan $Ca_3(PO_4)_2$, dan 4% kandungan bahan-bahan organik (Stadelman, 2005). Limbah padat cangkang telur ayam ini tidak berbahaya, dan umumnya dibuang di tempat pembuangan sampah dan tidak membutuhkan *pretreatment* apapun karena tidak memiliki kegunaan khusus.

Dari penelitian sebelumnya yang dilakukan oleh (El-Gendy & Deriase, 2015) dengan memvariasikan molar rasio metanol terhadap minyak jelantah, konsentrasi katalis, dan waktu reaksi serta menggunakan katalis kalsium oksida cangkang telur dengan suhu kalsinasi 800^{o}C. Minyak jelantah dapat menghasilkan biodiesel maksimum sebesar 90%. Pada penelitian tugas akhir ini akan disintesis biodiesel dengan memanfaatkan limbah minyak jelantah dan pengaruh suhu kalsinasi dan konsentrasi katalis kalsium oksida (CaO) yang didapatkan dari cangkang telur ayam yang akan dianalisis hasil pembuatan biodiesel tersebut.

1.2 Perumusan Masalah

Berdasarkan latar belakang yang telah dipaparkan, maka permasalahan yang akan dibahas dalam tugas akhir ini adalah sebagai berikut:

a. Seberapa besar pengaruh variasi temperatur kalsinasi dalam sintesis katalis kalsium oksida (CaO) limbah cangkang telur ayam untuk proses produksi biodiesel dari minyak jelantah?
b. Seberapa besar pengaruh konsentrasi perbandingan massa kandungan katalis kalsium oksida (CaO) dari limbah cangkang telur ayam terhadap minyak jelantah dalam proses sintesis biodiesel?
c. Bagaimana karakteristik biodiesel minyak jelantah yang telah mengalami *pre-treatment* menggunakan katalis kalsium oksida (CaO) dari limbah cangkang telur ayam dalam proses produksinya?

1.3 Tujuan

Tujuan dilakukannya penelitian tugas akhir ini adalah sebagai berikut:

a. Untuk mengetahui pengaruh perbandingan massa kandungan katalis kalsium oksida (CaO) dari limbah cangkang telur ayam terhadap minyak jelantah dalam proses sintesis biodiesel.
b. Untuk mengetahui pengaruh variasi temperatur kalsinasi dalam sintesis katalis kalsium oksida (CaO) limbah cangkang telur ayam untuk proses produksi biodiesel dari minyak jelantah.
c. Untuk mengetahui karakteristik biodiesel minyak jelantah yang telah mengalami *pre-treatment* menggunakan katalis kalsium oksida (CaO) dari limbah cangkang telur ayam.

1.4 Batasan Masalah

Adapun batas ruang lingkup dari tugas akhir ini antara lain:

a. Ukuran serbuk cangkang telur ayam sebesar 60 mesh.
b. Pada proses ekstraksi kalsium oksida (CaO) sebagai katalis digunakan variasi suhu kalsinasi, yaitu: 600°C, 700°C, 800°C, 900°C berdasarkan hasil uji TGA (*Thermogravimetric Analysis*).
c. Dalam proses sintesis biodiesel digunakan variasi perbandingan massa katalis terhadap volume minyak jelantah, yaitu: 3 wt%, 6 wt%, dan 9 wt% terhadap berat minyak jelantah.

BAB II
TINJAUAN PUSTAKA

2.1 Karakteristik Minyak Jelantah (*Waste Cooking Oil*)

Minyak jelantah (*waste cooking oil*) merupakan minyak goreng bekas yang diperoleh dari minyak nabati hasil penggorengan yang pemakaiannya sudah lebih dari dua kali. Minyak jelantah berasal dari minyak nabati dapat diperoleh dari tumbuh-tumbuhan. Minyak nabati memiliki kompisi trigliserida asam lemak (mempunyai kandungan terbanyak dalam minyak nabati hingga 95%), asam lemak bebas (*Free Fatty Acid*/FFA), mono- dan digliserida, serta beberapa komponen lain seperti *phosphoglycerides*, vitamin, mineral, atau sulfur (Mitellbach & Remscmidt, 2004).

Menurut (Mahreni, 2010), proses pemanasan yang terjadi saat minyak goreng digunakan akan mengubah sifat fisika-kimia minyak. Pemanasan dapat mempercepat hidrolisis trigliserida dan meningkatkan kandungan asam lemak bebas (FFA) di dalam minyak. Secara fisik, minyak jelantah lebih kental dibandingkan dengan minyak goreng segar. Hal ini disebabkan oleh pembentukan dimer dan polimer asam dan gliserida di dalam minyak goreng bekas karena pemanasan sewaktu digunakan.

Beberapa studi pengujian kimiawi terhadap minyak jelantah telah dilakukan memberikan hasil bahwa kualitas minyak goreng menurun terutama pada bilangan peroksida dan bilangan asam apabila dibandingkan dengan nilai standar yang disyaratkan (Siti & Kuntanti, 2001). Berdasarkan penelitian yang dilakukan oleh (Mahreni, 2010) kandungan asam lemak pada minyak jelantah ditunjukkan pada Tabel 2.1 berikut ini.

Tabel 2.1 Komposisi asam lemak pada minyak jelantah (Mahreni, 2010)

Asam Lemak	Kandungan pada Minyak Jelantah
Lauric (12:0)	9,95
Myristic (14:0)	0,19
Palmitic (16:0)	8,9
Palmitoleic (16:0)	0,22
Searic (18:0)	3,85
Oleic (18:0)	30,71
Linoleic (18:3)	54,35
Linonelic (18:3)	0,27
Arachidic (20:0)	0,29
Gidoleic (20:1)	0,18

Nilai standar yang digunakan untuk minyak goreng berdasarkan Standar Nasional Indonesia (SNI) seperti pada Tabel 2.2 di bawah ini.

Tabel 2.2 Syarat mutu minyak goreng menurut SNI 01-3741-2002 (Standar Nasional Indonesia, 2002)

Kriteria Uji	Satuan	Mutu
Keadaan: - Bau		Normal
- Rasa		Normal
- Warna		Putih kuning pucat sampai kuning
Kadar air	% b/b	0,01 - 0,30
Asam lemak bebas		
• Asam laurat*	% b/b	Maks 0,30
• Asam linolenat	% b/b	Maks 2,00
• Asam palmilat*	% b/b	Maks 0,30
• Asam oleat*	% b/b	Maks 0,30
Bilangan asam	mg KOH/g	Maks 0,60
Bilangan peroksida	mg O_2/100 g	Maks 1,00

*SNI 01-3741-1995

Meskipun minyak jelantah bersifat limbah karsinogenik tetapi minyak jelantah dapat didaur ulang menjadi energi terbarukan, salah satunya menjadi produksi biodiesel melalui tahapan proses kimiawi dan pemanasan. Ada beberapa keuntungan dalam mendaur ulang minyak jelantah (Departemen Teknologi Pertanian USU, 2005), yaitu:

a. Minyak jelantah merupakan sumber energi terbarukan, minyak goreng bekas dapat dikonversi menjadi bahan bakar diesel yang terbarukan.
b. Dapat digunakan sebagai biodiesel, banyak perusahaan menggunakan minyak goreng sebagai bahan baku untuk memproduksi bahan bakar berkualitas tinggi yang disebut biodiesel.
c. Dapat menurunkan emisi gas rumah kaca
d. Alternatif yang lebih murah sebagai sumber energi terbarukan
e. Ramah lingkungan dan tidak mencemari lingkungan
f. Memiliki titik nyala lebih tinggi (minimal 130°C) dan karena itu lebih aman dibandingkan solar biasa (minimal 52°C)
g. Memiliki Karbon monoksida (CO) dan partikulat yang lebih rendah

2.2 Karakteristik Biodiesel

Biodiesel merupakan jenis bahan bakar dengan senyawa mono alkil ester dari asam-asam lemak rantai panjang yang diperoleh melalui proses reaksi transesterifikasi dan esterifikasi minyak nabati atau lemak hewani untuk digunakan sebagai bahan bakar mesin diesel. Biodiesel merupakan bahan bakar alternatif yang digunakan sebagai pengganti bahan bakar fosil sebagai sumber energi transportasi utama dunia yang sumbernya *renewable limit*, dikenal sebagai bahan bakar yang ramah lingkungan dan menghasilkan emisi gas buang yang relatif lebih bersih dibandingkan bahan bakar konvensional. Biodiesel memiliki sifat tidak beracun, *biodegradable* atau dapat terurai, hampir tidak mengandung sulfur, dan serta pengaplikasiannya yang sederhana (Akbar, 2011).

Pembuatan biodiesel dilakukan melalui tahap reaksi esterifikasi asam lemak bebas atau reaksi transesterifikasi trigliserida yang berlangsung cenderung lambat sehingga membutuhkan bantuan katalis yang berfungsi untuk mempercepat reaksi yang akan menghasilkan senyawa kimia baru yang disebut metil ester asam lemak (*Fatty Acids Methyl Esters*/FAME) sebagai produk utama biodiesel dan gliserol sebagai produk samping.

Biodiesel memiliki jumlah rantai karbon antara 12 sampai 20 yang mengandung oksigen. Adanya oksigen pada biodiesel membedakannya dengan *petroleum diesel* (solar) yang komponen utamanya hanya terdiri dari hidrokarbon (Soerawidjaja, 2006). Tabel 2.3 menunjukkan perbandingan karakteristik antara biodiesel dengan *petroleum diesel* (solar).

Tabel 2.3 Perbandingan karakteristik biodiesel dengan solar (Haryono, dkk. 2010)

Karakteristik	Biodiesel	Solar
Komposisi	Metil ester	Campuran hidrokarbon
Bilangan setana	62,4	53
Massa jenis, g/ml	0,8624	0,8750
Viskositas,cSt	5,55	4,6
Titik kilat, ^{o}C	172	98
Energi yang dihasilkan	40,1 MJ/kg	45,3 MJ/kg
Lingkungan	Ramah lingkungan	Bahaya (10x dari biodiesel)
Keberadaan	Terbarukan	Tak Terbarukan

Dalam sintesis biodiesel adanya karakteristik uji dan parameternya dapat menunjukkan keberhasilan pembuatan biodiesel yang dapat ditinjau dari kandungan gliserol total, gliserol bebas, dan angka asam dari biodiesel hasil produksi.

Parameter yang digunakan sebagai acuan pembuatan biodiesel yaitu berdasarkan Standar Nasional Indonesia (SNI) SNI-04-7182-2015. Terpenuhinya semua persyaratan SNI-04-7182-2015 dalam sintesis biodiesel menunjukkan bahwa biodiesel tersebut tidak hanya telah dibuat dari bahan mentah yang baik, melainkan juga dengan tata cara pemrosesan serta pengolahan yang benar. Tabel 2.4 berikut merupakan persyaratan biodiesel menurut SNI-04-7182:2015.

Tabel 2.4 Persyaratan kualitas biodiesel menurut SNI-04-7182:2015 (Badan Pengkajian dan Penerapan Teknologi , 2015)

Parameter dan Satuannya	Batas nilai	Metode Uji
Massa jenis pada 40°C,	850-890	ASTM D 1298
Viskositas kinematik (cSt)	2,3-6,0	ASTM D 445
Angka setana	Min 51	ASTM D 613
Titik nyala °C	Min 100	ASTM D 93
Titik kabut, °C	Max 18	ASTM D 2500
Korosi bilah tembaga		ASTM D 130
Residu karbon, %w		
-dalam contoh asli	Max 0,05	ASTM D 4530
-dalam 10% ampas distilasi	Max 0,03	
Air dan sedimen, %-vol	Max 0,05	ASTM D 2709
Temperatur distilasi °C	Max 360	ASTM D 1160
Abu tersulfatkan, %-berat	Max 0,02	ASTM D 874
Belerang, ppm-b (mg/kg)	Max 100	ASTM D 5453
Fosfor, ppm-b (mg/kg)	Max 10	AOCS Ca 12-55
Angka asam, mg-KOH/g	Max 0,5	AOCS Cd 3-63
Gliserol bebas, %-berat	Max 0,02	AOCS Ca 14-56
Gliserol total, %-berat	Max 0,24	AOCS Ca 14-56
Kadar ester alkil, %-berat	Min 96,5	dihitung
Angka iodium, $g^{-1}2^{/(100\ g)}$	Max 115	AOCS Cd 1-25
Uji Halphen negatif	negatif	AOCS Cb 1-25

Menurut (Departemen Teknologi Pertanian USU, 2005), biodiesel memiliki beberapa kelebihan, di antaranya adalah:

a. Mengurangi emisi dari mesin
b. Mempunyai rasio keseimbangan energi yang baik (minimum 1-2,5)
c. Energi lebih rendah 10-12% dari bahan bakar diesel minyak bumi 37-38 MJ/Kg. (menimbulkan peningkatan efisiensi pembakaran biodiesel sebesar 5-7%. Juga menghasilkan penurunan torsi 5% dan efisiensi bahan bakar).
d. Bahan bakar alternatif pengganti minyak bumi
e. Produk yang dihasilkan tidak mencemari lingkungan
f. Jika 0,4 – 5 % dicampur dengan bahan bakar diesel minyak bumi otomatis akan meningkatkan daya lumas bahan bakar.
g. Titik nyala tinggi 100 – 150°C (meletup tidak spontan atau menyala dalam keadaan normal).

2.3 Proses Pembuatan Biodiesel

Dalam proses pembuatan biodiesel, dibutuhkan minyak nabati sebagai bahan baku utama yang mengandung trigliserida (Ketaren, 2005). Minyak nabati ini dikelompokkan menjadi tiga jenis berdasarkan kandungan asam lemak bebas (FFA) (Kinast, 2003), yaitu:

a. *Refined oils*: minyak nabati dengan kandungan FFA kurang dari 1,5 %
b. Minyak nabati dengan kandungan FFA rendah kurang dari 4%
c. Minyak nabati dengan kandungan FFA tinggi lebih dari 20 %

Berdasarkan kandungan FFA dalam minyak nabati maka proses pembuatan biodiesel dibedakan menjadi 2 yaitu:

A. Esterifikasi dengan katalis asam (umumnya menggunakan asam sulfat) untuk minyak nabati dengan kandungan FFA tinggi dilanjutkan dengan transesterifikasi dengan katalis basa.

B. Transesterifikasi dengan katalis basa (sebagian besar menggunakan kalium hidroksida) untuk bahan baku *refined oil* atau minyak nabati dengan kandungan FFA rendah.

2.3.1 Reaksi Esterifikasi

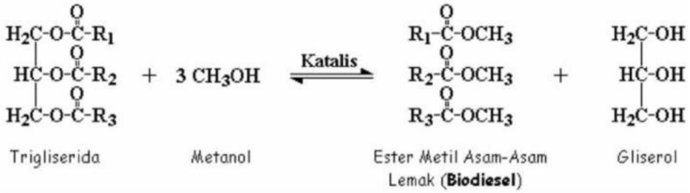
Reaksi Esterifikasi merupakan suatu reaksi dimana asam lemak bebas diubah menjadi ester. Reaksi Esterifikasi melakukan reaksi antara minyak lemak dengan alkohol. Dalam reaksi ini diperlukan katalis untuk mempercepat reaksi. Jenis katalis yang cocok yaitu katalis berkarakter asam kuat. Untuk mendorong agar reaksi dapat berlangsung dengan sempurna pada temperatur rendah, reaktan metanol harus ditambahkan dalam jumlah yang sangat dan air produk ikutan reaksi harus disingkirkan dari fasa reaksi, yaitu fasa minyak. Melalui kombinasi-kombinasi yang tepat dari kondisi-kondisi reaksi dan metode penyingkiran air, konversi sempurna asam-asam lemak ke ester metilnya dapat dituntaskan dalam 1 sampai beberapa jam (Putri, 2007). Reaksi esterifikasi dapat dilihat pada persamaan (2.1).

$$\underset{\text{Asam lemas bebas}}{\mathbf{R_1COOH}} + \underset{\text{Metanol}}{\mathbf{CH_3OH}} \underset{\uparrow\ \text{Katalis Asam}}{\longleftrightarrow} \underset{\text{Metil Ester (Biodiesel)}}{\mathbf{R_1COOCH_3}} + \underset{\text{Air}}{\mathbf{H_20}} \qquad (2.1)$$

2.3.2 Reaksi Transesterifikasi

Reaksi transesterifikasi merupakan suatu reaksi dimana trigliserida atau minyak nabati diubah menjadi alkil ester. Reaksi transesterifikasi juga disebut alkoholisis dimana molekul trigliserida atau kompleks asam lemak, menetralisir asam lemak bebas, menghilangkan gliserol, dan membentuk alkil ester. Reaksi ini dapat dilihat pada persamaan (2.2). Dalam reaksi ini biasanya juga diperlukan katalis. Katalis dalam reaksi ini bertujuan untuk memperbesar laju reaksi dan rendemen. Secara teoritis, reaksi transesterifikasi adalah reaksi kesetimbangan. Dalam reaksi ini sejumlah besar alkohol digunakan untuk mengarahkan reaksi ekuilibrium ke kanan dan memproduksi metil ester, produk akhir yang diinginkan, dalam jumlah tinggi (Mahreni, 2010).

Reaksi transesterifikasi dengan katalis basa biasanya menggunakan logam alkali alkoksida, NaOH, KOH, dan $NaHCO_3$ sebagai katalis. Pada reaksi transesterifikasi ini, sebagai reaktan dapat digunakan metanol atau etanol. Pada proses ini dipilih metanol sebagai reaktan karena merupakan alkohol yang paling reaktif. Reaksi transesterifikasi merupakan reaksi yang bersifat reversibel. Karena sifatnya yang reversibel, maka pergeseran reaksi ke kanan (ke arah produk) biasanya dilakukan dengan menggunakan alkohol secara berlebih dari kesetimbangan stoikhiometri (Dising, 2006).



(2.2)

Proses transesterifikasi dipengaruhi oleh beberapa faktor yaitu :

a. Pengaruh air dan kandungan asam lemak bebas

   Minyak nabati yang akan ditransesterifikasi harus bebas air dan kandungan asam lemak bebas lebih kecil dari 0,5% (Gnanaprakasam & Sivakumar, 2013). Adanya kandungan air dalam minyak goreng akan mempercepat reaksi hidrolisis dan sekaligus mengurangi jumlah pembentukan metil ester (Leung, dkk., 2010).

b. Perbandingan molar alkohol dengan minyak

   Secara stoikiometri jumlah alkohol yang dibutuhkan untuk reaksi, 3 mol untuk setiap 1 mol trigliserida untuk menghasilkan 3 mol alkil ester dan 1 mol gliserol (Schuchatdr, dkk., 1998). Semakin banyak jumlah alkohol yang digunakan maka konversi ester yang dihasilkan akan bertambah banyak. Pada rasio 1 : 6 setelah 1 jam konversi yang dihasilkan 98–99%, sedangkan pada rasio molar 1 : 3 adalah 78 – 89 % (Sidik, 2011).

c. Katalis

Katalis berfungsi mempercepat reaksi dan menurunkan energi aktivasi sehingga reaksi dapat berlangsung pada suhu kamar. Sedangkan tanpa katalis reaksi dapat berlangsung pada suhu 250^oC C (Kirk & Othmer, 1980). Katalis yang biasa digunakan dalam reaksi transesterifikasi adalah katalis basa seperti KOH dan NaOH (Darnoko, dkk., 2001). Reaksi transesterifikasi dengan katalis basa akan menghasilkan konversi minyak nabati menjadi ester yang optimum (94 -99 %) dengan jumlah katalis 0,5 – 1,5% b/b minyak nabati. Jumlah KOH yang efektif untuk menghasilkan konversi optimum pada reaksi transesterifikasi adalah 1% b/b minyak nabati (Darnoko, dkk., 2001). KOH mempunyai kelebihan dibanding katalis lainnya. Pada akhir reaksi KOH yang tersisa dapat dinetralkan dengan asam (H_2SO_4, HCl, H_3PO_4, dan asam organik) menjadi pupuk sehingga proses produksi biodiesel tidak menghasilkan limbah cair yang berbahaya bagi lingkungan.

d. Temperatur

Kecepatan reaksi akan meningkat sejalan dengan kenaikan temperatur, berarti semakin banyak energi yang digunakan oleh reaktan untuk mencapai energi aktivasi. Ini menyebabkan tumbukan terjadi lebih sering antara molekul-molekul reaktan (Rahayu & Raswadi, 2003). Reaksi transesterifikasi akan berlangsung lebih cepat bila suhu dinaikkan mendekati titik didih alkohol yang digunakan.

e. Waktu reaksi

Semakin lama waktu reaksi semakin banyak ester yang dihasilkan karena akan memberikan kesempatan terhadap molekul-molekul reaktan untuk semakin lama bertumbukan (Gnanaprakasam & Sivakumar, 2013).

f. Pengadukan

Pengadukan (*vigorous mixing*) dilaporkan sebagai salah satu cara untuk mencapai homogenitas antara gliserida dan alkohol. Semakin tinggi kecepatan pengadukan akan menaikkan pergerakan molekul dan menyebabkan terjadinya tumbukan. Pada awal terjadinya reaksi, pengadukan menyebabkan terjadinya difusi antara minyak atau lemak sampai terbentuk alkil ester (Gnanaprakasam & Sivakumar, 2013).

2.4 Katalis dalam Pembuatan Biodiesel

Dalam reaksi pembuatan biodiesel diperlukan katalis karena reaksi cenderung berjalan lambat. Katalis berfungsi menurunkan energi aktifasi reaksi sehingga reaksi dapat berlangsung lebih cepat. Katalis yang digunakan dalam pembuatan biodiesel dapat berupa katalis basa maupun katalis asam. Dengan katalis basa reaksi berlangsung pada suhu kamar sedangkan dengan katalis asam reaksi baru berjalan baik pada suhu sekitar 100°C. Bila tanpa katalis, reaksi membutuhkan suhu minimal 250°C (Kirk & Othmer, 1980).

Penggunaan katalis asam atau basa masih memiliki beberapa kelemahan. Penggunaan katalis asam diketahui membutuhkan waktu reaksi yang cukup lama (Schuchardt, dkk., 1998) dan pemisahan katalis dan produk sangat sulit sehingga di butuhkan perlakuan khusus untuk memisahkannya. Di samping itu, reaksi harus dilangsungkan tanpa air karena adanya air akan meningkatkan pembentukan asam karboksilat sehingga mengurangi rendemen reaksi. Dibanding dengan katalis asam, katalis basa menghasilkan reaksi dengan laju yang lebih tinggi. Namun demikian, penggunaan katalis ini dapat menghasilkan air dari reaksi antara hidroksida dan alkohol. Pembentukan air ini akan mengakibatkan terjadinya reaksi hidrolisis ester yang sudah terbentuk, menghasilkan sabun yang tidak hanya mengurangi rendemen reaksi akan tetapi juga menyulitkan pemisahan gliserol akibat pembentukan emulsi (Freedman, dkk., 1986).

2.4.1 Katalis Basa

Terdapat dua jenis katalis basa yang dapat digunakan dalam pembuatan biodiesel, yaitu katalis basa homogen dan katalis basa heterogen. Katalis basa homogen seperti NaOH (natrium hidroksida) dan KOH (kalium hidroksida) merupakan katalis yang paling umum digunakan dalam proses pembuatan biodiesel karena dapat digunakan pada temperatur dan tekanan operasi yang relatif rendah serta memiliki kemampuan katalisator yang tinggi (Soerawidjaja, 2006). Akan tetapi, katalis basa homogen sangat sulit dipisahkan dari campuran reaksi sehingga tidak dapat digunakan kembali dan pada akhirnya akan ikut terbuang sebagai limbah yang dapat mencemarkan lingkungan (Santoso, dkk,. 2013).

Di sisi lain, katalis basa heterogen seperti CaO, meskipun memiliki kemampuan katalisator yang sedikit lebih rendah dibandingkan dengan katalis basa homogen, dapat menjadi alternatif yang baik dalam proses pembuatan biodiesel (Wei, dkk., 2009). Katalis basa heterogen dapat dengan mudah dipisahkan dari campuran reaksi sehingga dapat digunakan kembali, mengurangi biaya pengadaan dan pengoperasian peralatan pemisahan yang mahal serta meminimasi persoalan limbah yang dapat berdampak negatif terhadap lingkungan (Santoso, dkk,. 2013).

Meskipun katalis basa memiliki kemampuan katalisator yang tinggi serta harganya yang relatif lebih murah dibandingkan dengan katalis asam, untuk mendapatkan performa proses yang baik, penggunaan katalis basa dalam reaksi transesterifikasi memiliki beberapa persyaratan penting, diantaranya alkohol yang digunakan harus dalam keadaan anhidrous dengan kandungan air < 0,1 – 0,5 %-berat serta minyak yang digunakan harus memiliki kandungan asam lemak bebas < 0,5% (Lotero, dkk., 2005). Keberadaan air dalam reaksi transesterifikasi sangat penting untuk diperhatikan karena dengan adanya air, alkil ester yang terbentuk akan terhidrolisis menjadi asam lemak bebas. Lebih lanjut, kehadiran asam lemak bebas dalam sistem reaksi dapat menyebabkan reaksi penyabunan yang sangat menggangu dalam proses pembuatan biodiesel seperti yang ditunjukkan pada persamaan (2.3).

$$\mathbf{R\text{-}COOH \;+\; KOH \longrightarrow R\text{-}COOK \;+\; H_2O} \qquad (2.3)$$

(As.lemak bebas) (Alkali) (Sabun) (Air)

Akibat reaksi samping ini, katalis basa harus terus ditambahkan karena sebagian katalis basa akan habis bereaksi membentuk produk samping berupa sabun. Kehadiran sabun dapat menyebabkan meningkatnya pembentukkan gel dan viskositas pada produk biodiesel serta menjadi penghambat dalam pemisahan produk biodisel dari campuran reaksi karena menyebabkan terjadinya pembentukan emulsi (Ketaren, 2005). Hal ini secara signifikan akan menurunkan keekonomisan proses pembuatan biodiesel dengan menggunakan katalis basa.

2.4.2 Katalis Asam

Alternatif lain yang dapat digunakan untuk pembuatan biodiesel adalah dengan menggunakan katalis asam. Selain dapat mengkatalisis reaksi transesterifikasi minyak tumbuhan menjadi biodiesel, katalis asam juga dapat mengkatalisis reaksi esterifikasi asam lemak bebas yang terkandung di dalam minyak menjadi biodiesel seperti yang ditunjukkan persamaan (2.4):

$$\mathbf{R\text{-}COOH \;+\; CH_3OH \longrightarrow R\text{-}COOCH_3 \;+\; H_2O} \qquad (2.4)$$

(As.lemak bebas) (Metanol) (Biodiesel) (Air)

Katalis asam umumnya digunakan dalam proses *pretreatment* terhadapat bahan baku minyak tumbuhan yang memiliki kandungan asam lemak bebas yang tinggi namun sangat jarang digunakan dalam proses utama pembuatan biodiesel. Katalis asam homogen seperti asam sulfat, bersifat sangat korosif, sulit dipisahkan dari produk dan dapat ikut terbuang dalam pencucian sehingga tidak dapat digunakan kembali sekaligus dapat menyebabkan terjadinya pencemaran lingkungan. Katalis asam heterogen seperti Nafion, meskipun tidak sekorosif katalis asam homogen dan dapat dipisahkan untuk digunakan kembali, cenderung sangat mahal dan memiliki kemampuan katalisasi yang jauh lebih rendah dibandingkan dengan katalis basa.

2.5 Katalis Kalsium Oksida (CaO) dari Bahan Dasar Cangkang Telur Ayam

Kalsium oksida (CaO) adalah jenis katalis yang lebih aktif dan telah lama diteliti untuk reaksi transestrifikasi karena harganya yang murah, memiliki kekuatan basa yang tinggi (Liu dkk, 2008) serta sedikit larut dalam metanol dibandingkan dengan oksida atau hidroksida logam alkali tanah yang lain seperti SrO dan $Ba(OH)_2$ yang terlarut secara penuh dalam media reaksi (Granados, dkk., 2007). Kebanyakan katalis CaO yang digunakan dalam reaksi transesterifikasi masih berukuran mikro, seperti yang dilaporkan oleh (Xin, dkk., 2009), yang menggunakan kristal CaO dengan diameter berukuran 4-8 µm untuk reaksi transesterifikasi. Oleh sebab itu, sintesis CaO berukuran nano sangat diperlukan dalam upaya mendapatkan katalis CaO dengan aktivitas yang lebih tinggi.

Katalis basa heterogen CaO dapat dibuat melalui proses kalsinasi $CaCO_3$. Salah satu sumber $CaCO_3$ yang mudah diperoleh disekitar kita adalah cangkang telur. Cangkang telur memiliki kandungan $CaCO_3$ (kalsium karbonat) sebanyak 94%, $MgCO_3$ (magnesium karbonat) sebanyak 1%, $Ca_3(PO4)_2$ (kalsium fosfat) sebanyak 1% dan bahan-bahan organik sebanyak 4% (Stadelman, 2000).

Beberapa literatur menyebutkan bahwa terdapat dua metode utama yang menjelaskan tentang preparasi CaO, di antaranya adalah dekomposisi termal dan sol-gel. Melalui metode sol-gel diperoleh partikel CaO berukuran nano yang sekitar 4 nm (Rahmawati, dkk., 2012), akan tetapi memerlukan biaya yang tinggi serta proses yang sangat kompleks dan memakan banyak waktu, sehingga sangat sulit untuk mengaplikasikan metode sol-gel pada industri. Metode dekomposisi termal memiliki beberapa keuntungan seperti proses yang sederhana, biaya murah, kemudahan memperoleh produk dengan kemurnian tinggi. Akan tetapi pada metode dekomposisi termal, CaO seringkali dihasilkan melalui kalsinasi $CaCO_3$ secara langsung dengan suhu tinggi (Tang, dkk., 2007). Proses kalsinasi bertujuan untuk menghilangkan kandungan air, senyawa organik, serta karbon dioksida yang terdapat di dalam kulit telur (Wei, dkk., 2009). Air dan senyawa organik umumnya dapat dihilangkan dari kulit telur pada temperatur di bawah 600^{o}C sementara karbon dioksida baru dapat dilepaskan dari kulit telur pada temperatur sekitar 700–800^{o}C. Oleh karena itu, untuk mendapatkan katalis CaO yang baik dari kulit telur, temperatur kalsinasi yang digunakan harus di atas 800^{o}C (Henry, dkk,. 2013).

2.6 Gliserol

Gliserol merupakan hasil samping yang dihasilkan dari proses pembuatan biodiesel. Jumlah gliserol bebas dalam kandungan biodiesel merupakan parameter keberhasilan purifikasi biodiesel. Kandungan gliserol bebas yang diperbolehkan maksimum 0,02% (mol/mol). Gliserol dapat menyebabkan korosi *non ferrous* pada logam, terutama logam tembaga, kromium dan seng. Gliserol juga dapat menyebabkan deposit pada saringan bahan bakar yang dapat meningkatkan emisi aldehid (Panjaitan, dkk., 2005). Rumus kimia gliserol adalah C_3H_8O dengan nama kimia 1,2,3-propanatriol. Berat molekul gliserol sebesar 92,10 dengan massa jenis 1,23 g/cm^3. Gliserol bersifat mudah larut dalam air, dapat meningkatkan viskositas larutan, mengikat air, merupakan cairan dengan rasa pahit-manis yang mempunyai kelarutan tinggi, yaitu sebesar 71 g/100 g air pada suhu 250°C (Andika, 2007). Karakteristik gliserol dapat dilihat pada Tabel 2.5.

Laporan (Andika, 2007) mengatakan bahwa gliserol banyak terdapat di alam sebagai ester asam lemak pada minyak atau lemak. Gliserol merupakan produk samping yang prospektif dari proses pembuatan biodiesel karena harganya lebih tinggi daripada reaktan metanol. Fasa gliserol dihasilkan dari proses transesterifikasi minyak dan alkohol, dimana pada akhir proses akan terpisah dengan metil ester (biodiesel) akibat adanya perbedaan berat jenis. Selain itu, sifat gliserol yang tidak mudah larut dalam metil ester juga mempermudah dan mempercepat proses pemisahan kedua fasa tersebut, baik dengan cara pengendapan (*settling*) atau sentrifugasi. Gliserol yang diperoleh setelah proses pemisahan ini mengandung sebagian kecil metanol dan sebagian besar sisa katalis serta sabun (Andika, 2007).

Tabel 2.5 Karakteristik gliserol (Andika, 2007)

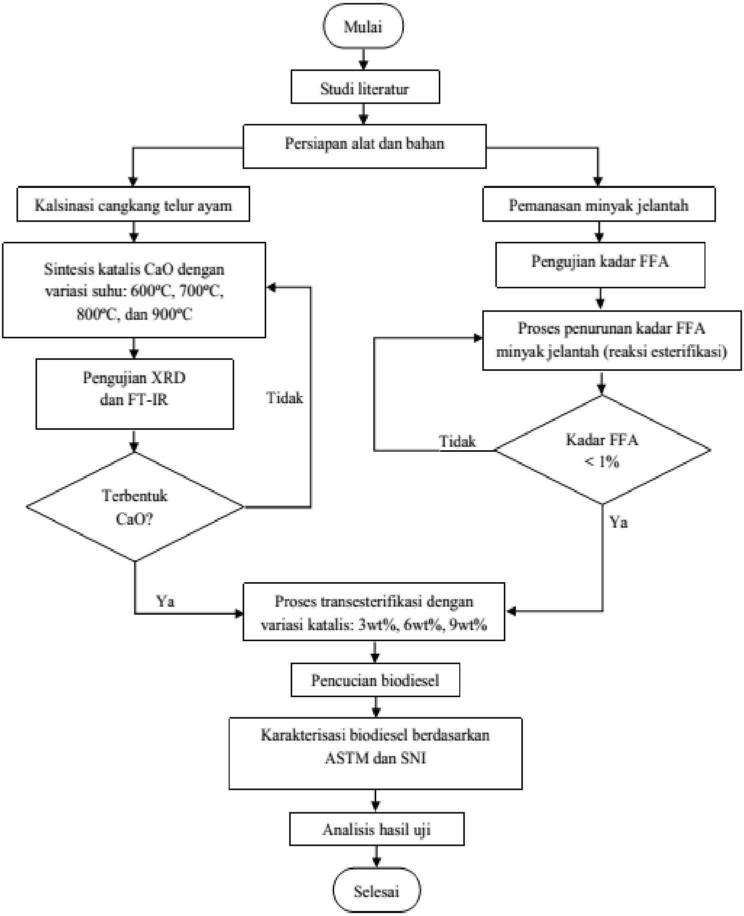
Parameter dan Satuannya	**Nilai**
Massa jenis pada 25°C (g/cm^3)	1,262
Viskositas (20°C, mPa.s)	1499
Titik cair (°C)	18,17
Titik didih (°C)	
0,53 kPa	14,9
1,33 kPa	166,1
13,33 kPa	222,4
101,2 kPa	290
Kadar air (%-vol)	0,5
Kadar gliserol total (%-berat)	99,5
Kadar ester alkil, %-berat	Min 96,5

Gliserol harus dipisahkan dari biodiesel karena gliserol dapat membentuk senyawa akrolein dan terpolimerisasi menjadi senyawa plastis yang agak padat. Senyawa ini akan membentuk deposit pada pompa injektor sehingga menyebabkan kerusakan pada mesin diesel. Selama ini gliserol hasil samping produksi biodiesel masih bernilai ekonomis rendah, karena kemurniannya masih belum memenuhi standar. Gliserol hasil samping produksi biodiesel belum dapat dimanfaatkan, baik dalam bidang farmasi maupun makanan sebagaimana lazimnya gliserol paling banyak digunakan. Jumlah gliserol yang dihasilkan dari setiap produksi biodiesel kurang lebih 10 % dari total produksi biodiesel.

Menurut penelitian (Islami, 2008), warna *crude glyserol* dari pembuatan biodiesel dari minyak goreng bekas jauh lebih gelap dibandingkan dengan gliserol murni. *Crude glyserol* mempunyai warna coklat kehitaman, sedangkan gliserol murni bening (tidak berwarna). Warna gelap ini disebabkan terdapatnya sisa reaktan yang tidak bereaksi yaitu minyak goreng bekas yang juga mempunyai warna coklat kehitaman. Menurut (Anas, 2011), bahan dominan yang terkandung dalam gliserol hasil samping produksi biodiesel jarak pagar adalah sisa metanol yang tidak bereaksi dan sabun sebagai hasil reaksi antara asam lemak bebas dengan katalis basa yang digunakan selama proses transesterifikasi.

BAB III
METODOLOGI PENELITIAN

Gambar 3.1 merupakan diagram alir penelitian yang dilakukan:



Gambar 3.1 Skema diagram alir penelitian

3.1 Alat dan Bahan

Pada penelitian ini, peralatan yang akan dibutuhkan antara lain sebagai berikut:

a. *Oven*

Digunakan untuk menghilangkan kadar air dan debu yang masih menempal pada cangkang telur ayam dengan suhu kerja 100^{o}C selama 24 jam.

b. *Blender*

Digunakan untuk menghancurkan, memperhalus serta memperkecil ukuran partikel cangkang telur ayam yang sudah dihilangkan kadar airnya.

c. *Siever* atau ayakan 60 mesh

Digunakan untuk mengayak serbuk cangkang telur ayam dengan ukuran maksimum 60 mesh.

d. Tungku

Digunakan untuk proses pemansan atau kalsinasi serbuk cangkang telur ayam dengan suhu kerja 600 ^{o}C, 700 ^{o}C, 800 ^{o}C, 900^{o}C.

e. *Crucible* 100 ml

Digunakan sebagai wadah pada proses kalsinasi cangkang telur ayam menjadi katalis kalsium oksida.

f. *Hot plate* dan *magnetic stirrer*

Digunakan untuk proses pengadukan, pecampuran sampel minyak jelantah dengan bahan lain serta digunakan untuk proses pemanasan selama reaksi sintesis biodiesel berlangsung.

g. Gelas beker 250 ml, 500 ml, 1000 ml

Digunakan sebagai wadah penyimpanan minyak jelantah dan biodiesel, serta untuk mengukur volume sampel, pengukuran kadar FFA, proses *pre-treatment* atau esterifikasi, serta proses transesterifikasi sintesis biodiesel.

h. Gelas ukur

Digunakan untuk mengukur volume sampel dalam jumlah yang lebih kecil contohnya dalam proses titrasi pengujian kadar FFA.

i. Tabung reaksi
   Digunakan untuk pengujian sampel biodiesel, seperti: titik tuang, titik kabut pada sampel biodiesel.
j. Neraca digital
   Digunakan untuk mengukur massa sampel minyak jelantah, katalis, dan biosiesel
k. Termometer digital
   Digunakan untuk mengukur suhu reaksi selama proses penelitian biodiesel dilakukan
l. Pipet tetes
   Digunakan sebagai alat pembantu dalam meneteskan atau menuangkan larutan sampel dalam proses pengujian kadar FFA
m. Corong pemisah (*Buchner Funnel*)
   Untuk memisahkan antara lapisan biodiesel dengan lapisan air atau lapisan gliserol pada saat proses reaksi esterifikasi dan reaksi transesterifikasi

Adapun bahan-bahan yang dibutuhkan dalam penelitian ini terbagi menjadi 3 bagian. Pertama, bahan yang dibutuhkan untuk menghasilkan katalis kalsium oksida (CaO), yaitu: limbah cangkang telur ayam, air.

a. Limbah cangkang telur ayam
   Limbah ini diperoleh dari penjual makanan dan digunakan sebagai bahan utama penghasil katalis kalsium oksida (CaO) yang akan $CaCO_3$ melalui proses kalsinasi atau pemanasan.
b. Air
   Bahan ini digunakan untuk membersihkan limbah cangkang telur ayam dari kotoran-kotoran yang masih menempel.

Kedua, bahan yang dibutuhkan untuk melakukan pengujian kadar asam lemas bebas (FFA) dan proses *pre-treatment* atau pemurnian minyak jelantah dari asam lemak bebas (FFA), yaitu: limbah minyak jelantah, kertas saring kasar, larutan NaOH

0,05M, indikator *phenolphthalein*, methanol 95% dan larutan H_2SO_4.

a. Limbah minyak jelantah

   Limbah ini diperoleh dari penjual makanan dan gorengan yang ada di sekitar kawasan Keputih, Sukolilo. Bahan ini digunakan untuk menguji kadar asam lemak bebas (FFA). Bahan ini juga digunakan sebagai bahan utama dalam proses esterifikasi atau *pre-treatment*.

b. Kertas saring kasar

   Bahan ini gunakan untuk menyaring limbah minyak jelantah yang masih bercampur dengan sisa hasil penggorengan.

c. Larutan NaOH 0,05M

   Bahan ini digunakan pada proses titrasi dalam pengujian kadar asam lemak bebas (FFA) pada limbah minyak jelantah.

d. Indikator *phenolphthalein*

   Bahan ini digunakan dalam proses pengujian kadar FFA dimana penggunaannya sebagai acuan dalam memberikan perubahan warna sampel minyak jelantah menjadi warna merah muda.

e. Larutan H_2SO_4

   Bahan digunakan dalam proses esterifikasi atau *pre-treatment* yang bertujuan untuk menurunkan kandungan asam lemak bebas (FFA) pada sampel minyak jelantah sampai < 1%

Ketiga, bahan yang dibutuhkan untuk melakukan proses sintesis Biodiesel, yaitu:

a. Minyak jelantah dengan kadar FFA < 1%

   Bahan ini diperoleh dari proses esterifikasi yang digunakan sebagai bahan baku utama dalam proses sintesis biodiesel.

b. Methanol 95%

   Bahan ini digunakan dalam proses esterifikasi dan transesterifikasi untuk menurunkan kadar FFA.

c. Katalis kalsium oksida (CaO)

   Bahan digunakan untuk mempercepat reaksi dan energi aktivasi pada proses transesterifikasi

d. Kertas saring
   Bahan ini digunakan untuk menyaring sampel biodiesel.

3.2 Persiapan Sampel Cangkang Telur Ayam

Bagian cangkang telur ayam yang akan digunakan adalah bagian cangkang yang terdiri dari kutikula dan lapisan bunga karang atau *calcareus*. Limbah cangkang telur ayam digunakan sebagai sumber untuk menghasilkan katalis kalsium oksida (CaO). Pertama, limbah cangkang telur ayam dicuci terlebih dahulu menggunakan air untuk menghilangkan cairan kental isi telur dan pengotor lain seperti debu seperti yang ditunjukkan pada Gambar 3.2 (a). Cangkang telur yang sudah dibersihkan kemudian dikeringkan di dalam oven pada suhu 100^{o}C selama 24 jam untuk menghilangkan kadar air dan debu yang menempel. Setelah itu, cangkang telur yang sudah dipanaskan didinginkan di udara terbuka sekitar 10 menit lalu simpan di dalam desikator seperti yang ditunjukkan pada Gambar 3.2 (b).

Gambar 3.2 Sampel cangkang telur (a) sebelum dikeringkan (b) setelah dikeringkan

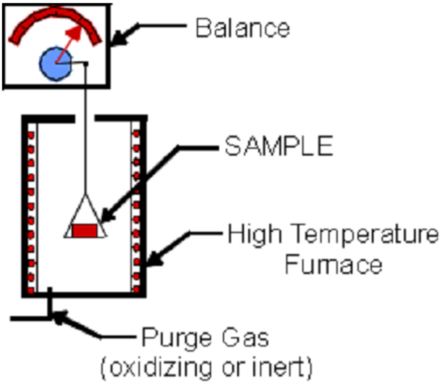
Karena partikel cangkang telur yang sudah dikeringkan masih cukup besar maka perlu dilakukan proses pengecilan ukuran partikel dengan menggunakan *blender*. Dalam penelitian tugas akhir ini digunakan ukuran partikel katalis kalsium oksida (CaO) sebesar 60 mesh. Setelah ukuran partikel sudah cukup halus kemudian dilakukan proses pengayakan menggunakan *siever* dengan ukuran 60 mesh seperti yang ditunjukkan pada Gambar 3.3.

Gambar 3.3 Proses pengayakan dengan *Siever* atau ayakan 60 mesh

Partikel yang tidak lolos dalam proses pengayakan digerus atau dihancurkan kembali menggunakan *mortar* dan kemudian diayak hingga seluruh partikel cangkang telur berukuran 60 mesh.

3.3 Prinsip Kerja Uji TGA (*Thermogravimetric Analysis*)

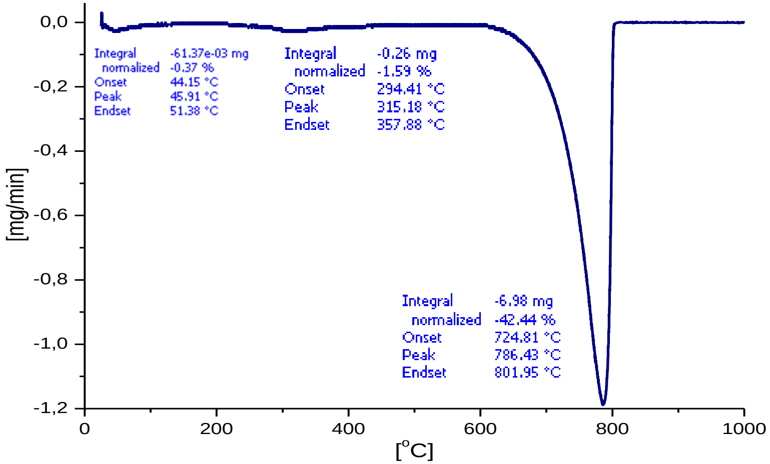
Analisa termogravimetrik (TGA) merupakan salah satu metode analisis termal prinsip kerjanya secara otomatis merekam perubahan berat sampel ketika suhu lingkungan berubah dengan waktu tertentu atau fungsi dari suhu maupun waktu yang dapat dilihat pada Gambar 3.4.



Gambar 3.4 Skema kerja pengujian TGA (Tarasov, 2012)

Sampel dipanaskan di bawah nitrogen dengan laju suhu yang konstan, sementara perbedaan massa selama proses ini diukur. Kehilangan massa menunjukkan bahwa degradasi zat yang diukur terjadi (Tarasov, 2012). Analisa TGA dapat memberikan informasi tentang fenomena fisik, seperti orde kedua fase transisi, termasuk penguapan, sublimasi, penyerapan, adsorpsi, dan desorpsi. Demikian juga, TGA dapat memberikan informasi tentang fenomena kimia termasuk *chemisorptions, desolvation* (terutama dehidrasi), dekomposisi, dan reaksi padat-gas (misalnya, oksidasi atau reduksi).

Hasil analisa TGA biasanya berupa rekaman diagram yang kontinu. Sampel yang digunakan, dengan berat beberapa miligram, dipanaskan pada laju konstan, berkisar antara 1–20^{o}C/menit, mempertahan berat awalnya, sampai mulai terdekomposisi pada suhu T (Setiabudi, 2012). Pengujian TGA ini dilakukan di Laboratorium Energi LPPM ITS. Sekitar 16,5 mg sampel cangkang telur, dengan menggunakan cawan platina, dengan pemanasan awal dari suhu 25°C sampai 1000°C dalam atmosfir nitrogen dinamis dengan laju pemanasan 10°C/menit. Dari hasil uji TGA serbuk cangkang telur ayam didapatkan grafik kontinyu yang ditunjukkan pada Gambar 3.5.



Gambar 3.5 Grafik uji TGA serbuk cangkang telur

Kurva termogravimetrik (Gambar 3.5) yang diperoleh untuk kalsium karbonat ($CaCO_3$) menunjukkan stabilitas termal hingga suhu 600°C dengan massa kecil yang hilang (Δm = 1,59%). Proses dekomposisi terjadi dengan jelas terjadi antara kisaran suhu dari 610 sampai 805°C, dengan Δm = 42,44%. Proses dekomposisi ini karena adanya pelepasan karbon dioksida, yang diberikan pada kalsium oksida: $CaCO_3$ (s) → CO_2 (g) + CaO (s). (Santoso, dkk., 2013). Pengujian ini sesuai dengan pernyataan (Kibbe, dkk., 2000) dimana kalsium karbonat ($CaCO_3$) biasanya terurai pada suhu di atas 600°C tanpa proses fusi.

Dari dari kurva pengujian TGA dapat dihitung persentase pembentukan fraksi CaO yang dilihat pada Lampiran A. Dari perhitungan, fraksi pembentukan CaO dapat dilihat pada Tabel 3.1. Dari tabel, laju pembentukan CaO terjadi secara linear. Apabila suhu semakin tinggi fraksi pembentukan CaO akan selesai pada suhu 900°C. sehingga dalam sintesisnya, suhu dekomposisi lebih efektif untuk menghasilkan katalis kalsium oksida (CaO).

Tabel 3.1 Persentase fraksi pembentukan katalis CaO

No.	Suhu Dekomposisi (°C)	Fraksi Pembentukan CaO (%)
1.	600	0
2.	700	19
3.	800	51
4.	900	100

Dari data pengujian yang telah dihasilkan pada penelitian tugas akhir ini, sehingga proses kalsinasi cangkang telur dilakukan dengan variasi suhu kalsinasi, yaitu: 600°C, 700 °C, 800 °C, dan 900 °C. Dimana penyusutan massa pada suhu 600°C saat sebelum partikel cangkang telur belum terdekomposisi menjadi kalsium oksida, suhu 700°C saat partikel cangkang telur sedang terdekomposisi menjadi kalsium oksida, suhu 800°C saat partikel cangkang telur tepat terdekomposisi menjadi kalsium oksida, dan suhu 900°C saat partikel cangkang telur sudah melewati suhu dekomposisi dan telah membentuk katalis kalsium oksida.

3.4 Sintesis Katalis Kalsium Oksida (CaO) dari Cangkang Telur Ayam

Selanjutnya dilakukan pembuatan katalis kalsium oksida (CaO) melalui proses kalsinasi dari partikel cangkang telur yang telah diayak. Tujuan proses kalsinasi cangkang telur adalah untuk menghilangkan senyawa karbon dioksida melalui reaksi dekomposisi kalsium karbonat ($CaCO_3$) yang terkandung dalam kulit telur sehingga diperoleh senyawa kalsium oksida. Persamaan (3.1) menunjukkan reaksi yang terjadi pada saat proses kalsinasi adalah sebagai berikut (Santoso, dkk., 2013):

$$CaCO_3 \longrightarrow CaO + CO_2 \qquad (3.1)$$

Setelah proses kalsinasi selesai, katalis yang sudah diekstrak disimpan di dalam desikator untuk menjaga kondisi katalis tetap kering dan terhindar dari uap air di udara.

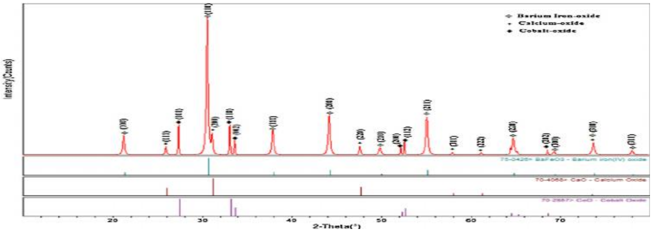
3.5 Karakterisasi Katalis

Setelah proses kalsinasi selesai dilakukan, dilakukan analisa pengujian pada sampel katalis kalsium oksida (CaO) untuk mengetahui karakteristik fisik dan kimia katalis cangkang telur ayam. Uji sampel yang diperlukan meliputi uji *X-Ray Diffraction* (XRD), uji *Fourier Trasform Infra Red* (FT-IR), dan uji *Brunauer–Emmett–Teller* (BET).

3.5.1 Uji *X-Ray Diffraction* (XRD)

Pengujian *X-Ray Diffraction* (XRD) dilakukan di Laboratorium Karakterisasi Material, Jurusan Teknik Material dan Metalurgi ITS. Karakterisasi uji XRD untuk mengidentifikasi fasa-fasa kristal yang terbentuk dari katalis, struktur mikro kristal, dan senyawa yang terkandung pada katalis tersebut.

Prinsip kerja XRD yaitu sampel uji berbentuk serbuk ditempatkan di suatu plat kaca. Kemudian sinar-X ditembakkan pada sampel uji dan mendifraksikan sinar ke segala arah. Detektor bergerak dengan kecepatan sudut yang konstan untuk mendeteksi berkas sinar-X yang didifraksikan oleh sampel. Representasi dari pengujian XRD berupa grafik yang menunjukkan besar intesitas terhadap sudut difraksi seperti yang ditunjukkan pada Gambar 3.6. Berdasarkan sudut difraksi, dapat diketahui jenis senyawa yang terkandung pada sampel uji. Dari grafik tersebut juga dapat dilihat puncak difraksi, dimana setiap puncak yang muncul pada pola XRD mewakili satu bidang kristal yang memiliki orientasi tertentu dalam sumbu tiga dimensi.



Gambar 3.6 Contoh grafik hasil uji XRD (Martín-Ramos & Díaz-Hernández, 2011)

Untuk menganalisa senyawa yang terkandung dari grafik karakterisasi XRD dapat dilakukan dengan cara mencocokkan data XRD dengan data JCPDS (*Joint Committee on Powder Diffraction Standards*) sebagai pembandingnya. Apabila senyawa dari data sudah teridentifikasi maka dari data karakterisasi XRD ini dapat dihitung persentase fraksi yang terkandung pada sampel uji. Untuk menghitung persentase komposisi senyawa yang terkandung dalam sampel uji, digunakan rumus RIR (*Reference Intensity Ratio*) yang tunjukkan pada Persaman (3.2) (Martín-Ramos & Díaz-Hernández, 2011):

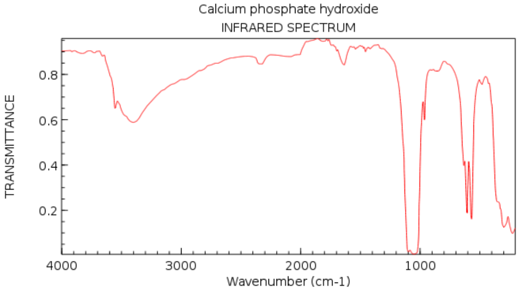
$$Fraksi\ R\ (\%) = \frac{\sum \frac{I_i}{I_{max}}}{\sum \frac{I_p}{I_{max}}}\, x\ 100\% \qquad (3.2)$$

Dimana I_i merupakan intensitas masing-masing komponen pada salah satu titik puncak, I_i merupakan intensitas keseluruhan komponen pada salah satu titik puncak, dan I_{max} merupakan intensitas maksimum pada satu puncak tertentu yang digunakan sebagai referensi.

3.5.2 *Fourier Transforms Infrared Spectroscopy* (FT-IR)

Pengujian *Fourier Transforms Infrared Spectroscopy* (FTIR) dilakukan di Laboratorium Karakterisasi Material, Jurusan Teknik Material dan Metalurgi ITS dengan menggunakan alat Thermo Nicolet i51. Pengukuran dilakukan pada temperatur ruang dan kristal KBr digunakan sebagai matriks (perbandingan massa antara sampel dengan KBr adalah m 1:100). Karaterisasi uji FTIR pada sampel uji digunakan untuk mengidentifikasi senyawa kimia, struktur molekul suatu senyawa pada sampel uji dan dapat juga digunakan untuk mengetahui fasa yang terbentuk dari sampel.

Prinsip kerja FTIR pada dasarnya menguji sampel yang diperlukan untuk memperoleh spektrum penyerapan selama analisis FTIR. Sinar inframerah diradiasikan pada sampel yang akan diuji yang selanjutnya akan diserap atau diteruskan oleh sampel sehingga akan ada perbedaan intensitas spektrum yang ditangkap oleh detektor. Sampel dianalisis dengan *Fourier Transform* dan menghasilkan spektrum yang menunjukkan ikatan kimia dan struktur molekul bahan sampel. Pada Gambar 3.7 menunjukkan contoh grafik pengujian FTIR sampel kalsium oksida.



Gambar 3.7 Contoh grafik hasil uji FTIR (Wei, dkk., 2009)

3.5.3 *Brunauer Emmet Teller* (BET)

Pengujian *Brunauer Emmet Teller* (BET) dilakukan di Laboratorium Nano Material Jurusan Teknik Kimia ITS dengan menggunakan alat NOVA Quantachrome Instrument Version 10.01 yang ditunjukkan pada Gambar 3.8. Karaterisasi uji BET pada sampel uji digunakan untuk mengetahui luas permukaan, volume pori, dan diameter pori dari sampel uji.

Gambar 3.8 NOVA Quantachrome Instrument Version 10.01

Prinsip kerja alat ini menggunakan mekanisme adsorpsi gas alat ini menggunakan nitrogen pada permukaan sampel yang akan dikarakterisasi dan pada dasarnya hanya mengukur jumlah gas yang dapat diserap oleh suatu permukaan padatan pada tekanan dan suhu tertentu (Zulichatun, dkk., 2015). Persiapan utama dari sampel sebelum dianalisa adalah dengan menghilangkan gas-gas yang terserap (*degassing*). Selanjutnya, gas nitrogen dialirkan sebagai adsorbat atau zat terlarut pada sampel uji. Dari banyaknya gas nitrogen yang diadsorb pada permukaan sampel ini selanjutnyaa akan dianalisa dan menghasilkan data luas permukaan, volume, distribusi ukuran pori yang ingin diketahui (Martin & Cammarata, 1993). Secara sederhana, jika kita mengetahui berapa volume gas spesifik yang dapat diserap oleh suatu permukaan padatan pada suhu dan tekanan tertentu, dan kita mengetahui secara teori luas permukaan dari satu molekul gas yang diserap, maka luas permukaan total padatan tersebut dapat dihitung.

3.6 Persiapan Sampel Minyak Jelantah

3.6.1 Preparasi Sampel Minyak Jelantah

Sampel minyak jelantah dikumpulkan dari berbagai sumber, seperti: penjual gorengan dan rumah makan. Sebelum dilakukan proses transesterifikasi terhadap minyak jelantah, sampel minyak jelantah terlebih dahulu dipreparasi yang bertujuan untuk mengurangi kandungan air yang terdapat pada bahan baku minyak jelantah. Langah yang perlu dilakukan pertama minyak jelantah disaring menggunakan kertas saring kasar berukuran untuk menghilangkan kotoran-kotoran yang terdapat didalamnya, kemudian minyak jelantah dipanaskan dengan menggunakan *hotplate* pada suhu 120^{o}C selama ± 10 menit yang dapat dilihat pada Gambar 3.9.

Gambar 3.9 Proses pemanasan minyak jelantah

3.6.2 *Pre-treatment* Sampel Minyak Jelantah

Langkah selanjutnya adalah proses *pre-treatment* atau reaksi esterifikasi pada sampel minyak jelantah. Proses *pre-treatment* bertujuan untuk mengurangi ataupun menghilangkan kandungan asam lemak Bebas (*Free Fatty Acid~ FFA*) yang terdapat pada sampel minyak jelantah yang menjadi bahan baku dasar dalam sintesis biodiesel.

Sebelum dilakukan proses *pre-treatment* perlu dilakukan pengujian kadar FFA pada minyak jelantah. Untuk mengetahui kandungan asam lemak bebas yang ada di dalam bahan baku minyak jelantah, sebanyak 10 gram sampel minyak jelantah diaduk dengan *magnetic stirrer* di atas *hotplate*. Selanjutnya ditambahkan etanol 96% sebanyak 50 ml dan indikator fenolftalein sebanyak 5 tetes, kemudian dititrasi dengan larutan NaOH 0,1 M hingga sampel minyak jelantah berubah warna menjadi merah muda yang ditunjukkan pada Gambar 3.10.

Gambar 3.10 Pengujian kadar FFA sampel minyak jelantah

Volume NaOH yang dibutuhkan dicatat untuk kemudian digunakan dalam menentukan kandungan asam lemak bebas pada sampel minyak dengan menggunakan persamaan (3.3) (Soerawidjaja, 2006):

$$FFA\ (\%) = \frac{V_{NaOH}\ x\ N_{NaOH}\ x\ MW_{asam\ lemak}}{m_{sampel}}\ x\ 100\% \qquad (3.3)$$

dengan:

V_{NaOH} : volume NaOH yang terpakai hingga terjadi perubahan warna merah muda pada sampel minyak jelantah (ml)

N_{NaOH} : normalitas larutan NaOH (M)

$MW_{asam\ lemak}$: berat molekul

m_{sampel} : massa minyak jelantah (gram)

Dalam penelitian ini kadar FFA pada minyak jelantah yang diinginkan adalah < 1%. Apabila kadar FFA pada minyak jelantah < 1%, mengindikasikan bahwa minyak jelantah dapat langsung digunakan untuk pembuatan biodiesel melalui reaksi transesterifikasi sehingga tidak perlu dilakukan proses *pre-treatment*. Apabila kadar FFA pada minyak jelantah > 1%, dapat memicu terjadinya reaksi samping yaitu reaksi saponifikasi atau reaksi penyabunan sehingga perlu dilakukan proses *pre-treatment* atau reaksi esterifikasi. Dalam penelitian ini, proses reaksi esterifikasi menggunakan katalis asam H_2SO_4. Langkah-langkah yang dilakukan pertama sampel minyak jelantah sebanyak 300ml di panaskan menggunakan *hotplate* hingga sampel minyak mencapai suhu 55-65^{o}C. Sesaat sedang terjadi pemanasan, dibuat larutan antara metanol dan katalis asam H_2SO_4. Kadar metanol yang digunakan sebanyak 15% dari massa minyak jelantah dan kadar H_2SO_4 sebanyak 1% dari berat minyak jelantah. Setelah itu campuran larutan methanol dan H_2SO_4 dimasukkan ke dalam sampel minyak jelantah dengan suhu reaksi 60^{o}C selama 2 jam. Setelah reaksi selesai sampel minyak dicuci menggunakan akuades dan akan terbentuk 2 lapisan yaitu lapisan minyak jelantah dan lapisan akuades. Kemudian kedua lapisan ini dipisahkan menggunakan corong pemisah yang dapat dilihat pada Gambar 3.11.

Gambar 3.11 a. Proses pencucian sampel minyak jelantah
b. Proses pemisahan sampel minyak jelantah

3.7 Proses Transesterifikasi Biodiesel

Biodiesel disintesis melalui reaksi transesterifikasi dengan bantuan katalis basa. Sampel minyak jelantah yang telah mengalami *pre-treatment* dibagi menjadi 13 bagian untuk dibuat menjadi biodiesel. Tiap sampel dipanaskan kembali pada suhu 120^{o}C selama 10 menit menggunakan *magnetic stirrer* di atas *hot plate*. Langkah selanjutnya yaitu membuat larutan *lye* dengan mencampurkan katalis kalsium oksida (CaO) dengan metanol dengan molar metanol 6:1 terhadap sampel minyak jelantah atau sekitar 30 gram berat metanol. Penambahan katalis kalsium oksida (CaO) divariasikan sebagai berikut: 0%, 3wt%, 6wt%, 9wt% terhadap berat minyak jelantah. Setelah dilakukan pencampuran aduk larutan *lye* dengan menggunakan *magnetic stirrer* selama 10 menit kemudian dimasukkan ke dalam sampel biodiesel, kemudian suhu pemanasan diturunkan menjadi 65^{o}C yang dijadikan sebagai acuan suhu reaksi dengan lama reaksi 2 jam. Setelah reaksi transesterifikasi selesai, sampel biodiesel didiamkan selama 1 malam untuk memisahkan fasa atas yang mengandung biodiesel dan fasa bawah yang mengandung gliserol. Rancangan penelitian dalam pembuatan biodiesel ini dapat direpresentasikan dalam Tabel 3.2.

Tabel 3.2 Rancangan penelitian sintesis biodiesel

Exp No.	Faktor				Yield (%)
	Suhu Kalsinasi (^{o}C)	Konsentrasi Katalis (wt%)	Rasio Metanol: Minyak (wt%)	Lama Reaksi (Jam)	
1	600	3	6:1	1	X1
2		6	6:1	1	X2
3		9	6:1	1	X3
4	700	3	6:1	1	X4
5		6	6:1	1	X5
6		9	6:1	1	X6
7	800	3	6:1	1	X7
8		6	6:1	1	X8
9		9	6:1	1	X9
10	900	3	6:1	1	X10
11		6	6:1	1	X11
12		9	6:1	1	X12

3.8 Pencucian Biodiesel

Sampel biodiesel yang didiamkan selama 1 malam akan membentuk bentuk 2 fasa. Fasa atas merupakan biodiesel yang diperoleh dari reaksi transesterifikasi dan fasa bawah merupakan hasil samping berupa gliserol. Proses pencucian biodiesel bertujuan untuk memisahkan antara biodiesel dengan gliserol. Sampel biodiesel dicuci menggunakan air untuk menghilangkan sisa-sisa gliserol dan zat lain yang masih tertinggal. Kemudian sampel didiamkan sekitar 4 jam hingga terbentuk endapan putih. Sampel biodiesel kemudian dapat disaring menggunakan kertas saring untuk mendapatkan hasil total biodiesel. Hasil biodiesel dihitung seperti persamaan (3.4) (Zhang, dkk., 2014):

$$y\ (\%) = \frac{M_{BO}}{M_O}\ x\ 100\% \tag{3.4}$$

dengan:

M_{BO} : berat hasil konversi biodiesel (gram)
M_O : massa awal minyak jelantah (gram)

3.9 Uji Kuantitatif dan Kualitatif Biodiesel

Produk biodiesel yang dihasilkan kemudian diuji secara kuanitatif dengan cara mencampurkannya dengan air dengan perbandingan volume 1:1. Jika hasil pencampuran tersebut dengan cepat terpisah kembali membentuk dua fasa, maka dapat dipastikan bahwa produk fasa atas tersebut bukan metanol.

Lapisan fasa atas yang terbentuk setelah pencampuran dengan air kemudian dipisahkan. Fase atas hasil pemisahan tersebut kemudian dicampur kembali dengan metanol. Jika pencampuran tersebut membentuk campuran homogen maka dapat dipastikan bahwa produk fasa atas yang diuji merupakan biodiesel. Jumlah produk akhir biodiesel yang dihasilkan dicatat kemudian dihitung *yield* yang dihasilkan pada tiap sampel biodiesel terhadap sampel minyak jelantah ketika belum mengalami proses transesterifikasi.

Selanjutnya produk biodiesel yang dihasil diuji secara kualitatif terhadap karakteristiknya, di antaranya yaitu: uji massa jenis biodiesel, uji viskositas kinematik biodiesel, uji titik nyala biodiesel, uji titik kabut dan titik tuang biodiesel.

3.9.1 Uji Massa Jenis Biodiesel

Pengujian massa jenis dalam penelitian ini mengacu pada standar ASTM D1298. Pengujian ini dilakukan dengan cara sampel biodiesel sebanyak 10 ml diukur massanya, setelah itu sampel biodiesel dipanaskan pada suhu 40°C, adanya perubahan volume yang terjadi ketika pemanasan dicatat. Nilai massa jenis sampel biodiesel kemudian dihitung dari perbandingan massa dengan volume yang tercatat dan memiliki satuan kg/m^3.

3.9.2 Uji Viskositas Kinematik

Pengujian viskositas kinematik mengacu pada standar ASTM D445-97. Pengujian ini dilakukan di Laboratorium Energi LPPM ITS dengan menggunakan alat *kinematic viscosity bath* yang ditunjukkan pada Gambar 3.12.

Gambar 3.12 *Kinematic viscosity bath*

Data pengujian dicatat, yang diperoleh berupa waktu selama fluida mengalir dalam pipa dari batas pertama sampai batas kedua pipa kemudian nilai viskositas dihitung dengan persamaan (3.5) (Santoso, dkk., 2013):

$$cSt = C \,.\, t \tag{3.5}$$

dengan:

cSt : viskositas kinematik
C : konstanta viskometer (0,00874 mm^2/s^2 atau cSt/s)
t : waktu alir (s)

3.9.3 Uji Titik Nyala (*Flash Point)*

Pengujian titik nyala (*flash point*) mengacu pada standar ASTM D93-80. Pengujian ini dilakukan dengan mengamati suhu paling rendah yang dimiliki sampel biodiesel untuk dapat menyala ketika dipicu dengan api. Langkah-langkah pengujian yaitu sebanyak 5 ml sampel biodiesel dituangkan pada cawan pembakaran, kemudian dipanaskan hingga suhu tertentu sambil mengamati perubahan suhunya. Setelah suhu sampel biodiesel mencapai suhu 100°C, sampel biodiesel kemudian dipicu dengan api hingga sampel mampu terbakar pada suhu tertentu. Pada suhu sampel biodiesel dapat terbakar yang dijadikan acuan sebagai sebagai titik nyalanya.

3.9.4 Uji Titik Kabut (*Cloud Point*) dan Titik Tuang (*Pour Point)*

Pengujian titik kabut (*cloud point*) mengacu pada standar ASTM D97. Pengujian titik kabut pada biodiesel diperoleh ketika sampel biodiesel berubah menjadi berwarna keruh saat didinginkan pada suhu tertentu. Sedangkan pengujian titik tuang merupakan suhu terendah dimana biodiesel mulai terbentuk kristal. Pengujian titik tuang (*pour point*) mengacu pada standar ASTM D2500. Cara menguji titik kabut dan titik tuang dapat dilakukan dengan mengambil sampel biodiesel kurang lebih 2 ml, kemudian biodiesel didinginkan dengan merendamnya dalam air es sambil diamati suhu dan penampilan biodiesel. Ketika biodiesel telah menunjukkan warna keruh seperti berkabut, maka suhu pada keadaan tersebutlah yang merupakan titik kabut biodiesel. Sedangkan untuk mendapatkan titik tuang biodiesel adalah dengan menurunkan suhu biodiesel dengan merendamnya pada air es lebih lama hingga terbentuk kristal paraffin pada biodiesel. Suhu yang menunjukkan terjadinya pembentukan kristal paraffin inilah yang merupakan titik tuang biodiesel.

“Halaman ini sengaja dikosongkan”

BAB IV
HASIL DAN PEMBAHASAN

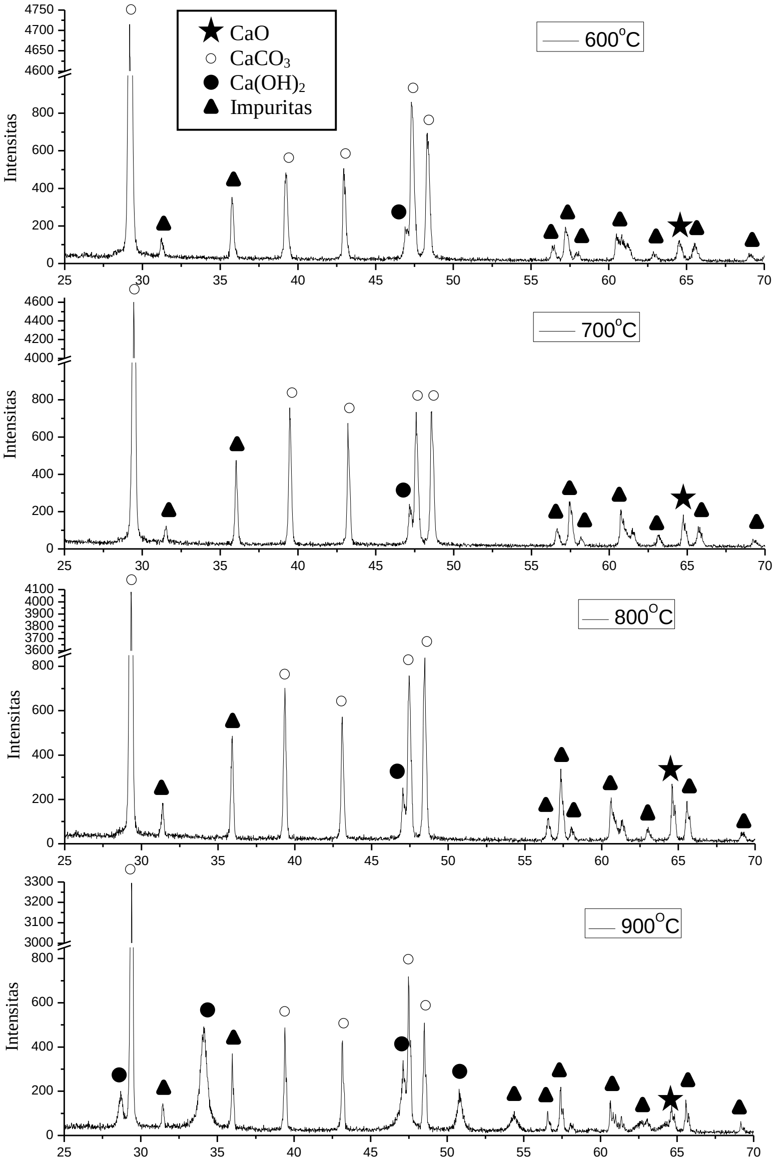
4.1 Pengaruh Suhu Dekomposisi Terhadap Sifat Fisik Katalis

Serbuk cangkang telur ayam yang didekomposisi di dalam tungku dengan variasi suhu 600ºC, 700°C, 800°C, dan 900°C selama 6 jam. Secara fisik, warnanya berbeda dengan serbuk telur sebelum dikalsinasi. Hasil kalsinasi pada suhu 600°C menghasilkan serbuk yang berwarna abu-abu gelap, pada suhu 700°C menghasilkan serbuk berwarna abu-abu pucat, pada suhu 800°C menghasilkan serbuk yang berwarna abu-abu pucat dengan sedikit yang berwarna putih, pada suhu kalsinasi 900°C diperoleh serbuk yang secara keseluruhan berwarna putih dengan sedikit abu-abu. Semakin tinggi suhu kalsinasi, maka semakin banyak oksida logam yang terbentuk yang ditunjukkan dari perubahan warna serbuk cangkang telur ayam menjadi putih (Mohadi, dkk., 2016). Oksida logam yang dimaksud pada sampel serbuk cangkang telur tersebut kemungkinan adanya CaO dan $Ca(OH)_2$. $Ca(OH)_2$ dapat terbentuk karena adanya interaksi CaO dengan uap air di udara (Mohadi, dkk., 2016), dimana CaO dan $Ca(OH)_2$ memiliki warna fisik yang sama yaitu berwarna putih (Lesbani, 2003). Serbuk cangkang telur ayam sebelum dan setelah didekomposisi pada variasi suhu dapat dilihat pada Gambar 4.1.

Gambar 4.1 Serbuk cangkang telur ayam (a) sebelum kalsinasi; dan setelah kalsinasi dengan variasi suhu (b) 600^{o}C, (c) 700^{o}C, (d) 800^{o}C, (e) 900^{o}C

4.2 Karakterisasi XRD Serbuk Cangkang Telur Ayam

Hasil karakterisasi XRD serbuk cangkang telur ayam setelah kalsinasi pada variasi suhu yang berbeda, yaitu: 600^{o}C, 700^{o}C, 800^{o}C, dan 900^{o}C menunjukkan perbedaan pola difraksi XRD, dimana masing-masing pola menunjukkan struktur senyawa yang berbeda-beda. Perbedaan pola difraksi cangkang telur ayam setelah proses kalsinasi ditunjukkan pada Gambar 4.2.



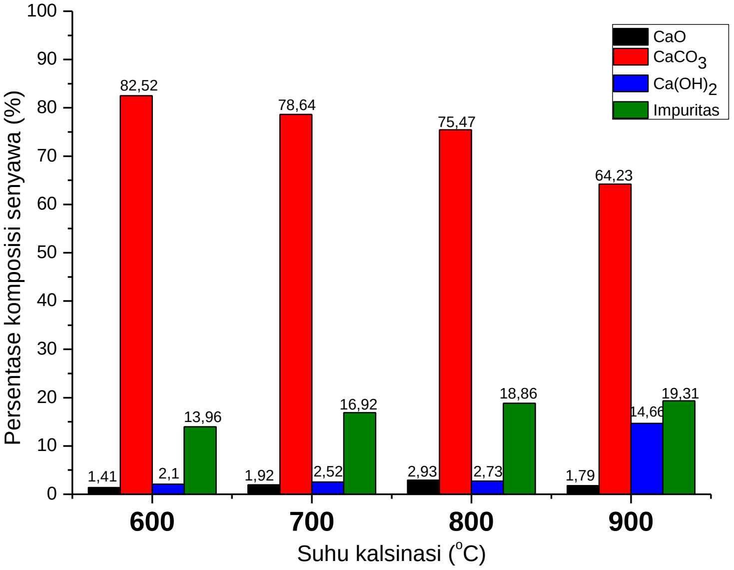
Gambar 4.2 Pola difraksi XRD cangkang telur kalsinasi 2 jam

Dari hasil karakterisasi XRD pada Gambar 4.2, didapatkan grafik hubungan antara intensitas terhadap puncak difraksi sepanjang nilai 2θ. Pengukuran difraksi sinar-X pada 2θ dari 25^o sampai 70^o. Dari grafik difraksi sinar-X, puncak yang dihasilkan dicocokkan dengan data standar JCPDS (*Joint Committee on Powder Diffraction Standards*) sebagai pembanding. Pola difraksi sinar-X dapat merepresentasikan adanya $CaCO_3$, puncak yang mengalami pengurangan dan penyempitan yang menunjukkan adanya konversi $CaCO_3$ menjadi CaO dan pelepasan gas CO_2. Selain itu, pola difraksi yang dihasilkan dapat juga mengidentifikasikan keberadaan $Ca(OH)_2$ dan impuritas. $Ca(OH)_2$ dapat terbentuk karena adanya interaksi CaO dengan uap air di udara (Mohadi, dkk., 2016). Pola difraksi standar dari data JCPDS dan data dari difraksi cangkang telur ayam pada variasi suhu kalsinasi ditunjukkan pada Tabel 4.1.

Tabel 4.1 Data XRD serbuk cangkang telur ayam kalsinasi 2 jam

Sampel	**Senyawa**	**2θ (^{o})**				
Data JCPDS	CaO	32,2	37,3	53,9	64,1	67,3
	$CaCO_3$	29,4	39,4	43,2	47,4	48,5
	$Ca(OH)_2$	28,6	34,1	47,1	50,8	-
600^{o}C	CaO	-	-	-	64,5	-
	$CaCO_3$	29,1	39,2	43,0	47,3	48,3
	$Ca(OH)_2$	-	-	47,0	-	-
700^{o}C	CaO	-	-	-	64,7	-
	$CaCO_3$	29,4	39,4	43,2	47,5	48,6
	$Ca(OH)_2$	-	-	47,1	-	-
800^{o}C	CaO	-	-	-	64,6	-
	$CaCO_3$	29,3	39,3	43,1	47,4	48,4
	$Ca(OH)_2$	-	-	47,0	-	-
900^{o}C	CaO	-	-	-	64,6	-
	$CaCO_3$	29,4	39,4	43,1	47,4	48,5
	$Ca(OH)_2$	28,6	34,1	47,1	50,7	-

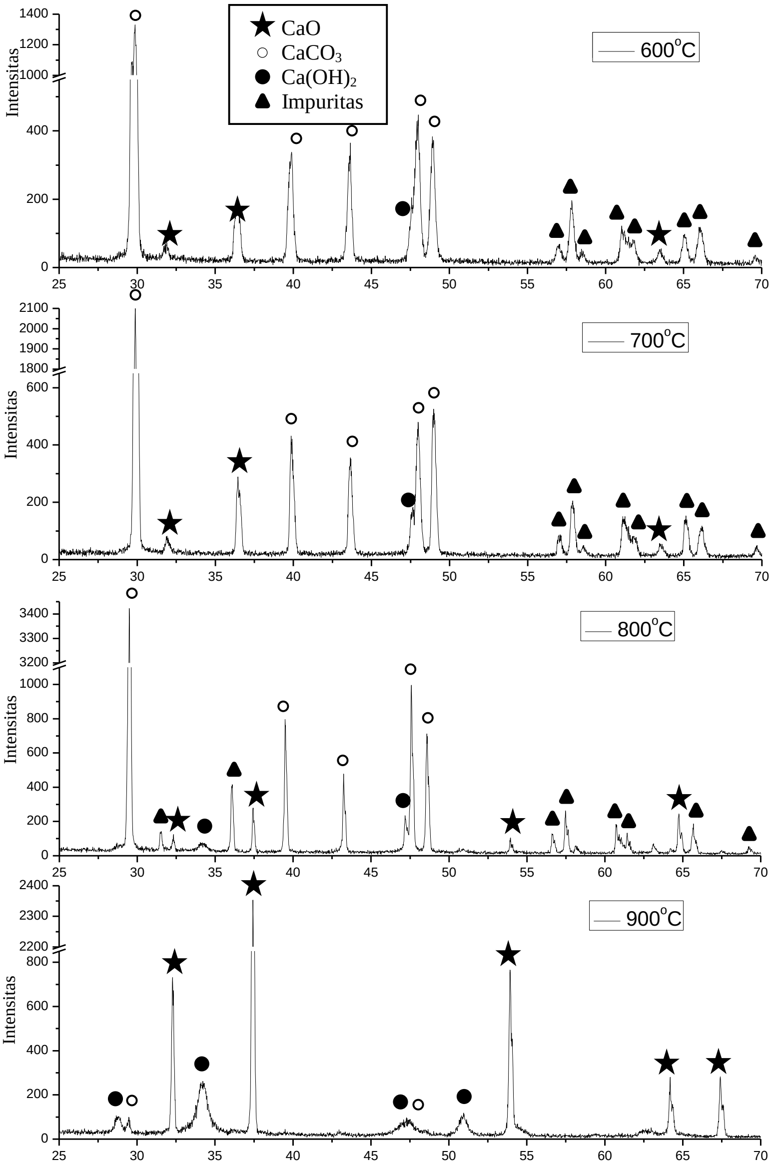
Dari pola difraksi pada Gambar 4.2 sampel serbuk cangkang telur pada semua variasi suhu kalsinasi menunjukkan adanya karakteristik CaO tetapi tidak dominan jika dibandingkan dengan adanya $CaCO_3$. Puncak yang menunjukkan adanya CaO memiliki intensitas yang sangat rendah, tetapi puncak yang menunjukkan adanya $CaCO_3$ sangat tajam dengan intensitas yang tinggi berada pada 2θ 29,4^o sehingga dapat dikatakan bahwa untuk semua suhu kalsinasi mengindikasikan masih terdapat mayoritas senyawa $CaCO_3$. Untuk mendapatkan senyawa secara spesifik, selanjutnya dihitung komposisi yang terkandung pada serbuk cangkang telur ayam (Lampiran B) yang ditunjukkan pada Gambar 4.3.



Gambar 4.3 Komposisi terkandung pada serbuk cangkang telur ayam kalsinasi 2 jam

Dari Gambar 4.3 komposisi yang terbentuk dari semua variasi suhu kalsinasi memang terdapat $CaCO_3$ yang paling dominan serta impuritas yang cukup tinggi, sehingga untuk sampel katalis ini dapat dikatakan masih banyak juga pengotor. Dari penelitian yang dilakukan oleh (Mohadi, dkk., 2016) yang juga melakukan variasi suhu kalsinasi 600ºC, 700ºC, 800ºC, 900ºC selama 3 jam, memberikan hasil yang sama untuk suhu 600ºC, 700ºC, 800ºC bahwa senyawa mayoritas yang terbentuk adalah $CaCO_3$ meskipun di suhu 800ºC sudah mulai terbentuk CaO. Tetapi hasil yang tidak sama untuk suhu kalsinasi 900ºC dimana seharusnya senyawa yang terbentuk adalah mayoritas CaO, hasil yang tidak sesuai ini juga didukung berdasarkan penelitian yang dilakukan oleh (Tangboriboon, dkk., 2012) yang menunjukkan pola difraksi suhu 900ºC dengan waktu kalsinasi 1 jam sudah menghasilkan mayoritas CaO. Sehingga pada penelitian ini suhu kalsinasi 900ºC belum memberikan hasil optimal yang akan berdampak pada reaksi transesterifikasi.

Setelah ditinjau ulang, terdapat beberapa faktor yang mengakibatkan tidak terbentuknya CaO secara optimal, yaitu: pada saat pencucian cangkang telur ayam lapisan membran luar dan membran dalam belum sepenuhnya dipisahkan dari cangkang telur ayam, perlakuan serbuk cangkang telur setelah kalsinasi juga mempengaruhi dimana pada saat setelah kalsinasi serbuk cangkang telur ayam disimpan di dalam gelas ditutupi plastik tetapi tetapi seharusnya serbuk cangkang disimpan di dalam tempat kedap udara (desikator) dikarenakan CaO yang terbentuk mudah bereaksi dengan uap air yang ada di udara untuk menghasilkan $Ca(OH)_2$. Lebih lanjut dilakukan pengulangan proses kalsinasi dengan menambah waktu prosesnya yaitu selama 6 jam. Pola difraksi sinar-X setelah proses kalsinasi selama 6 jam ditunjukkan pada Gambar 4.4.



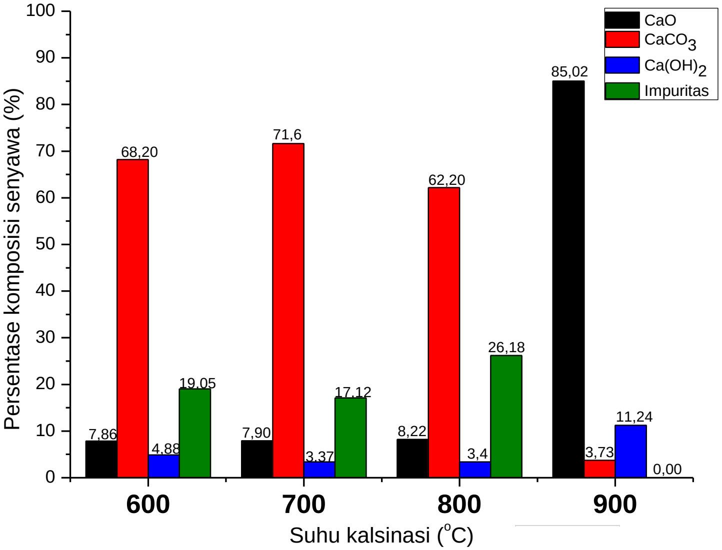
Gambar 4.4 Pola difraksi XRD cangkang telur kalsinasi 6 jam

Dari grafik difraksi sinar-X, puncak yang dihasilkan dicocokkan kembali dengan JCPDS (*Joint Committee on Powder Diffraction Standards*) yang ditunjukkan pada Tabel 4.2.

Tabel 4.2 Data XRD serbuk cangkang telur ayam kalsinasi 6 jam

Sampel	**Senyawa**	**2θ (°)**				
Data JCPDS	CaO	32,2	37,3	53,9	64,1	67,3
	$CaCO_3$	29,4	39,4	43,2	47,4	48,5
	$Ca(OH)_2$	28,6	34,1	47,1	50,8	-
600°C	CaO	31,8	36,4	-	63,5	-
	$CaCO_3$	29,8	39,8	43,6	48,0	48,9
	$Ca(OH)_2$	-	-	47,5	-	-
700°C	CaO	32,0	37,4	-	63,4	-
	$CaCO_3$	29,8	39,9	43,6	47,9	49,0
	$Ca(OH)_2$	-	-	47,6	-	-
800°C	CaO	32,1	37,4	53,9	64,7	-
	$CaCO_3$	29,4	39,4	43,2	47,5	48,5
	$Ca(OH)_2$	-	34,1	47,1	-	-
900°C	CaO	32,2	37,4	53,9	64,2	67,4
	$CaCO_3$	29,4	-	-	47,3	-
	$Ca(OH)_2$	28,6	34,2	47,2	50,9	-

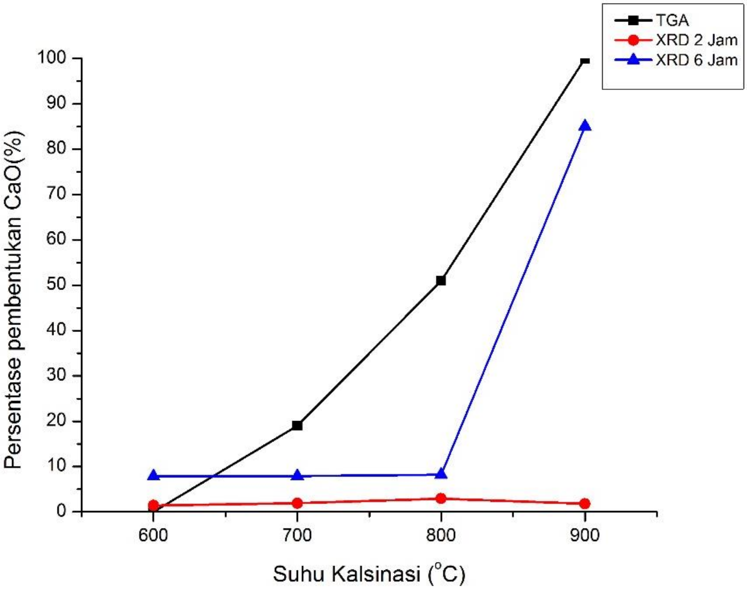
Pada data pola difraksi pada Tabel 4.3 dari hasil kalsinasi cangkang telur ayam pada suhu 900°C sudah dihasilkan struktur CaO kristalin yang ditunjukkan dengan munculnya puncak-puncak tajam yang mengindikasikan peningkatan kritalinitas CaO yang dihasilkan, namun masih terdapat pola difraksi yang berhubungan dengan fase $CaCO_3$ yang muncul pada 2θ (°) = 29,4 dan 47,3 dan $Ca(OH)_2$ yang muncul pada 2θ (°) = 28,6; 34,2; 47,2 dan 50,9 serta bersamaan dengan keberadaan beberapa puncak CaO pada 2θ (°) = 32,2; 37,4; 53,9; 64,2 dan 67,4. Puncak-puncak ini sudah sesuai dengan hasil yang dipublikasikan oleh (Mohadi, dkk., 2016) dan (Tangboriboon, dkk., 2012) untuk pola difraksi CaO. Secara detail, kemudian dihitung juga komposisi tiap senyawa (Lampiran B) yang tunjukkan pada Gambar 4.5.



Gambar 4.5 Komposisi terkandung pada serbuk cangkang telur ayam kalsinasi 6 jam

Pada Gambar 4.5 menunjukkan pada suhu kalsinasi 600ºC, 700ºC, 800ºC mempunyai komposisi yang paling tinggi adalah $CaCO_3$ yaitu sekitar 68%-86%, mempunyai komposisi CaO yang minoritas yaitu sekitar 7-8%, komposisi $Ca(OH)_2$ sekitar 3%-5%, serta komposisi impuritas terbilang cukup tinggi sekitar 11%-19%. Ini menunjukkan bahwa pada suhu kalsinasi 600ºC, 700ºC, 800ºC hanya sedikit $CaCO_3$ yang terkonversi menjadi CaO. Oleh sebab itu, sampel dengan suhu kalsinasi 600ºC, 700ºC, 800ºC tidak menjadi pilihan yang tepat untuk digunakan sebagai katalis. Untuk suhu kalsinasi 900ºC, komposisi CaO sudah optimal terbentuk yaitu 85,02% dan memiliki sekitar 3,73% $CaCO_3$, 11,24% $Ca(OH)_2$, dan sudah bersih dari impuritas. Sehingga dari data yang dihasilkan dan penjelasan sebelumnya dapat disimpulkan dengan jelas bahwa suhu kalsinasi yang paling optimal untuk menghasilkan katalis CaO dari cangkang telur ayam dengan impuritas yang rendah adalah suhu kalsinasi 900ºC.

Fraksi pembentukan CaO pada kedua sampel juga dibandingkan dengan fraksi pada pengujian TGA (*thermogravimetric analysis*). Secara grafik, perbandingannya dapat dilihat pada Gambar 4.6

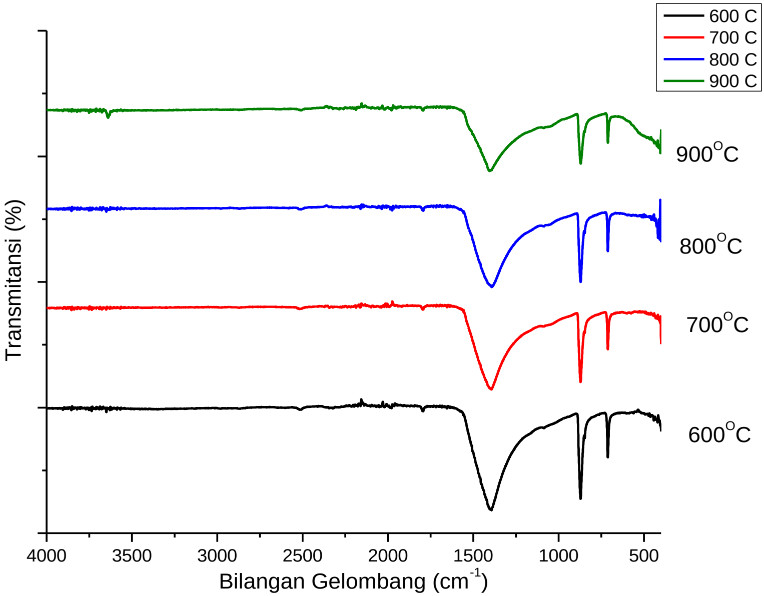


Gambar 4.6 Perbandingan laju pembentukan CaO pada pengujian TGA dan XRD

Pada Gambar 4.6 menunjukkan laju pembentukan CaO pengujian TGA berlangsung secara linier, dimana tiap kenaikan suhu dekomposisi terdapat pembentukan CaO yang semakin banyak. Pada pengujian XRD waktu kalsinasi 2 jam, pembentukan CaO terlihat konstan dan tidak memberikan hasil secara signifikan. Berbeda dengan pada pengujian XRD waktu 6 jam, pada suhu sampai 800°C memang pembentukan CaO masih stagnan, tetapi pada saat suhu mencapai 900°C terjadi pembentukan CaO secara signifikan. Dari perbandingan ini dapat disimpulkan bahwa laju pembentukan CaO pada pengujian TGA kurang lebih sama dengan laju pembentukan CaO pada pengujian XRD pada kalsinasi 6 jam.

4.3 Karakterisasi FTIR Katalis Kalsium Oksida

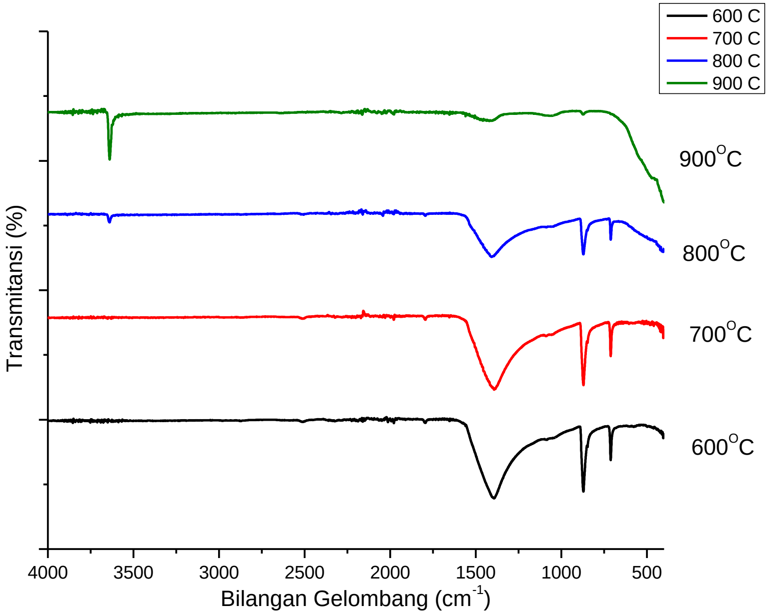
Spektroskopi inframerah dilakukan bertujuan untuk mengidentifikasi gugus fungsi yang terdapat dalam suatu senyawa. Analisis FTIR pada katalis kalsium oksida (CaO) dilakukan pada panjang gelombang 4000-400 cm^{-1} yang ditunjukkan pada Gambar 4.7 untuk waktu kalsinasi 2 jam dan Gambar 4.8 untuk waktu kalsinasi 6 jam.



Gambar 4.7 Karakterisasi FTIR serbuk cangkang telur ayam kalsinasi 2 jam

Spektra FTIR dari sampel sintesis serbuk cangkang telur ayam menunjukkan puncak pada bilangan gelombang di daerah sekitar 3600 cm^{-1} menunjukkan adanya pita OH, pita CH di bilangan gelombang 2300-2900 cm^{-1}, adanya pita CO antara

1600–1800 cm^{-1}; di atas 1530–1620 cm^{-1}; di bawah 1530-1300 cm^{-1}; di sekitar 875 cm^{-1}; di sekitar 713 cm^{-1}, serta adanya pita CaO pada daerah sekitar 400 cm^{-1} (Rahmawati, dkk., 2012).



Gambar 4.8 Karakterisasi FTIR serbuk cangkang telur ayam kalsinasi 6 jam

Pita dari gugus OH muncul pada bilangan gelombang 3735,48 cm^{-1} hinga 3854,01 cm^{-1} pada sampel cangkang telur ayam yang dikalsinasi dengan suhu 600°C, 700°C, serta 900°C, tetapi sama sekali tidak muncul pada pada sampel kalsinasi dengan suhu 800°C pada suhu kalsinasi 2 jam. Untuk kalsinasi 6 jam, pita gugus OH muncul pada bilangan gelombang 3639,06 cm^{-1} hingga 3760,21 cm^{-1} untuk suhu kalsinasi 800°C dan muncul sangat tajam pada suhu 900°C, tetapi tidak muncul pada suhu 600°C dan 700°C. Gugus OH merupakan karakteristik dari CaO

(Ruiz, dkk., 2009), sehingga kemunculan gugus OH tersebut menunjukkan adanya kecocokan puncak antara ketiga sampel. Akan tetapi, kemunculan gugus OH tersebut tidak dapat begitu saja memastikan bahwa sampel yang dianalisis benar-benar merupakan kalsium oksida (CaO) karena indikasi adanya $Ca(OH)_2$ juga memiliki karakteristik puncak di daerah sekitar 3643 cm^{-1} seperti hasil analisis yang dilakukan oleh (Granados, dkk., 2007) yang mengatakan bahwa adanya gugus OH dari $Ca(OH)_2$ sehingga ada kemungkinan bahwa puncak tersebut menunjukkan keberadaan air yang teradsorb pada permukaan CaO dimana CaO sangat mudah menyerap uap air dari udara. Oleh sebab itu maka perlu ditemukannya ciri khas puncak yang meyakinkan bahwa sampel benar-benar mengandung CaO.

Pita dengan puncak di daerah sekitar 1700 cm^{-1} menunjukkaan adanya gugus C=O (karbonil) yang disebabkan oleh ikatan C=O *stretching*, dimana pada sampel yang dikalsinasi pada suhu 600^{o}C, 700^{o}C, dan 900^{o}C muncul puncak di panjang gelombang 1749,50 cm^{-1} hingga 1793,97 cm^{-1} tetapi tidak muncul pada suhu 800^{o}C untuk waktu kalsinasi 2 jam dan muncul juga pada suhu kalsinasi 600^{o}C, 700, dan 800 pada panjang gelombang 1979,07 cm^{-1} hingga 1793,64 cm^{-1} tetapi tidak muncul pada suhu 800^{o}C untuk waktu kalsinasi 6 jam.

Puncak yang sangat lebar pada semua sampel muncul pada panjang gelombang 1400 cm^{-1} yang menunjukkan adanya ikatan O-C-O dari karbonat, tetapi puncaknya semakin melemah pada suhu kalsinasi 900^{o}C waktu 6 jam. Hal ini sesuai dengan penelitian yang dilakukan oleh (Granados, dkk., 2007), bahwa pita pada bilangan gelombang 1479 cm^{-1} dan 1419 cm^{-1} dapat katakan adanya ikatan O-C-O dari karbonat monodentat pada permukaan CaO. Sedangkan vibrasi tekuk C-O dari gugus karbonat muncul pada bilangan gelombang sekitar 870 cm^{-1} pada semua sampel dan juga 713 cm^{-1} pada semua sampel kecuali pada sampel suhu kalsinasi 900^{o}C waktu 6 jam. Puncak di sekitar 870 cm^{-1} dan 713 cm^{-1} merupakan karakteristik puncak yang biasanya muncul pada $CaCO_3$ dan $Ca(OH)_2$ (Ruiz dkk., 2009). Hal ini menunjukkan bahwa sampel mengandung senyawa lain selain CaO yang mengindikasikan sampel hasil sintesis belum murni. Hasil ini sangat didukung dengan pernyataan yang telah dijelaskan pada subbab 4.2 bahwa memang pada semua sampel masih terdapat $CaCO_3$ dan $Ca(OH)_2$ tetapi persentasinya sangat menurun pada suhu kalsinasi 900^{o}C waktu 6 jam.

Pada bilangan gelombang di daerah sekitar 400 cm^{-1} dapat dijadikan acuan untuk memastikan adanya CaO pada sampel, hal ini dikarenakan di antara spektrum CaO standar, $CaCO_3$ standar dan $Ca(OH)_2$ standar tampak hanya CaO standar yang memiliki puncak yang melebar pada panjang gelombang tersebut sebab puncak di daerah sekitar 400-500 cm^{-1} berhubungan dengan ikatan Ca-O vibrasi ulur. Pada sampel suhu kalsinasi 900^{o}C waktu 6 jam mengindikasikan banyaknya muncul Ca-O karena puncak yang muncul sangat lebar. Secara spesifik, kemuncul panjang gelombang pada sampel cangkang telur ayam dapat dilihat pada Tabel 4.3.

Tabel 4.3 Bilangan gelombang dan gugus fungsi serbuk cangkang telur ayam kalsinasi 2 jam dan 6 jam

Gugus Fungsi	Bilangan gelombang (cm^{-1})							
	Kalsinasi 2 jam				Kalsinasi 6 jam			
	600^{o}C	700^{o}C	800^{o}C	900^{o}C	600^{o}C	700^{o}C	800^{o}C	900^{o}C
Vibrasi ulur -OH dari Ca(OH)$_2$	3736,1 3649,8	3854,0 3735,4	-	3640,1	-	-	3760,2 3639,8	3639,0
Gugus CH	-	-	-	-	2508,7	2171,4 2029,5	2042,4	-
Gugus karbonil C=O	1749,5	1793,9	-	1793,1	1789,9	1979,0	1793,6	-
Ikatan O-C-O	1393,7	1393,7	1392,9	1403,7	1393,8	1393,0	1408,8	1420,1
Ikatan O-C-O	871,69	871,72	871,47	871,11	871,48	871,30	871,64	868,60
Vibrasi tekuk dari gugus karbonat	712,07	711,98	711,89	711,50	711,94	711,95	711,61	-
Adanya CaO (υCa−O))	442,47 420,25	421,60 406,11	504,38 457,41 446,06 425,97 418,19 408,35	424,48 409,89 403,71	-	519,18 482,73 460.04 431,46 426,93 422,43 418,17 413,72 409,17 404,37	421,79 405,14	-

4.4 Pengaruh Proses *Pre-treatment* Terhadap Penurunan Kadar FFA

Untuk mengetahui penurunan kadar asam lemak bebas (FFA) pada sampel minyak jelantah, terlebih dahulu dihitung kadar FFA yang terkandung pada sampel minyak jelantah. Dengan mentitrasi sampel minyak jelantah dan larutan NaOH kemudian digunakan persamaan (3.2) untuk mendapatkan kadar FFA. Kadar FFA yang terkandung dalam sampel mempunyai kadar FFA yang cukup tinggi yaitu 4,045%, sehingga perlu dilakukan *pre-treatment* atau reaksi esterifikasi untuk menurunkan kandungan asam lemak sebelum dilakukan reaksi transesterifikasi. Penelitian ini menggunakan metanol sebanyak 15% dari massa minyak jelantah dan menggunakan katalisator asam homogen H_2SO_4 sebanyak 1% dari berat minyak jelantah dengan lama reaksi 2 jam. Kriteria tersebut dijadikan sebagai acuan berdasarkan penelitian yang dilakukan oleh (Hasahatan, dkk., 2012) yang memberikan hasil terbaik bahwa penurunan kadar FFA terbaik dengan konversi 92,06%.

Dari hasil reaksi esterifikasi didapatkan kadar FFA untuk sampel minyak jelantah dapat turun dari 4,045% menjadi 0,775%. Reaksi ini mampu menurunkan kadar FFA sebesar 80,84%. Reaksi ini menandakan terjadinya reaksi antara FFA dengan metanol yang dipercepat dengan bantuan katalis asam H_2SO_4 untuk menghasilkan metil ester. Faktor yang memengaruhi penurunan kadar FFA ini adalah lamanya waktu reaksi, temperatur reaksi, dan jumlah katalis asam. Menurut (Aziz, 2007) lamanya waktu reaksi esterifikasi akan menyebabkan molekul-molekul senyawa untuk bereaksi semakin besar, sehingga FFA yang tersisa semakin berkurang. Dalam penelitian (Ramadhas, dkk., 2005) juga menyebutkan bahwa kelebihan katalis (H_2SO_4) akan menyebabkan larutan produk berwarna lebih gelap, terbentuknya dimetil eter dari reaksi antara H_2SO_4 dengan metanol.

4.5 Hasil Sintesis Biodiesel Minyak Jelantah

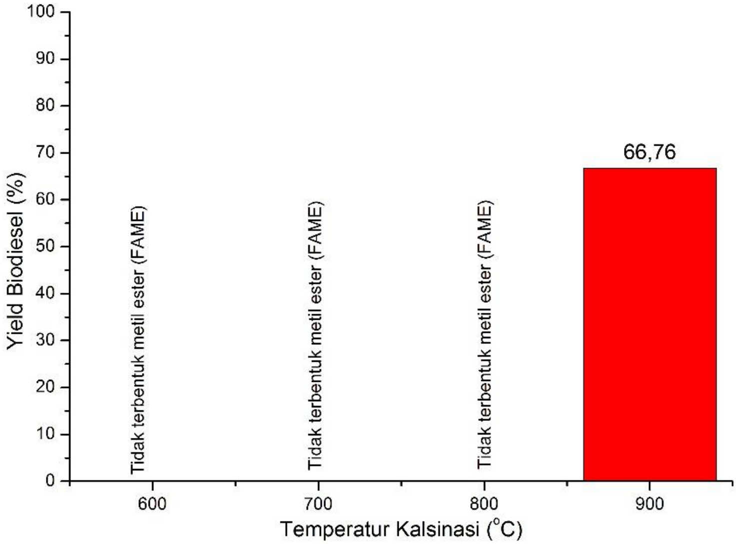
Sintesis biodiesel pada penelitian ini dilakukan pada kondisi temperatur 65ºC dengan perbandingan mol minyak-metanol 1:6, waktu reaksi selama 2 jam, dan menggunakan serbuk cangkang telur ayam yang berperan sebagai katalis kalsium oksida (CaO) dimana proses sintesis katalis ini divariasikan dengan suhu kalsinasi 600ºC, 700ºC, 800ºC, dan 900ºC selama 6 jam. Konversi biodiesel (*free acid methyl esters*/FAME) yang dihitung menggunakan persamaan (3.4). Matriks prediksi dari hasil biodiesel menggunakan katalis CaO yang berbeda yang dibuat dari cangkang telur ayam disajikan pada Tabel 4.4.

Tabel 4.4 Data hasil sintesis biodiesel dari proses transesterifikasi

Exp No.	Faktor		Hasil Biodiesel		
	Suhu Kalsinasi (°C)	Konsentrasi Katalis (wt%)	Gliserol (Y/T)	Massa Biodiesel (gram)	Massa FAME (%)
1	Tanpa Katalis	0	T	122,67	89,67
2	600	3	T	118,4	86,55
3		6	T	123,6	90,35
4		9	T	124,7	91,15
5	700	3	T	109,8	80,2
6		6	T	117,3	85,74
7		9	T	112,8	87,45
8	800	3	T	96,2	70,32
9		6	T	113,1	82,67
10		9	T	125,9	92,03
11	900	3	Y	73,1	53,43
12		6	Y	89,5	65,42
13		9	Y	111,4	81,43
14	CaO Komersil	3	Y	71,8	52,48
15		6	Y	88,5	64,69
16		9	Y	114,1	83,59

4.5.1 Pengaruh Suhu Dekomposisi Katalis CaO Terhadap Hasil Biodiesel

Suhu kalsinasi sangat mempengaruhi sifat struktural dan katalitik katalis. Oleh sebab itu aktivitas katalitik dari sampel serbuk cangkang telur ini kemudian diuji melalui proses transesterifikasi untuk mengkonversi trigliserida menjadi biodiesel (*free acid methyl esters*/FAME). Untuk data pengujian dapat dilihat pada Tabel 4.4 yang disajikan pada Gambar 4.9.



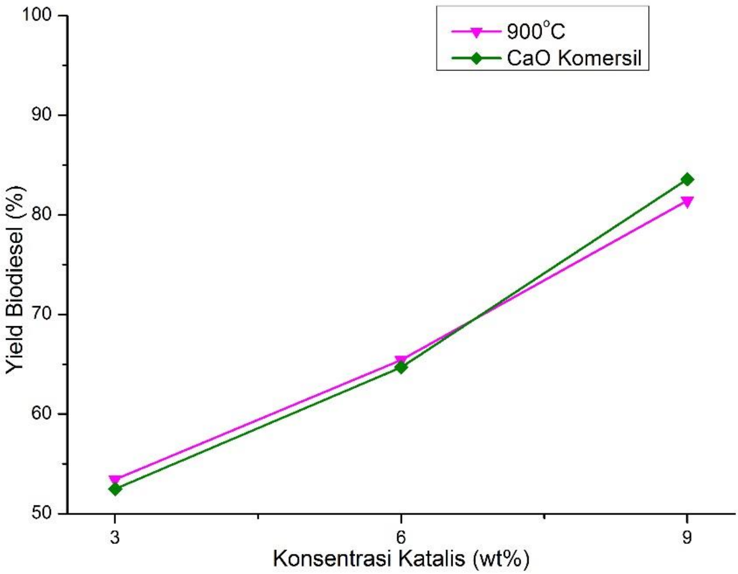
Gambar 4.9 Grafik pengaruh temperatur kalsinasi terhadap hasil konversi biodiesel

Dari Gambar 4.9 terlihat bahwa konversi trigliserida menjadi biodiesel meningkat seiring dengan meningkatnya suhu kalsinasi. Jika dikorelasikan pada penjelasan pada subbab 4.2 dimana pada suhu kalsinasi 600ºC, 700ºC, dan 800ºC fraksi katalis kalsium oksida (CaO) sangat minoritas, dapat dikatakan hasil reaksi transesterifikasi bukanlah merupakan biodiesel. Hal ini ditandai pada saat reaksi selesai tidak ada gliserol yang terbentuk dan tidak ada juga metil ester (FAME) yang terbentu. Sesuai dengan persamaan (2.2), biodiesel terbentuk apabila menghasilkan gliserol, sedangkan hanya pada suhu 900ºC yang membentuk gliserol. Hal ini terutama disebabkan oleh kehadiran katalis CaO dimana pada suhu 600ºC, 700ºC, dan 800ºC serbuk cangkang telur berperan sebagai $CaCO_3$ atau kalsit. Sama halnya seperti yang dilaporkan (Yoosuk, dkk., 2010) bahwa jika kalsium karbonat ($CaCO_3$) yang paling dominan tidak mampu untuk mengkatalisis dan menurunkan energi aktivasi pada reaksi transesterifikasi.

Suhu kalsinasi 900ºC dapat dijadikan acuan terbentuknya biodiesel. Pada suhu ini mampu memberikan hasil biodiesel rata-rata 66,76%. Hal ini disebabkan oleh kenaikan Jumlah CaO (dekomposisi $CaCO_3$ dan $Ca(OH)_2$) dengan meningkatnya temperatur kalsinasi dimana sifat katalitik juga akan meningkat pada proses transesterifikasi. Selain itu terbentuknya gliserol dapat memperkuat dugaan bahwa pada suhu ini merupakan biodiesel karena sudah terpenuhinya reaksi transesterifikasi seperti pada persamaan (2.2). Sama halnya seperti penelitian yang dilakukan oleh (Kouzu, dkk., 2008) yang menyimpulkan bahwa pada suhu kalsinasi 900 ºC merupakan katalis yang sangat aktif pada proses reaksi transesterifikasi. Sehingga hal ini meluruskan seperti pernyataan (Xie, dkk., 2006) dan (Verziu, dkk., 2009) yang mengklaim bahwa reaksi transesterifikasi sangat bergantung pada dasar katalis.

4.5.2 Pengaruh Konsentrasi Katalis CaO Terhadap Hasil Biodiesel

Dalam sintesis biodiesel, konsentrasi katalis juga sangat berperan dalam menurunkan energi aktivasi dalam proses transesterifikasi. Gambar 4.10 menunjukkan pengaruh konsentrasi terhadap biodiesel yang dihasilkan.



Gambar 4.10 Grafik pengaruh konsentrasi katalis CaO terhadap hasil konversi biodiesel

Dari Gambar 4.10 dapat diamati bahwa hasil biodiesel meningkat seiring dengan meningkatnya konsentrasi katalis kalsium oksida (CaO). Peningkatan ini secara konsisten terjadi pada semua sampel serbuk cangkang telur ayam. Jika melihat hasil tanpa katalis (Tabel 4.4), massa yang dihasilkan setelah proses transesterifikasi cukup besar. Tetapi hasil ini mengindikasikan bukan biodiesel yang terbentuk karena tidak adanya gliserol. Tidak adanya katalis yang berperan dalam proses transesterifikasi sebenarnya dapat menghasilkan biodiesel tetapi memerlukan kondisi suhu reaksi yang tinggi (Tan, dkk., 2011).

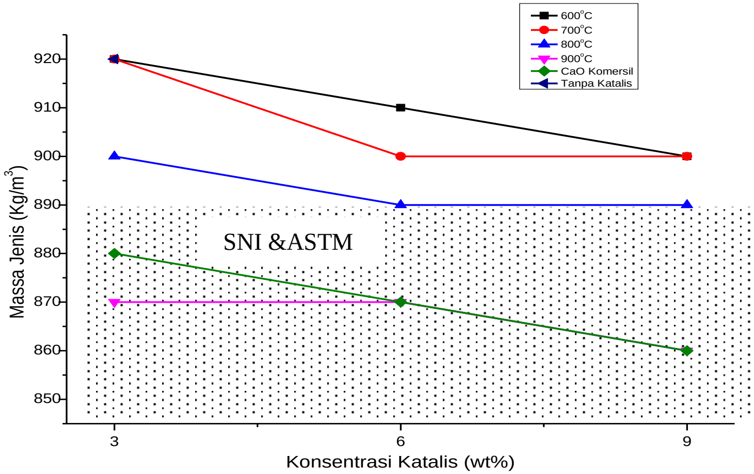
Pada suhu 900^{o}C dengan konsentrasi katalis CaO 9wt% memberikan kontribusi terbesar dalam mengkonversi trigliserida menjadi biodiesel sebesar 81,43%. Jika dibandingkan dengan katalis CaO komersil hasilnya tidak jauh berbeda. Pada CaO komersil menghasilkan konversi biodiesel tertinggi pada konsentrasi katalis 9wt% yaitu sebesar 83,59%. Katalis CaO komersil memiliki keakftifan yang paling tinggi pada konsentrasi yang sangat tinggi. Tetapi pada konsentrasi katalis 3wt% dan 6wt% pada suhu kalsinasi 900^{o}C hasil konversi biodiesel masih lebih tinggi dibandingkan dengan CaO komersil. Hal ini disebabkan oleh peningkatan laju reaksi dimana semakin besarnya konsentrasi katalis yang bekerja memiliki keaktifan yang tinggi sehingga dapat menurunkan menurunkan energi aktivasi (Kiakalaieh, dkk., 2013). Hal ini juga dapat dikaitkan bahwa katalis CaO membutuhkan lebih banyak alkohol untuk meningkatkan hasil biodiesel karena reaksi antar muka. Mekanisme reaksi katalis padat memerlukan peningkatan permukaan pori-pori katalis yang akan bereaksi dengan metanol yang tersedia sebelum bereaksi dengan minyak untuk membentuk produk. Permukaan katalis yang meningkat memerlukan lebih banyak metanol untuk bereaksi guna meningkatkan laju reaksi yang akan selalu mengoptimalkan hasil produk (Akhihiero, dkk., 2013).

4.6 Karakteristik Biodiesel Minyak Jelantah

Produk biodiesel yang dihasilkan kemudian diuji secara kualitatif dimana pengujian ini untuk menentukan standarisasi apakah layak digunakan. Pengujian ini mencakup massa jenis, viskositas kinematic, titik nyala, titik kabut, dan titik tuang.

4.6.1 Massa Jenis

Pengujian massa jenis dalam penelitian ini mengacu pada standar ASTM D1298. Sebagai standar, digunakan pembanding dengan SNI-04-7182:2015 dan ASTM D6751. Tabel hasil pengujian dapat dilihat pada Lampiran F, hasil pengujian kemudian diplot dalam kurva sebagai pengaruh konsentrasi katalis kalsium oksida (CaO) dengan massa jenis sampel biodiesel yang ditunjukkan pada Gambar 4.11.

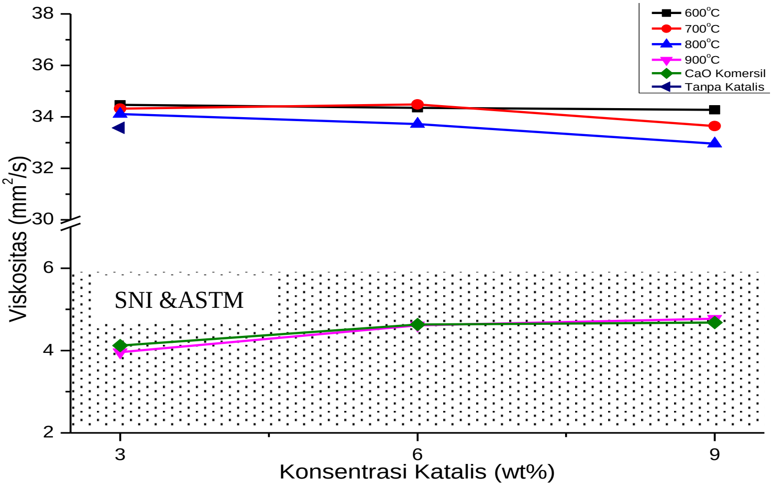


Gambar 4.11 Pengaruh konsentrasi katalis CaO terhadap massa jenis biodiesel

Berdasarkan Gambar 4.11 menunjukkan hasil pengujian biodiesel dengan konsentrasi katalis pada suhu kalsinasi 900°C, CaO komersil telah memenuhi standar SNI dan ASTM. Gambar 4.11 menunjukkan tren yang relatif turun tetapi tidak signifikan. Sehingga dapat disimpulkan semakin besar konsentrasi katalis CaO maka nilai massa jenis juga cenderung semakin kecil. Apabila dibandingkan dengan diesel konvensial (solar) nilai massa jenis sampel biodiesel yang telah memenuhi standar tidak jauh berbeda yaitu sekitar 0,87 kg/m^3. Hal ini sesuai dengan pernyataan (Moraes, dkk., 2009) menyebutkan bahwa diesel konvensional (solar) dan biodiesel memiliki kepadatan yang sangat mirip, namun harus dipertimbangkan bahwa kepadatan biodiesel dipengaruhi oleh sumber bahan baku dalam produksinya. Sumber bahan baku ini bisa saja berupa zat-zat pengotor, seperti sabun dan gliserol hasil reaksi penyabunan, asam-asam lemak yang tidak terkonversi menjadi metil ester (biodiesel), ataupun sisa metanol yang terdapat dalam biodiesel. Jika massa jenis biodiesel melebihi standar ketentuan sebaiknya biodiesel ini tidak digunakan karena akan meningkatkan keausan mesin dan akan menyebabkan kerusakan mesin (Setiawati & Edwar, 2012).

4.6.2 Viskositas Kinematik

Pengujian viskositas kinematik biodiesel dalam penelitian ini mengacu pada standar ASTM D445. Sebagai standar, digunakan pembanding dengan SNI-04-7182:2015 dan ASTM D6751. Tabel hasil pengujian dapat dilihat pada Lampiran F, hasil pengujian kemudian diplot dalam kurva sebagai pengaruh konsentrasi katalis kalsium oksida (CaO) dengan viskositas kinematik sampel biodiesel yang ditunjukkan pada Gambar 4.12.



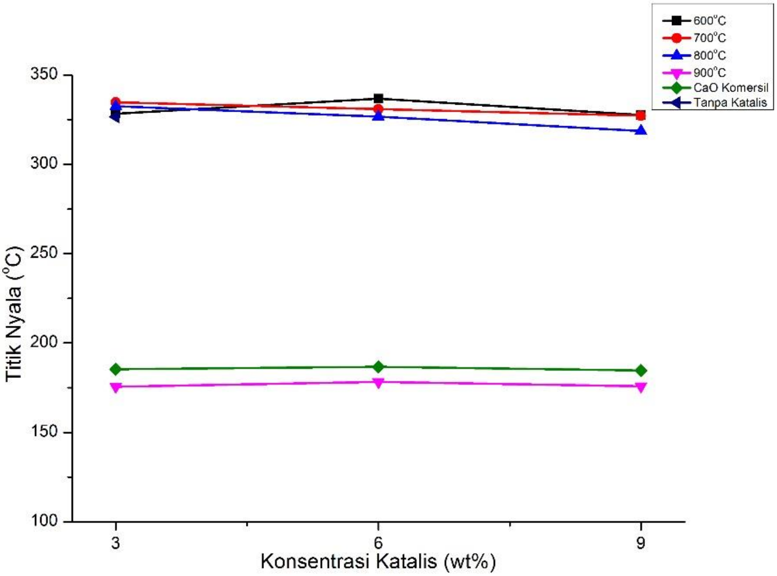
Gambar 4.12 Pengaruh konsentrasi katalis CaO terhadap viskositas kinematik biodiesel

Gambar 4.12 menunjukkan hasil pengujian biodiesel dengan konsentrasi katalis pada suhu kalsinasi 900°C dan CaO komersil katalis telah memenuhi standar SNI dan ASTM yang ditandai pada sifat fisik yang agak encer, sedangkan untuk konstrasi katalis pada suhu kalsinasi 600°C, 700°C, 800°C, dan tanpa katalis tidak memenuhi standar yang ditandai pada sifat fisik yang kental. Apabila dibandingkan dengan diesel konvensial (solar) nilai viskositas kinematik sampel biodiesel yang telah memenuhi standar tidak jauh berbeda yaitu sekitar 4,6 mm^2/s. Hal ini berarti katalis CaO dengan suhu kalsinasi 900^oC dan CaO komersil dapat menurunkan viskositas kinematik minyak jelantah secara optimal dengan mengkonversinya menjadi biodiesel. Gambar 4.12 dapat dilihat bahwa tren yang naik seiring dengan penambahan konsentrasi katalis. Sehingga dapat disimpulkan bahwa semakin tiggi konsentrasi katalis maka viskositas kinematik semakin tinggi (Yasin, dkk., 2013). Jika bahan bakar terlalu kental, maka dapat menyulitkan aliran, pemompaan, dan penyala pada mesin. Sebaliknya, jika bahan bakar terlalu encer, maka menyulitkan penyebaran bahan bakar sehingga sulit terbakar dan akan menyebabkan kebocoran dalam pipa injeksi (Setiawati & Edwar, 2012).

Apabila dihubungkan dengan massa jenis dan hasil konversi biodiesel, maka semakin tinggi konsentrasi katalis CaO maka kemampuan katalitik pada semakin aktif yang bekerja sama dengan metanol, peningkatan konsentrasi ini meningkatkan hasil konversi biodiesel dan nilai viskositas kinematik serta menurunkan massa jenis dari biodiesel tersebut. Hal ini dipengaruhi karena konsentrasi asam lemak bebas (FFA) yang rendah dalam biodiesel. Selain itu proses transesterifikasi juga mempengaruhi dimana mengubah minyak jelantah menjadi biodiesel sangat mengurangi viskositas.

4.6.3 Titik Nyala (*Flash Point*)

Pengujian titik nyala (*flash point*) biodiesel dalam penelitian ini mengacu pada standar ASTM D93. Sebagai standar, digunakan pembanding dengan SNI-04-7182:2015 dan ASTM D6751. Tabel hasil pengujian dapat dilihat pada Lampiran F, hasil pengujian kemudian diplot dalam kurva sebagai pengaruh konsentrasi katalis kalsium oksida (CaO) dengan titik nyala sampel biodiesel yang ditunjukkan pada Gambar 4.13.

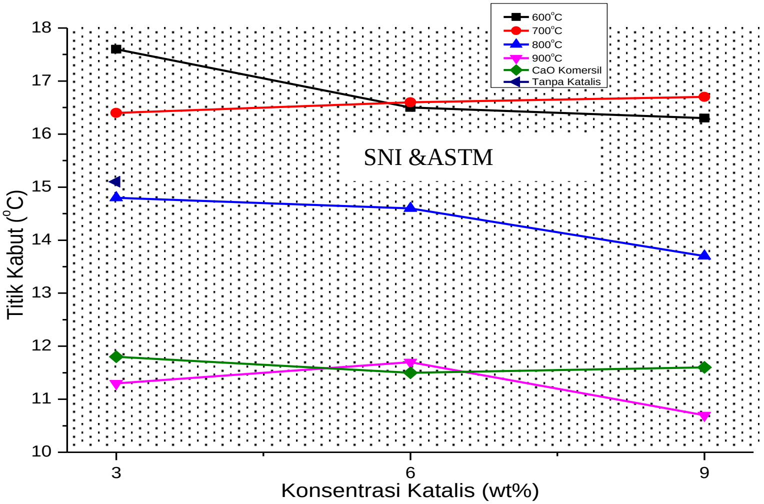


Gambar 4.13 Pengaruh konsentrasi katalis CaO terhadap titik nyala biodiesel

Berdasarkan Gambar 4.13 hasil pengujian seluruh sampel biodiesel telah memenuhi standar SNI (minimal 100°C) dan ASTM (minimal 130°C) sehingga semua sampel biodiesel ini berada dalam batas aman terhadap bahaya kebakaran selama penyimpanan, penanganan dan transportasi. Hal ini menunjukkan bahwa biodiesel dari minyak jelantah pada penelitian ini memiliki kualitas yang bagus karena memiliki titik nyala yang tinggi. Dari Gambar 4.13 tersebut dapat dilihat bahwa peningkatan konsentrasi katalis tidak terlalu mempengaruhi titik nyala biodiesel. Tetapi nilai titik nyala antara CaO pada suhu kalsinasi 900°C dan CaO komersil dengan katalis CaO pada suhu kalsinasi 600°C, 700°C, 800°C, dan tanpa katalis memiliki perbedaan yang sangat signifikan yaitu hampir dua kali lipatnya. Perlu diperhatikan bahwa titik nyala yang terlalu tinggi juga tidak baik digunakan karena biodiesel akan sulit melakukan menyalakan dirinya sendiri (Yasin, dkk,. 2013). Titik nyala juga mengindikasikan tinggi rendahnya volalitas dan kemampuan untuk terbakar dari suatu bahan bakar (Setiawati & Edwar, 2012). Sehingga dapat disimpulkan bahwa dalam penggunaannya, biodiesel dengan katalis suhu kalsinasi 900°C dan katalis CaO komersil lebih direkomendasikan.

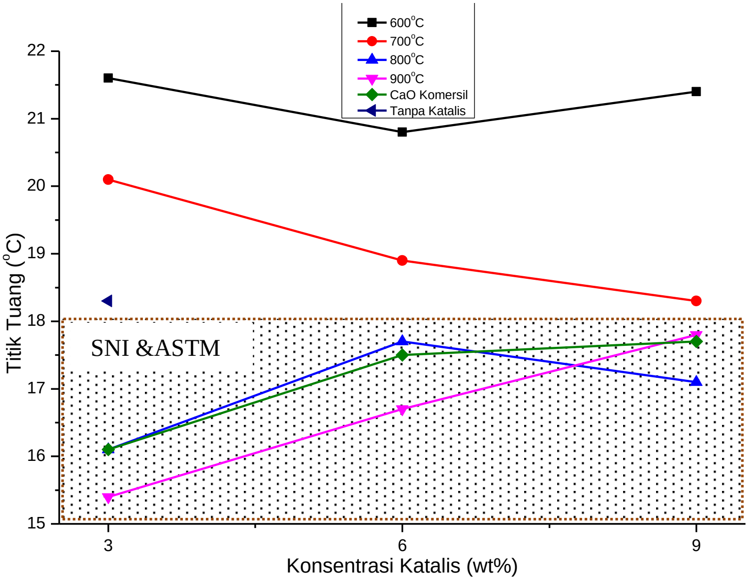
4.6.4 Titik Titik Kabut (*Cloud Point*) dan Titik Tuang (*Pour Point)*

Pengujian titik kabut (*cloud point*) dan titik tuang (*pour* point) biodiesel dalam penelitian ini mengacu pada standar ASTM D97 dan ASTM D2500. Sebagai standar, digunakan pembanding dengan SNI-04-7182:2015 dan ASTM D6751. Tabel hasil pengujian dapat dilihat pada Lampiran F. Hasil pengujian kemudian diplot dalam kurva sebagai pengaruh konsentrasi katalis kalsium oksida (CaO) dengan titik kabut dan titik tuang sampel biodiesel yang ditunjukkan pada Gambar 4.14 dan Gambar 4.15.



Gambar 4.14 Pengaruh konsentrasi katalis CaO terhadap titik kabut biodiesel

Berdasarkan Gambar 4.14 hasil pengujian seluruh sampel biodiesel telah memenuhi standar SNI (maksimal 18°C) dan ASTM (maksimal 18°C) yang ditandai adanya kabut yang berarti adanya krista-kristal lilin yang muncul pada saat pengujian. Hal ini menunjukkan bahwa biodiesel dari minyak jelantah pada penelitian ini memiliki kualitas yang baik karena memiliki titik kabut di bawah 18°C. Dari Gambar 4.14 tersebut dapat dilihat tren yang turun lebih sering muncul, sehingga dapat disimpulkan bahwa peningkatan konsentrasi katalis relatif dapat menurunkan titik kabut biodiesel.



Gambar 4.15 Pengaruh konsentrasi katalis CaO terhadap titik tuang biodiesel

Berdasarkan Gambar 4.15 hasil pengujian biodiesel dengan konsentrasi katalis pada suhu kalsinasi 800°C, 900°C, CaO komersil, telah memenuhi standar SNI (maksimal 18°C) dan ASTM (maksimal 18°C). Hal ini menunjukkan bahwa biodiesel dari minyak jelantah pada penelitian ini memiliki kualitas yang baik karena memiliki titik tuang di bawah 18°C. Sedangkan untuk konsentrasi katalis pada suhu kalsinasi 600°C, 700°C, dan tanpa katalis tidak memenuhi standar yang ada sehingga tidak direkomendasikan. Menurut (Susila & Darmawa, 2013) biodiesel dengan titik kabut dan titik tuang yang telah memenuhi standar dapat digunakan untuk daerah yang bersuhu rendah atau dingin seperti di Eropa dan tetap aman digunakan di daerah tropis.

4.7 Analisa Biaya Produksi Biodiesel Minyak Jelantah

Penghitungan biaya produksi biodiesel minyak jelantah ini bertujuan untuk mengetahui biaya yang harus dikeluarkan dalam produksi biodiesel serta kelayakan dalam penjualannya. Dalam produksi biodiesel bahan baku minyak dan alkohol yang digunakan memiliki peran penting dalam menentukan biaya produksinya (Boateng, dkk., 2013). Selain itu biaya penyewaan alat juga mempengaruhi dalam produksi biosiesel dalam penelitian.

1. Analisa Biaya Sintesis Katalis CaO

Tabel 4.5 Biaya langsung dan biaya tidak langsung pada produksi katalis CaO dari cangkang telur ayam

BIAYA LANGSUNG : BAHAN BAKU LANGSUNG			
Bahan baku	**Kuantitas**	**Harga**	**Jumlah**
Cangkang telur ayam	1 kg	-	-
Akuades	4000 ml	Rp 0.9,-/ml	Rp 3.600
BIAYA TIDAK LANGSUNG : BIAYA OVERHEAD PRODUKSI			
Penyewaan oven	24 jam	Rp 5.000,-/jam	Rp 120.000
Penyewaan furnace	6 jam	Rp 10.000,-/jam	Rp 60.000
Energi listrik	10 jam	Rp 605,-/kWh	Rp 6.050
Kertas saring	1 lembar	Rp 6.500,-/lembar	Rp 6.500
TOTAL			**Rp 196.150**
Hasil Katalis			850 gram
Harga katalis sintesis per gram			Rp 230
Harga katalis CaO komersil per gram			Rp 350,-

2. Analisa Biaya Proses Esterifikasi 1 Liter Minyak Jelantah

Tabel 4.6 Biaya langsung dan biaya tidak langsung pada esterifikasi 1 liter minyak jelantah

BIAYA LANGSUNG : BAHAN BAKU LANGSUNG			
Bahan baku	**Kuantitas**	**Harga**	**Jumlah**
Minyak jelantah	1000 ml	Rp 10,-/ml	Rp 10.000
Asam sulfat (H_2SO_4)	10 ml	Rp 110,-/ml	Rp 3.300,-
Metanol	150 ml	Rp 160,-/ml	Rp 24.000,-
BIAYA TIDAK LANGSUNG : BIAYA OVERHEAD PRODUKSI			
Energi listrik	2 jam	Rp 605,-/kWh	Rp 1.210,-
TOTAL			**Rp 38.510,-**
Hasil minyak jelantah setelah esterifikasi			980 ml
Harga minyak jelantah setelah esterifikasi/ml			Rp 39,3 ,-

3. Analisa Biaya Proses Produksi Biodiesel dengan Katalis CaO Sintesis

Tabel 4.7 Biaya langsung dan biaya tidak langsung pada produksi biodiesel CaO sintensis

BIAYA LANGSUNG : BAHAN BAKU LANGSUNG			
Bahan baku	**Kuantitas**	**Harga**	**Jumlah**
Minyak hasil *pre-treatment*	1000 ml (912 gram)	Rp 39,3 ,-/ml	Rp 39.300,-
Katalis CaO	82 gram	Rp 230,-/gram	Rp 18.860,-
Metanol	254 ml (201 gram)	Rp 160,-/ml	Rp 40.640,-
BIAYA TIDAK LANGSUNG : BIAYA OVERHEAD PRODUKSI			
Energi listrik	1 jam	Rp 605,-/kWh	Rp 605,-
TOTAL			**Rp 99.405,-**
Hasil biodiesel			854 ml (742 gram)
Harga biodiesel per ml			Rp 116,4 ,-
Harga biodiesel per liter			Rp 116.400,-

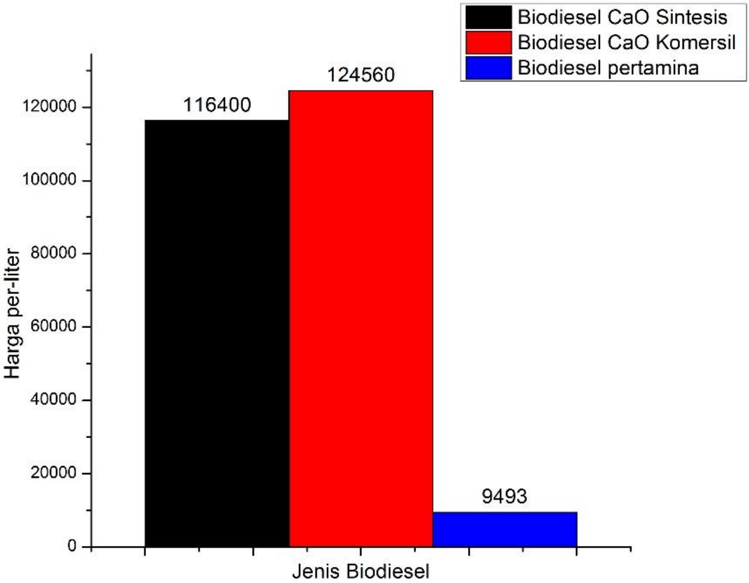
4. Analisa Biaya Proses Produksi Biodiesel dengan Katalis CaO Komersil

Tabel 4.8 Biaya langsung dan biaya tidak langsung pada produksi biodiesel CaO komersil

BIAYA LANGSUNG : BAHAN BAKU LANGSUNG			
Bahan baku	**Kuantitas**	**Harga**	**Jumlah**
Minyak hasil *pre-treatment*	1000 ml (912 gram)	Rp 39,296 ,-/ml	Rp 39.300,-
Katalis CaO Komersil	82 gram	Rp 350,-/gram	Rp 28.700,-
Metanol	254 ml (201 gram)	Rp 160,-/ml	Rp 40.640,-
BIAYA TIDAK LANGSUNG : BIAYA OVERHEAD PRODUKSI			
Energi listrik	1 jam	Rp 605,-/kWh	Rp 605,-
TOTAL			**Rp 109.245,-**
Hasil biodiesel			877 ml (762 gram)
Harga biodiesel per ml			Rp 124,56 ,-
Harga biodiesel per liter			Rp 124.560,-

Dari perhitungan biaya produksi biodiesel penelitian ini, didapatkan harga jual pasar biodiesel menggunakan CaO sintesis adalah Rp 116.400 dan biodiesel CaO komersil adalah Rp 124.560. Perbandingan harga penjualan biodiesel dapat dilihat pada Gambar 4.16. Dari gambar dapat dilihat bahwa harga penjualan per liter biodiesel CaO sintesis dan CaO komersil sangat mahal apabila dibandingkan dengan harga jual biodiesel pertamina.

Biaya pengembangan biodiesel memang masih cukup mahal karena ini merupakan energi alternatif yang relatif baru. Faktor utama yang menekan biaya produksi adalah biaya penyewaan alat seperti *oven* dan tungku serta harga metanol yang cukup tinggi. Sehingga berbanding lurus dengan pengeluaran biaya produksi yang tinggi pula.



Gambar 4.16 Perbandingan harga jual biodiesel

Dari perbandingan biaya produksi dengan harga penjualannya di pasar dapat disimpulkan bahwa pengembangan biodiesel dari minyak jelantah dengan menggunakan katalis kalsium oksida (CaO) masih kurang efektif karena harga yang relatif mahal. Namun, dengan berkembangnya teknologi dan meningkatnya penggunaan, pasti ke depan biodiesel akan mencapai keekonomian yang tinggi.

4.8 Analisa Prediksi Optimasi dan Validasi Parameter Biodiesel

Dari studi yang sudah pernah dilakukan, suhu reaksi, waktu reaksi, rasio molar metanol terhadap minyak jelantah dan konsentrasi katalis merupakan parameter yang secara signifikan mempengaruhi efisiensi hasil produksi biodiesel (Demirbas, 2005). Dari parameter ini dapat dibuat pemodelan kinetika dari reaksi transesterifikasi untuk mengamati pengaruh kondisi operasi terhadap hasil metil ester sebagai hasil yang valid (Velickovic, dkk., 2012). Parameter ini dipilih sebagai variabel independen, dan hasil metil ester sebagai variabel dependen. Dari penelitian sebelumnya, (El-Gendy, dkk., 2014) telah melakukan pemodelan kinetik biodiesel dari minyak jelantah dengan menggunakan katalis CaO yang disintesis dari cangkang kerang. Pemodelan kinetika tersebut dimodelkan berdasarkan desain dan data eksperimen D-Optimal yang digunakan sebagai acuan dalam penelitiannya. Konsep D-Optimal merupakan desain yang digunakan ketika desain simetris klasik tidak dapat digunakan, seperti ketika daerah eksperimen tidak berbentuk biasa, bila jumlah eksperimen yang dipilih oleh desain klasik terlalu besar atau bila salah satu Ingin menerapkan model yang menyimpang dari urutan pertama atau kedua yang biasa, dibantu komputer yang menciptakan rangkaian eksperimen yang optimal (Aguiar, dkk., 1995) yang diidentifikasi oleh (El-Gendy, dkk., 2014) pada persamaan (4.1) berikut:

$$\begin{aligned} Y = {} & 82{,}43 - 2{,}21A - 0{,}98B + 3{,}12C + 0{,}80D + 4{,}48A^2 + \\ & 1{,}89B^2 - 7{,}51C^2 - 2{,}56D^2 - 2{,}66AB - 1{,}16AC + \\ & 5{,}79AD + 2{,}50BC + 8{,}42BD + 0{,}87CD \end{aligned} \tag{4.1}$$

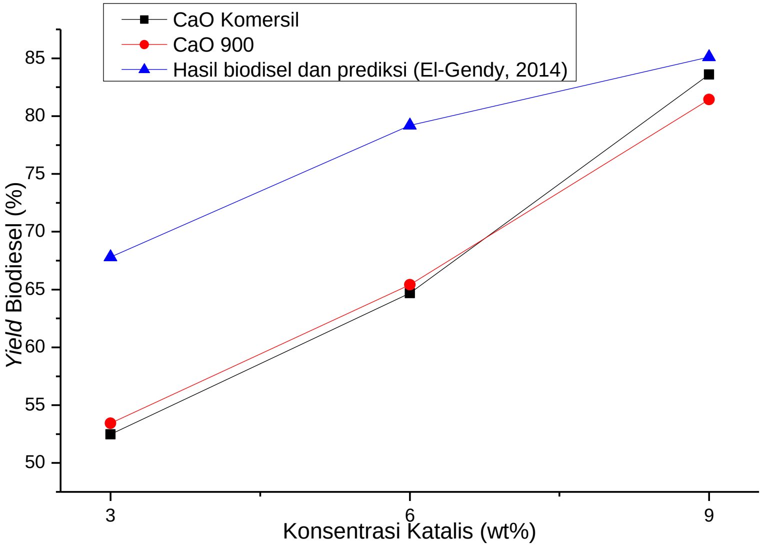
Dimana Y adalah hasil biodiesel dari proses transesterifikasi menggunakan katalis CaO, variabel A merupakan rasio molar metanol terhadap minyak jelantah, variabel B merupakan variabel konsentrasi katalis, variabel C merupakan variabel waktu reaksi, dan variabel D merupakan kecepatan reaksi yang diasumsikan bernilai 1. Matriks prediksi dari hasil biodiesel menggunakan katalis CaO yang berbeda yang dibuat dari cangkang telur ayam disajikan pada Tabel 4.9.

Tabel 4.9 Data hasil sintesis biodiesel dari proses transesterifikasi

Faktor				*Yield* Biodiesel (%)		*Error yield* (%)
Jenis Katalis	M:O (Rasio Molar) A	Konsentrasi Katalis (wt%) B	Waktu Reaksi (menit) C	Aktual	Prediksi (El-Gendy, dkk., 2014)	
CaO 900	6:1	3	120	53,43	67,80	21,2
	6:1	6	120	65,42	79,20	17,4
	6:1	9	120	81,43	85,10	4,3
CaO Komersil	6:1	3	120	52,48	67,80	22,6
	6:1	6	120	64,69	79,20	18,3
	6:1	9	120	83,59	85,10	1,8

Hubungan antara nilai prediksi dan aktual hasil biodiesel untuk CaO suhu kalsinasi 900°C dan CaO komersil ditunjukkan pada Gambar 4.17. Keterkaitan *yield* biodiesel antar variabel independen digunakan pendekatan nilai *error* antara jarak rata-rata (ΔY) kedua grafik linear aktual dan prediksi.

Gambar 4.17 menunjukkan adanya korelasi yang cukup tinggi, dengan nilai ΔY memiliki *error* mencapai 12% untuk jenis katalis CaO 900°C antara nilai prediksi dan aktual yang menunjukkan bahwa nilai prediksi dan aktual model tersebut dapat menjelaskan 88% variabilitasnya cukup berkesinambungan. Untuk CaO komersil, nilai ΔY memiliki *error* mencapai 11% yang menunjukkan bahwa nilai prediksi dan aktual model tersebut dapat menjelaskan 89% variabilitasnya cukup berkesinambungan. Dalam kaitannya terhadap variabel independen dan persamaan model kinetik, waktu reaksi memiliki dampak positif yang tinggi terhadap hasil reaksi. Namun, rasio molar metanol terhadap minyak jelantah (M:O) memiliki dampak negatif. Efek interaksi rasio molar M:O dan konsentrasi katalis memiliki dampak negatif yang lebih tinggi daripada M:O dan waktu reaksi pada hasil biodiesel (El-Gendy, dkk., 2014).



Gambar 4.17 Grafik aktual versus prediksi hasil produksi biodiesel

Dampak negatif ini disebabkan karena jumlah katalis CaO yang terdapat pada serbuk cangkang telur ayam belum murni. Seperi yang dijelaskan pada subbab 4.2, serbuk cangkang telur ayam mengandung CaO sebanyak 85%, $CaCO_3$ sebanyak 3,73%, $Ca(OH)_2$ sebanyak 11,24% yang dikalsinasi pada suhu 900°C dengan lama waktu 6 jam. Jika dibandingkan dengan penelitian (El-Gendy, dkk., 2014) yang disintesis dari cangkang kerang, CaO yang dihasilkan memiliki kemurnian 99%. Hal ini dapat dikatkan dengan tingkat kebasaan katalis, seperti yang dilaporkan (Yoosuk, dkk., 2013) semakin murni katalis basa heterogen maka tingkat kebasaannya semakin tinggi yang berpengaruh pada keaktifan katalitiknya. Ketidakmurnian yang dihasilkan dalam penelitian ini menyebabkan keaktifan dari katalis akan berkurang untuk mengkonversi menjadi biodiesel. $CaCO_3$ yang terkandung dalam serbuk cangkang telur ayam tidak cukup tinggi untuk mengkatalisis reaksi transesterifikasi. Begitu juga dengan $Ca(OH)_2$ yang terkandung, meskipun memiliki sifat basa tetapi memiliki keaktifan yang lemah dibandingkan dengan CaO. Secara jelas dilaporkan oleh (Yoosuk, dkk., 2013) untuk logam alkali tanah, senyawa yang bentuk oksida memiliki sifat basa yang lebih kuat daripada bentuk hidroksida. Sehingga dapat disimpulkan bahwa ketidaksesuaian antara hasil konversi biodiesel dengan prediksi (El-Gendy, dkk., 2014) disebabkan oleh ketidakmurnian dimana terdapat $CaCO_3$ dan $Ca(OH)_2$

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BAB V
PENUTUP

5.1 Kesimpulan

Berdasarkan hasil karakterisasi dan analisa yang telah dilakukan pada sampel katalis kalsium oksida (CaO) dan sampel biodiesel, maka kesimpulan dari penelitian ini adalah sebagai berikut :

a. Suhu kalsinasi 900ºC dapat dijadikan acuan terbentuknya biodiesel. Pada suhu ini mampu memberikan hasil biodiesel rata-rata 66,76%.

b. Pada suhu kalsinasi 900˚C dengan konsentrasi 9wt% memberikan hasil terbesar dalam pembentukan biodiesel yaitu 81,43%, hasil yang tidak berbeda jauh dengan CaO komersil dimana pada konsentrasi katalis 9wt% dapat mengkonversi biodiesel sebesar 83,59%.

c. Hasil pengujian karakteristik biodiesel (massa jenis, viskositas kinematik, titik nyala, titik kabut, dan titik tuang) yang memenuhi kualifikasi SNI-04-7182:2015 dan ASTM D6751 adalah biodiesel sampel CaO kalsinasi suhu 900˚C dan CaO komersil dengan konsentrasi katalis 3wt%, 6wt%, dan 9wt%.

5.2 Saran

Saran yang dapat diberikan sebagai pertimbangan dalam pengembangan lebih lanjut adalah sebagai berikut :

a. Dalam proses sintesis katalis kalsium oksida (CaO) perlu diperhatikan bahwa proses tahap pencucian cangkang telur ayam sangat mempengaruhi pembentukan CaO yang optimal.

b. Perlunya studi lebih lanjut dalam pemanfaat limbah cangkang telur ayam dan minyak jelantah dalam produksi biodiesel yang memiliki kualitas tinggi dan berdaya jual yang lebih murah sebagai energi alternatif yang berkelanjutan.

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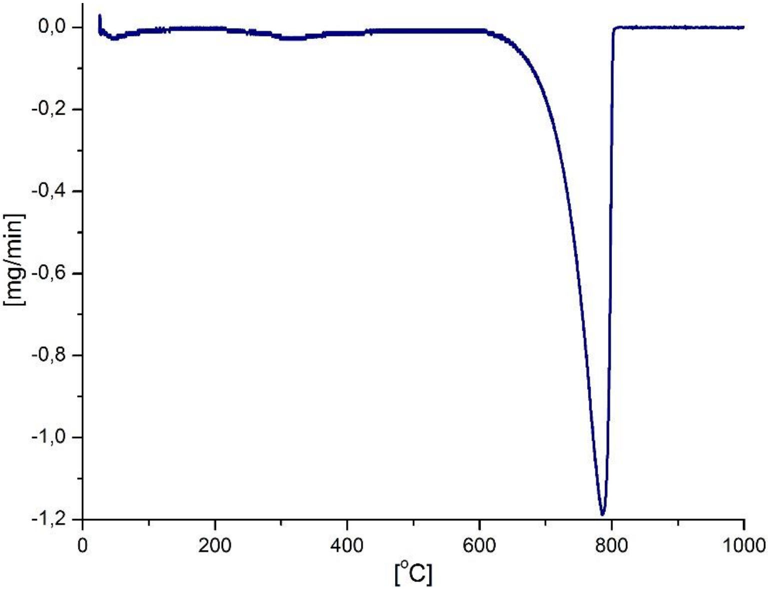
Lampiran A
Menghitung Fraksi Senyawa dari Kurva *Thermogravimetric*

- Kurva TGA



Dari kurva TGA didapatkan persamaan polynomial yang mendekati adalah sebagai berikut:

$$f(x) = 4.10^{-12}x^6 - 2.10^{-8}x^5 + 3.10^{-5}x^4 - 0{,}0256x^3 + 13{,}262x^2 + 3662{,}6x + 420873$$

- Menghitung daerah fraksi (luas pemukaan kurva)

$$F(x) = -\int 4.10^{-12}x^6 - 2.10^{-8}x^5 + 3.10^{-5}x^4 - 0{,}0256x^3 + 13{,}262x^2 + 3662{,}6x + 420873\, dx$$

$$F(x) = -\left(4.10^{-12}\frac{x^{6+1}}{6+1} - 2.10^{-8}\frac{x^{5+1}}{5+1} + 3.10^{-5}\frac{x^{4+1}}{4+1} - 0{,}0256\frac{x^{3+1}}{3+1} + 13{,}262\frac{x^{2+1}}{2+1} + 366{,}2\frac{x^{1+1}}{1+1} + 420873x + C\right)$$

$$F(x) = -\frac{x^7}{1750000000000} + \frac{x^6}{300000000} - \frac{3x^5}{500000} + \frac{4x^4}{625} - \frac{6631x^3}{1500} + \frac{18313x^2}{10} + 420873x + C$$

- Menghitung fraksi total (total luas pemukaan kurva)

$$F(x) = -\int_{600}^{900} 4.10^{-12}x^6 - 2.10^{-8}x^5 + 3.10^{-5}x^4 - 0{,}0256x^3 + 13{,}262x^2 + 3662{,}6x + 420873\,dx$$

$$F(900) = -\frac{900^7}{1750000000000} + \frac{900^6}{300000000} - \frac{3(900)^5}{500000} + \frac{4(900)^4}{625} - \frac{6631(900)^3}{1500} + \frac{18313(900)^2}{10} + 420873(900)$$

$$F(900) = 2080941300$$

$$F(600) = -\frac{600^7}{1750000000000} + \frac{600^6}{300000000} - \frac{3(600)^5}{500000} + \frac{4(600)^4}{625} - \frac{6631(600)^3}{1500} + \frac{18313(600)^2}{10} + 420873(600)$$

$$F(600) = 281320200$$

$F(600 - 900) = F(900) - F(600)$

$F(600 - 900) = 2080941300 - 281320200$

$F(600 - 900) = 1799621100$ satuan luas

- Fraksi CaO suhu dekomposisi 600°C

$$F(x) = -\int_{600}^{600} 4.10^{-12}x^6 - 2.10^{-8}x^5 + 3.10^{-5}x^4 - 0{,}0256x^3 + 13{,}262x^2 + 3662{,}6x + 420873\ dx$$

$$F(600-600) = F(600) - F(600)$$
$$F(600-600) = 0 \text{ satuan luas}$$
$$Fraksi\ CaO\ 600^oC = \frac{F(600-600)}{F(600-900)} x100$$
$$= \frac{0}{1799621100} x\ 100\% = 0\%$$

- Fraksi CaO suhu dekomposisi 700°C

$$F(x) = -\int_{600}^{700} 4.10^{-12}x^6 - 2.10^{-8}x^5 + 3.10^{-5}x^4 - 0{,}0256x^3 + 13{,}262x^2 + 3662{,}6x + 420873\ dx$$
$$F(700) = -\frac{700^7}{1750000000000} + \frac{700^6}{300000000} - \frac{3(700)^5}{500000} + \frac{4(700)^4}{625} - \frac{6631(700)^3}{1500} + \frac{18313(700)^2}{10} + 420873(700)$$
$$F(700) = 341757033{,}333$$

$$F(600-700) = F(700) - F(600)$$
$$F(600-700) = 341757033{,}333 - 281320200$$
$$F(600-700) = 60436833{,}333 \text{ satuan luas}$$
$$Fraksi\ CaO\ \ 700^oC = \frac{F(600-700)}{F(600-900)} x100\%$$
$$= \frac{60436833{,}333}{1799621100} x\ 100\% = 18{,}99\%$$

- Fraksi CaO suhu dekomposisi 800°C

$$F(x) = -\int_{600}^{800} 4.10^{-12}x^6 - 2.10^{-8}x^5 + 3.10^{-5}x^4 - 0{,}0256x^3 + 13{,}262x^2 + 3662{,}6x + 420873\, dx$$

$$F(800) = -\frac{800^7}{1750000000000} + \frac{800^6}{300000000} - \frac{3(800)^5}{500000} + \frac{4(800)^4}{625} - \frac{6631(800)^3}{1500} + \frac{18313(800)^2}{10} + 420873(800)$$

$$F(800) = 912072066{,}7$$

$F(600 - 800) = F(800) - F(600)$
$F(600 - 800) = 912072066{,}7 - 281320200$
$F(600 - 800) = 630751866{,}7$ satuan luas

$$Fraksi\ CaO\ \ 800^oC = \frac{F(600-800)}{F(600-900)} x100\% = \frac{630751866{,}7}{1799621100} x\ 100\% = 50{,}68\%$$

- Fraksi CaO suhu dekomposisi 900°C

$$F(x) = -\int_{600}^{900} 4.10^{-12}x^6 - 2.10^{-8}x^5 + 3.10^{-5}x^4 - 0{,}0256x^3 + 13{,}262x^2 + 3662{,}6x + 420873\, dx$$

$F(600 - 900) = F(600) - F(900)$
$F(600 - 900) = 1799621100$ satuan luas

$$Fraksi\ CaO\ \ 900^oC = \frac{F(600-900)}{F(600-900)} x100\% = \frac{1799621100}{1799621100} x\ 100\% = 100\%$$

Lampiran B
Penghitungan Fraksi Pembentukan CaO dari Pola Difraksi XRD

Fraksi pembentukan senyawa dapat dihitung dengan persamaan RIR (*Reference Intensity Ratio*) sebagai berikut:

$$Fraksi\ R\ (\%) = \frac{\sum \frac{I_i}{I_{max}}}{\sum \frac{I_p}{I_{max}}} x\ 100\%$$

- Suhu Kalsinasi 600°C waktu 2 jam

Senyawa	**2θ**	**Intensitas (I_i)**	**I_i/ I_{max}**	**∑ I_i**	**Persen Fraksi (%)**
CaO	64,5	124	0,0263	0,0263	1,41
$CaCO_3$	29,1	4715	1	1,54	82,52
	39,2	483	0,102		
	43,0	506	0,107		
	47,3	859	0,182		
	48,3	694	0,147		
$Ca(OH)_2$	47,0	185	0,039	0,039	2,1
Impuritas	31,1	129	0,027	0,26	13,96
	35,7	353	0,075		
	56,5	99	0,021		
	57,2	194	0,041		
	58,0	66	0,014		
	60,5	158	0,034		
	62,8	65	0,014		
	65,5	109	0,023		
	69,0	55	0,011		
				∑ I_p/ I_{max} = 1,865	

- Suhu Kalsinasi 700^{o}C waktu 2 jam

Senyawa	**2θ**	**Intensitas (I_i)**	**I_i/ I_{max}**	**∑ I_i**	**Persen Fraksi (%)**
CaO	64,7	183	0,039	0,039	1,91
$CaCO_3$	29,4	4601	1	1,631	78,64
	39,4	758	0,165		
	43,2	675	0,145		
	47,5	734	0,159		
	48,6	738	0,160		
$Ca(OH)_2$	47,1	241	0,052	0,052	2,52
Impuritas	31,5	107	0,023	0,351	16,92
	36,0	476	0,103		
	56,6	110	0,024		
	57,5	253	0,054		
	58,1	66	0,014		
	60,7	210	0,045		
	61,0	107	0,023		
	61,5	112	0,024		
	65,7	121	0,026		
	69,2	53	0,011		
				∑ I_p/ I_{max} = 2,074	

- Suhu Kalsinasi 800°C waktu 2 jam

Senyawa	**2θ**	**Intensitas (I_i)**	**I_i/ I_{max}**	**∑ I_i**	**Persen Fraksi (%)**
CaO	64,6	270	0,066	0,066	2,93
$CaCO_3$	29,3	4081	1	1,703	75,47
	39,3	702	0,172		
	43,1	572	0,140		
	47,4	758	0,186		
	48,4	839	0,205		
$Ca(OH)_2$	47,0	252	0,061	0,061	2,73
Impuritas	31,3	183	0,045	0,425	18,86
	35,9	486	0,119		
	56,5	116	0,028		
	57,3	337	0,082		
	58,0	77	0,018		
	60,9	108	0,026		
	61,3	109	0,026		
	63,0	75	0,018		
	65,5	192	0,047		
	69,1	54	0,013		
				∑ I_p/ I_{max} = 2,257	

- Suhu Kalsinasi 900^{o}C waktu 2 jam

Senyawa	**2θ**	**Intensitas (I_i)**	**I_i/ I_{max}**	**∑ I_i**	**Persen Fraksi (%)**
CaO	64,6	152	0,046	0,046	1,80
$CaCO_3$	29,4	3295	1	1,65	64,23
	39,4	487	0,148		
	43,1	428	0,129		
	47,4	718	0,218		
	48,5	509	0,154		
$Ca(OH)_2$	28,6	200	0,060	0,376	14,66
	34,1	492	0,149		
	47,1	339	0,102		
	50,7	210	0,063		
Impuritas	31,4	144	0,043	0,496	19,31
	35,9	370	0,112		
	54,3	110	0,033		
	56,5	109	0,033		
	57,4	219	0,066		
	57,5	121	0,036		
	57,5	121	0,036		
	60,6	158	0,048		
	63,1	76	0,023		
	65,6	144	0,043		
	69,1	63	0,019		
				∑ I_p/ I_{max} = 2,569	

- Suhu Kalsinasi 600°C waktu 6 jam

Senyawa	**2θ**	**Intensitas (I_i)**	**I_i/ I_{max}**	**∑ I_i**	**Persen Fraksi (%)**
CaO	31,8	74	0,055	0,248	7,86
	36,4	201	0,151		
	63,5	55	0,041		
$CaCO_3$	29,8	1331	1	0,601	68,20
	39,8	338	0,254		
	43,6	365	0,274		
	48,0	447	0,336		
	49,0	383	0,287		
$Ca(OH)_2$	47,5	205	0,154	0,154	4,89
Impuritas	57,0	69	0,052	0,601	19,05
	57,8	196	0,147		
	58,4	54	0,040		
	61,0	122	0,091		
	61,2	108	0,081		
	65,0	96	0,072		
	66,0	118	0,088		
	69,6	37	0,028		
				∑ I_p/ I_{max} = 3,154	

- Suhu Kalsinasi 700°C waktu 6 jam

Senyawa	**2θ**	**Intensitas (I_i)**	**I_i/ I_{max}**	**∑ I_i**	**Persen Fraksi (%)**
CaO	32,0	82	0,038	0,202	7,90
	37,4	289	0,136		
	63,4	57	0,027		
$CaCO_3$	29,8	2113	1	1,836	71,60
	39,9	421	0,199		
	43,6	356	0,168		
	47,9	480	0,227		
	49,0	511	0,241		
$Ca(OH)_2$	47,6	183	0,086	0,086	3,37
Impuritas	57,0	87	0,041	0,439	17,12
	57,8	205	0,097		
	58,6	50	0,023		
	61,2	150	0,070		
	61,4	116	0,054		
	65,1	153	0,072		
	66,1	117	0,055		
	69,7	50	0,023		
				∑ I_p/ I_{max} = 2,565	

- Suhu Kalsinasi 800^{o}C waktu 6 jam

Senyawa	**2θ**	**Intensitas (I_i)**	**I_i/ I_{max}**	**∑ I_i**	**Persen Fraksi (%)**
CaO	32,1	124	0,036	0,219	8,22
	37,4	279	0,081		
	53,9	105	0,030		
	64,7	244	0,071		
$CaCO_3$	29,4	3422	1	1,663	62,20
	39,4	796	0,232		
	43,2	477	0,139		
	47,5	996	0,291		
	48,5	712	0,208		
$Ca(OH)_2$	34,1	77	0,022	0,090	3,40
	47,1	234	0,068		
Impuritas	31,5	143	0,041	0,699	26,17
	36,1	415	0,121		
	48,5	712	0,208		
	56,6	129	0,037		
	57,4	263	0,077		
	58,1	60	0,017		
	60,7	184	0,053		
	60,9	124	0,036		
	61,0	108	0,031		
	63,1	71	0,020		
	65,6	186	0,0543		
				∑ I_p/ I_{max} = 2,673	

- Suhu Kalsinasi 900°C waktu 6 jam

Senyawa	**2θ**	**Intensitas (I_i)**	**I_i/ I_{max}**	**∑ I_i**	**Persen Fraksi (%)**
CaO	32,2	731	0,310	1,87	85,02
	37,4	2353	1		
	53,9	765	0,325		
	64,2	280	0,119		
	67,4	282	0,112		
$CaCO_3$	29,4	100	0,042	0,08	3,74
	47,3	94	0,040		
$Ca(OH)_2$	28,6	106	0,045	0,24	11,23
	34,2	262	0,111		
	47,2	97	0,041		
	50,9	118	0,050		
Impuritas	0	0	0	0	0
				∑ I_p/ I_{max} = 2,20	

Lampiran C
Penghitungan Berat Molekul Minyak Jelantah

- Komposisi produk
  1. Metil ester : 97,76 %
     - Metil laurat : 1,10 %
     - Metil palmitat : 43,60 %
     - Metil stearate : 4,50 %
     - Metil oleat : 40,50 %
     - Metil linoleat : 10,10 %
     - Metil linolenat : 0,20 %
  2. Gliserol bebas : 0,02 %
  3. Trigliserida : 0,4 %
  4. Asam lemak bebas (FFA) : 1,53 %
  5. Metanol : 0,30 %
  6. Air : 0,01 %

  (Sumber: Standar Mutu Biodiesel Indonesia (RSNI EB 020551); Standar Biodiesel Jerman (DIN 51606)

- Berat molekul tiap komposisi

No	Senyawa	Rumus Molekul	BM (kg/kmol)
1	Asam laurat	$C_{12}H_{24}O_2$	200
2	Asam palmitat	$C_{16}H_{31}O_2$	256
3	Asam stearat	$C_{18}H_{36}O_2$	284
4	Asam oleat	$C_{18}H_{34}O_2$	282
5	Asam linoleat	$C_{18}H_{32}O_2$	280
6	Asam linolenat	$C_{18}H_{30}O_2$	278
7	Metil laurat	$C_{13}H_{26}O_2$	214
8	Metil palmitat	$C_{17}H_{34}O_2$	270
9	Metil stearat	$C_{19}H_{38}O_2$	298
10	Metil oleat	$C_{19}H_{36}O_2$	296
11	Metil linoleat	$C_{19}H_{34}O_2$	294
12	Metil linolenat	$C_{19}H_{32}O_2$	292
13	Metanol	CH_4O	32

- Menghitung berat molekul

BM FFA rata-rata = {(1,1% x 200) + (43,6% x 256) + (4,50% x 284) + (40,50% x 282) + (10,10% x 280) + (0,2 % x 278)
= 269,642 kg/kmol

BM trigliserida (palmito-diolein) = 858 kg/kmol

LAMPIRAN D
PENGUJIAN KADAR ASAM LEMAK BEBAS (FFA)

- Sampel minyak jelantah sebelum proses *pre-treatment* atau reaksi esterifikasi

  Dengan menggunakaan persamaan 3.2:
  - V_{NaOH} : 15 ml
  - N_{NaOH} : 0,1 M
  - $MW_{asam\ lemak}$: 269,642 gr/mol
  - m_{sampel} : 10 gram

$$FFA\ (\%) = \frac{V_{NaOH}\ x\ N_{NaOH}\ x\ MW_{asam\ lemak}}{m_{sampel}\ x\ 1000} x\ 100\%$$

$$FFA\ (\%) = \frac{15ml\ x\ 0{,}1M\ x\ 269{,}642\ gr/mol}{10\ gr\ x\ 1000} x\ 100\%$$

$$FFA\ (\%) = 4{,}045\%$$

- Sampel minyak jelantah setelah proses *pre-treatment* atau reaksi esterifikasi

  Dengan menggunakaan persamaan 3.2:
  - V_{NaOH} : 3 ml
  - N_{NaOH} : 0,1 M
  - $MW_{asam\ lemak}$: 269,642 gr/mol
  - m_{sampel} : 10 gram

$$FFA\ (\%) = \frac{V_{NaOH}\ x\ N_{NaOH}\ x\ MW_{asam\ lemak}}{m_{sampel}\ x\ 1000} x\ 100\%$$

$$FFA\ (\%) = \frac{3ml\ x\ 0{,}1M\ x\ 269{,}642\ gr/mol}{10\ gr\ x\ 1000} x\ 100\%$$

$$FFA\ (\%) = 0{,}775\%$$

- Persentase penurunan kadar FFA

$$Penurunan\ Kadar\ FFA\ (\%) = \frac{4{,}045\% - 0{,}775\%}{4{,}045\%}\, x\ 100\%$$

$$Penurunan\ Kadar\ FFA\ (\%) = 80{,}84\%$$

LAMPIRAN E
MENGHITUNG MASSA METANOL DALAM PROSES TRANSESTERIFIKASI

- Larutan metanol terdiri dari 98% (%b) metanol dan 2% (%b) air

$$\text{BM larutan metanol} = \frac{100}{\frac{98}{32} + \frac{2}{18}}$$

$$\text{BM larutan metanol} = \frac{100}{3{,}0625 + 0{,}1111}$$

$$\text{BM larutan metanol} = 31{,}51\ kg/kmol$$

- Trigliserida : metanol = 1 : 6 (perbandingan rasio molar)

$$1 : 6 \quad = \frac{massa\ trigliserida}{BM\ trigliserida} : \frac{massa\ larutan\ metanol}{BM\ larutan\ metanol}$$

$$1 : 6 \quad = \frac{136{,}8\ gr}{858\ kg/kmol} : \frac{massa\ larutan\ metanol}{31{,}51\ kg/kmol}$$

$$\text{Massa lar. metanol} \ = \frac{6\ x\ 136{,}8\ gr\ x\ 31{,}51\ kg/kmol}{1\ x\ 858\ kg/kmol}$$

$$\text{Massa lar. metanol} \ = 30{,}14\ gram$$

“Halaman ini sengaja dikosongkan”

Designation: D 93 – 02a

An American National Standard

Designation: 34/99

Standard Test Methods for Flash Point by Pensky-Martens Closed Cup Tester[1]

This standard is issued under the fixed designation D 93; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

INTRODUCTION

This flash point test method is a dynamic test method and depends on definite rates of temperature increases to control the precision of the test method. The rate of heating may not in all cases give the precision quoted in the test method because of the low thermal conductivity of certain materials. To improve the prediction of flammability, Test Method D 3941, an equilibrium method, was developed in which the heating rate is slower. This allows the vapor above the test specimen and the test specimen to be at about the same temperature. If your specification requires Test Method D 93, do not substitute Test Method D 3941 or any other test method without obtaining comparative data and agreement from the specifier.

Flash point values are a function of the apparatus design, the condition of the apparatus used, and the operational procedure carried out. Flash point can therefore only be defined in terms of a standard test method, and no general valid correlation can be guaranteed between results obtained by different test methods, or with test apparatus different from that specified.

1. Scope *

1.1 These test methods cover the determination of the flash point of petroleum products in the temperature range from 40 to 360°C by a manual Pensky-Martens closed-cup apparatus or an automated Pensky-Martens closed-cup apparatus.

NOTE 1—Flash point determination as above 250°C can be performed, however, the precisions have not been determined above this temperature. For residual fuels, precisions have not been determined for flash points above 100°C.

1.2 Procedure A is applicable to distillate fuels (diesel, kerosine, heating oil, turbine fuels), new lubricating oils, and other homogeneous petroleum liquids not included in the scope of Procedure B.

1.3 Procedure B is applicable to residual fuel oils, cutback residua, used lubricating oils, mixtures of petroleum liquids with solids, petroleum liquids that tend to form a surface film under test conditions, or are petroleum liquids of such kinematic viscosity that they are not uniformly heated under the stirring and heating conditions of Procedure A.

1.4 These test methods is applicable for the detection of contamination of relatively nonvolatile or nonflammable materials with volatile or flammable materials.

1.5 The values stated in SI units shall be regarded as the standard. The values given in parentheses are provided for information only.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazards statements, see 6.4, 7.1, 9.3, 9.4, 11.1.2, 11.1.4, and 12.1.2.

2. Referenced Documents

2.1 *ASTM Standards:*

D 56 Test Methods for Flash Point by Tag Closed Cup Tester[2]

D 3941 Test Method for Flash Point by the Equilibrium Method with a Closed-Cup Apparatus[3]

D 4057 Practice for Manual Sampling for Petroleum and Petroleum Products[4]

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[1] These test methods are under the joint jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and are the direct responsibility of Subcommittee D02.08 on Volatility. In the IP, these test methods are under the jurisdiction of the Standardization Committee.

Current edition approved Dec. 10, 2002. Published March 2003. Originally approved in 1921. Last previous edition approved in 2002 as D 93–02.

[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 06.01.

[4] *Annual Book of ASTM Standards*, Vol 05.02.

***A Summary of Changes section appears at the end of this standard.**

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products[4]
E 1 Specification for ASTM Thermometers[5]
E 300 Practice for Sampling Industrial Chemicals[6]
E 502 Test Method for Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods[7]

2.2 *ISO Standards*[8]

Guide 34 Quality Systems Guidelines for the Production of Reference Materials
Guide 35 Certification of Reference Material—General and Statistical Principles

3. Terminology

3.1 *Definitions:*

3.1.1 *dynamic*, *adj—in petroleum products*—the condition where the vapor above the test specimen and the test specimen are not in temperature equilibrium at the time that the ignition source is applied.

3.1.1.1 *Discussion*—This is primarily caused by the heating of the test specimen at the constant prescribed rate with the vapor temperature lagging behind the test specimen temperature.

3.1.2 *equilibrium*, *n—in petroleum products*—the condition where the vapor above the test specimen and the test specimen are at the same temperature at the time the ignition source is applied.

3.1.2.1 *Discussion*—This condition may not be fully achieved in practice, since the temperature may not be uniform throughout the test specimen, and the test cover and shutter on the apparatus can be cooler.

3.1.3 *flash point*, *n—in petroleum products*, the lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg), at which application of an ignition source causes the vapors of a specimen of the sample to ignite under specified conditions of test.

3.1.3.1 *Discussion*—The test specimen is deemed to have flashed when a flame appears and instantaneously propagates itself over the entire surface of the test specimen.

3.1.3.2 *Discussion*—When the ignition source is a test flame, the application of the test flame may cause a blue halo or an enlarged flame prior to the actual flash point. This is not a flash point and shall be ignored.

4. Summary of Test Method

4.1 A brass test cup of specified dimensions, filled to the inside mark with test specimen and fitted with a cover of specified dimensions, is heated and the specimen stirred at specified rates, by either of two defined procedures (A or B). An ignition source is directed into the test cup at regular intervals with simultaneous interruption of the stirring, until a flash is detected (see 3.1.3.1). The flash point is reported as defined in 3.1.3.

5. Significance and Use

5.1 The flash point temperature is one measure of the tendency of the test specimen to form a flammable mixture with air under controlled laboratory conditions. It is only one of a number of properties which must be considered in assessing the overall flammability hazard of a material.

5.2 Flash point is used in shipping and safety regulations to define *flammable* and *combustible* materials. One should consult the particular regulation involved for precise definitions of these classifications.

NOTE 2—The U.S. Department of Transportation (DOT)[9] and U.S. Department of Labor (OSHA) have established that liquids with a flash point under 37.8°C (100°F) are flammable, as determined by these test methods, for those liquids which have a kinematic viscosity of 5.8 mm 2/s (cSt) or more at 37.8°C or 9.5 mm 2/s (cSt) or more at 25°C (77°F), or that contain suspended solids, or have a tendency to form a surface film while under test. Other classification flash points have been established by these departments for liquids using these test methods.

5.3 These test methods should be used to measure and describe the properties of materials, products, or assemblies in response to heat and an ignition source under controlled laboratory conditions and should not be used to describe or appraise the fire hazard or fire risk of materials, products, or assemblies under actual fire conditions. However, results of these test methods may be used as elements of a fire risk assessment which takes into account all of the factors which are pertinent to an assessment of the fire hazard of a particular end use.

5.4 These test methods provides the only closed cup flash point test procedures for temperatures up to 370°C (698°F).

6. Apparatus

6.1 *Pensky-Martens Closed Cup Apparatus (manual)*—This apparatus consists of the test cup, test cover and shutter, stirring device, heating source, ignition source device, air bath, and top plate described in detail in Annex A1. The assembled manual apparatus, test cup, test cup cover, and test cup assembly are illustrated in Figs. A1.1-A1.4, respectively. Dimensions are listed respectively.

6.2 *Pensky-Martens Closed Cup Apparatus (automated)*—This apparatus is an automated flash point instrument that is capable of performing the test in accordance with Section 11 (Procedure A) and Section 12 (Procedure B) of these test methods. The apparatus shall use the test cup, test cover and shutter, stirring device, heating source, and ignition source device described in detail in Annex A1.

6.3 *Temperature Measuring Device*—Is a thermometer having a range as shown as follows and conforming to the requirements prescribed in Specification E 1 or in Annex A3, or an electronic temperature measuring device, such as resistance thermometers or thermocouples. The device shall exhibit the same temperature response as the mercury thermometers.

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[5] *Annual Book of ASTM Standards*, Vol 14.03.

[6] *Annual Book of ASTM Standards*, Vol 15.05.

[7] *Annual Book of ASTM Standards*, Vol 14.02.

[8] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

[9] For information on U.S. Department of Transportation regulations, see Codes of U.S. Regulations 49 CFR Chapter 1 and the U.S. Department of Labor, see 29 CFR Chapter XVII. Each of these items is revised annually and may be procured from the Superintendent of Documents, Government Printing Office, Washington, DC 20402.

Temperature Range	Thermometer Number ASTM	IP
−5 to +110°C (20 to 230°F)	9C (9F)	15C
+10 to 200°C (50 to 392°F)	88C (88F)	101C
+90 to 370°C (200 to 700°F)	10C (10F)	16C

6.4 *Ignition Source*—Natural gas flame, bottled gas flame, and electric ignitors (hot wire) have been found acceptable for use as the ignition source. The gas flame device described in detailed in Fig. A1.4 requires the use of the pilot flame described in A1.1.2.3. The electric ignitors shall be of the hot-wire type and shall position the heated section of the ignitor in the aperture of the test cover in the same manner as the gas flame device. (**Warning—**Gas pressure supplied to the apparatus should not be allowed to exceed 3 kPa (12 in.) of water pressure.)

7. Reagents and Materials

7.1 *Cleaning Solvents*—Use suitable solvent capable of cleaning out the specimen from the test cup and drying the test cup and cover. Some commonly used solvents are toluene and acetone. (**Warning**—Toluene, acetone, and many solvents are flammable and a health hazard. Dispose of solvents and waste material in accordance with local regulations.)

8. Sampling

8.1 Obtain a sample in accordance with instructions given in Practices D 4057, D 4177, or E 300.

8.2 At least 75 mL of sample is required for each test. Refer to Practice D 4057. When obtaining a sample of residual fuel oil, the sample container shall be from 85 to 95 % full. For other types of samples, the size of the container shall be chosen such that the container is not more than 85 % full or less than 50 % full prior to any sample aliquot being taken.

8.3 Successive test specimens can be taken from the same sample container. Repeat tests have been shown to be within the precisions of the method when the second specimen is taken with the sample container at least 50 % filled. The results of flash point determinations can be affected if the sample volume is less than 50 % of sample container capacity.

8.4 Erroneously high flash points may be obtained if precautions are not taken to avoid the loss of volatile material. Do not open containers unnecessarily, to prevent loss of volatile material or possible introduction of moisture, or both. Avoid storage of samples at temperatures in excess of 35°C or 95°F. Samples for storage shall be capped tightly with inner seals. Do not make a transfer unless the sample temperature is at least the equivalent of 18°C or 32°F below the expected flash point.

8.5 Do not store samples in gas-permeable containers, since volatile material may diffuse through the walls of the enclosure. Samples in leaky containers are suspect and not a source of valid results.

8.6 Samples of very viscous materials shall be heated in their containers, with lid/cap slightly loosened to avoid buildup of dangerous pressure, at the lowest temperature adequate to liquefy any solids, not exceeding 28°C or 50°F below the expected flash point, for 30 min. If the sample is then not completely liquefied, extend the heating period for additional 30 min periods as necessary. Then gently agitate the sample to provide mixing, such as orbiting the container horizontally, before transferring to the specimen cup. No sample shall be heated and transferred unless its temperatures is more than 18°C or 32°F below its expected flash point. When the sample has been heated above this temperature, allow the sample to cool until its temperature is at least 18°C or 32°F below the expected flash point before transferring.

NOTE 3—Volatile vapors can escape during heating when the sample container is not properly sealed.

NOTE 4—Some viscous samples may not completely liquefy even after prolonged periods of heating. Care should be exercised when increasing the heating temperature to avoid unnecessary loss of volatile vapors, or heating the sample too close to the flash point.

8.7 Samples containing dissolved or free water may be dehydrated with calcium chloride or by filtering through a qualitative filter paper or a loose plug of dry absorbent cotton. Warming the sample is permitted, but it shall not be heated for prolonged periods or greater than a temperature of 18°C 32°F below its expected flash point.

NOTE 5—If the sample is suspected of containing volatile contaminants, the treatment described in 8.6 and 8.7 should be omitted.

9. Preparation of Apparatus

9.1 Support the manual or automated apparatus on a level steady surface, such as a table.

9.2 Tests are to be performed in a draft-free room or compartment. Tests made in a laboratory hood or in any location where drafts occur are not reliable.

NOTE 6—A shield, of the approximate dimensions 460 mm (18 in.) square and 610 mm (24 in.) high, or other suitable dimensions, and having an open front is recommended to prevent drafts from disturbing the vapors above the test cup.

NOTE 7—With some samples whose vapors or products of pyrolysis are objectionable, it is permissible to place the apparatus along with a draft shield in a ventilation hood, the draft of which is adjustable so that vapors can be withdrawn without causing air currents over the test cup during the ignition source application period.

9.3 Prepare the manual apparatus or the automated apparatus for operation in accordance with the manufacturer's instructions for calibrating, checking, and operating the equipment. (**Warning—**Gas pressure should not be allowed to exceed 3 kPa (12 in.) of water pressure.)

9.4 Thoroughly clean and dry all parts of the test cup and its accessories before starting the test, to ensure the removal of any solvent which had been used to clean the apparatus. Use suitable solvent capable of removing all of the specimen from the test cup and drying the test cup and cover. Some commonly used solvents are toluene and acetone. (**Warning—**Toluene, acetone, and many solvents are flammable. Health hazard. Dispose of solvents and waste material in accordance with local regulations.)

10. Verification of Apparatus

10.1 Adjust the automated flash point detection system (when used) in accordance with the manufacturer's instructions.

10.2 Verify that the temperature measuring device is in accordance with 6.3.

10.3 Verify the performance of the manual apparatus or the automated apparatus at least once per year by determining the flash point of a certified reference material (CRM) such as those listed in Annex A4, which is reasonably close to the expected temperature range of the samples to be tested. The material shall be tested according to Procedure A of these test methods and the observed flash point obtained in 11.1.8 or 11.2.2 shall be corrected for barometric pressure (see Section 13). The flash point obtained shall be within the limits stated in Table A4.1 for the identified CRM or within the limits calculated for an unlisted CRM (see Annex A4).

10.4 Once the performance of the apparatus has been verified, the flash point of secondary working standards (SWSs) can be determined along with their control limits. These secondary materials can then be utilized for more frequent performance checks (see Annex A4).

10.5 When the flash point obtained is not within the limits stated in 10.3 or 10.4, check the condition and operation of the apparatus to ensure conformity with the details listed in Annex A1, especially with regard to tightness of the lid (A1.1.2.2), the action of the shutter, the position of the ignition source (A1.1.2.3), and the angle and position of the temperature measuring device (A1.1.2.4). After any adjustment, repeat the test in 10.3 using a fresh test specimen, with special attention to the procedural details prescribed in these test methods.

PROCEDURE A

11. Procedure

11.1 *Manual Apparatus*:

11.1.1 Ensure that the sample container is filled to the volume capacity requirement specified in 8.2. Fill the test cup with the test specimen to the filling mark inside of the test cup. The temperature of the test cup and test specimen shall be at least 18°C or 32°F below the expected flash point. If too much test specimen has been added to the test cup, remove the excess using a syringe or similar device for withdrawal of fluid. Place the test cover on the test cup and place the assembly into the apparatus. Be sure the locating or locking device is properly engaged. If the temperature measuring device is not already in place, insert the device into its holder.

11.1.2 Light the test flame, and adjust it to a diameter of 3.2 to 4.8 mm (0.126 to 0.189 in.), or switch on the electric igniter and adjust the intensity in accordance with the manufacturer's instructions. (**Warning—**Gas pressure should not be allowed to exceed 3 kPa (12 in.) of water pressure.) (**Warning—**Exercise care when using a gas test flame. If it should be extinguished it will not ignite the vapors in the test cup, and the gas for the test flame that then enters the vapor space can influence the result.) (**Warning—**The operator should exercise and take appropriate safety precautions during the initial application of the ignition source, since test specimens containing low-flash material can give an abnormally strong flash when the ignition source is first applied.) (**Warning—**The operator should exercise and take appropriate safety precautions during the performance of these test methods. The temperatures attained during these test methods, up to 370°C (698°F), are considered hazardous.)

11.1.3 Apply the heat at such a rate that the temperature, as indicated by the temperature measuring device, increases 5 to 6°C (9 to 11°F)/min.

11.1.4 Turn the stirring device at 90 to 120 rpm, stirring in a downward direction. (**Warning—**Meticulous attention to all details relating to the ignition source, size of test flame or intensity of the electric ignitor, rate of temperature increase, and rate of dipping the ignition source into the vapor of the test specimen is desirable for good results.)

11.1.5 *Application of Ignition Source*:

11.1.5.1 If the test specimen is expected to have a flash point of 110°C or 230°F or below, apply the ignition source when the temperature of the test specimen is 23 ± 5°C or 41 ± 9°F below the expected flash point and each time thereafter at a temperature reading that is a multiple of 1°C or 2°F. Discontinue the stirring of the test specimen and apply the ignition source by operating the mechanism on the test cover which controls the shutter so that the ignition source is lowered into the vapor space of the test cup in 0.5 s, left in its lowered position for 1 s, and quickly raised to its upward position.

11.1.5.2 If the test specimen is expected to have a flash point above 110°C or 230°F, apply the ignition source in the manner described in 11.1.5.1 at each temperature increase of 2°C or 5°F, beginning at a temperature of 23 ± 5°C or 41 ± 9°F below the expected flash point.

11.1.6 When testing materials to determine if volatile material contamination is present, it is not necessary to adhere to the temperature limits for initial ignition source application as stated in 11.1.5.

11.1.7 When testing materials where the expected flash point temperature is not known, bring the material to be tested and the tester to a temperature of 15 ± 5°C or 60 ± 10°F. When the material is known to be very viscous at this temperature, heat the specimen to a starting temperature as described in 8.6. Apply the ignition source, in the manner described in 11.1.5.1, beginning at least 5°C or 10°F higher than the starting temperature.

NOTE 8—Flash Point results determined in an "unknown expected flash point mode" should be considered approximate. This value can be used as the expected flash point when a fresh specimen is tested in the standard mode of operation.

11.1.8 Record as the observed flash point the reading on the temperature measuring device at the time ignition source application causes a distinct flash in the interior of the test cup. The sample is deemed to have flashed when a large flame appears and instantaneously propagates itself over the entire surface of the test specimen. (**Warning—**For certain mixtures containing halogenated hydrocarbons, such as, methylene chloride or trichloroethylene, no distinct flash, as defined, is observed. Instead a significant enlargement of the test flame (not halo effect) and change in color of the test flame from blue to yellowish-orange occurs. Continued heating and testing of these samples above ambient temperature can result in significant burning of vapors outside the test cup, and can be a potential fire hazard. See Appendix X1 and Appendix X2 for more information.)

11.1.9 When the ignition source is a test flame, the application of the test flame may cause a blue halo or an enlarged flame prior to the actual flash point. This is not a flash and shall be ignored.

11.1.10 When a flash point is detected on the first application, the test shall be discontinued, the result discarded, and the test repeated with a fresh test specimen. The first application of the ignition source with the fresh test specimen shall be 23 ± 5°C or 41 ± 9°F below the temperature at which a flash point was detected on the first application.

11.1.11 When a flash point is detected at a temperature which is greater than 28°C or 50°F above the temperature of the first application of the ignition source, or when a flash point is detected at a temperature which is less than 18°C or 32°F above the temperature of the first application of the ignition source, the result shall be considered approximate, and the test repeated with a fresh test specimen. Adjust the expected flash point for this next test to the temperature of the approximate result. The first application of the ignition source with the fresh test specimen shall be 23 ± 5°C or 41± 9°F below the temperature at which the approximate result was found.

11.1.12 When the apparatus has cooled down to a safe handling temperature, less than 55°C (130°F), remove the test cover and the test cup and clean the apparatus as recommended by the manufacturer.

NOTE 9—Exercise care when cleaning and positioning the lid assembly so not to damage or dislocate the flash detection system or temperature measuring device. See the manufacturer's instructions for proper care and maintenance.

11.2 *Automated Apparatus*:

11.2.1 The automated apparatus shall be capable of performing the procedure as described in 11.1, including control of the heating rate, stirring of the test specimen, application of the ignition source, detection of the flash point, and recording the flash point.

11.2.2 Start the automated apparatus in accordance with the manufacturer's instructions. The apparatus shall follow the procedural details described in 11.1.3 through 11.1.8.

PROCEDURE B

12. Procedure

12.1 *Manual Apparatus*:

12.1.1 Ensure that the sample container is filled to the volume capacity requirement specified in 8.2. Fill the test cup with the test specimen to the filling mark inside of the test cup. The temperature of the test cup and test specimen shall be at least 18°C or 32°F below the expected flash point. If too much test specimen has been added to the test cup, remove the excess using a syringe or similar device for withdrawal of fluid. Place the test cover on the test cup and place the assembly into the apparatus. Be sure the locating or locking device is properly engaged. If the temperature measuring device is not already in place, insert the device into its holder.

12.1.2 Light the test flame and adjust it to a diameter of 3.2 to 4.8 mm (0.126 to 0.189 in.), or switch on the electric igniter and adjust the intensity in accordance with the manufacturer's instructions. (**Warning—**Gas pressure should not be allowed to exceed 3 kPa (12 in.) of water pressure.) (**Warning—**Exercise care when using a gas test flame. If it should be extinguished it will not ignite the vapors in the test cup and the gas for the test flame that then enters the vapor space can influence the result.) (**Warning—**The operator should exercise and take appropriate safety precautions during the initial application of the ignition source, since test specimens containing low-flash material may give an abnormally strong flash when the ignition source is first applied.) (**Warning—**The operator should exercise and take appropriate safety precautions during the performance of these test methods. The temperatures attained during these test methods, up to 370°C (698°F), are considered hazardous.)

12.1.3 Turn the stirring device at 250 ± 10 rpm, stirring in a downward direction.

12.1.4 Apply the heat at such a rate that the temperature as indicated by the temperature measuring device increases 1 to 1.6°C (2 to 3°F)/min.

12.1.5 Proceed as prescribed in Section 11, with the exception of the preceding requirements for rates of stirring and heating.

12.2 *Automated Apparatus*:

12.2.1 The automated apparatus shall be capable of performing the procedure as described in 12.1, including control of the heating rate, stirring of the test specimen, application of the ignition source, detection of the flash point, and recording the flash point.

12.2.2 Start the automated apparatus in accordance with the manufacturer's instructions. The apparatus shall follow the procedural details in accordance with 12.1.3 through 12.1.5.

PRECISION, CALCULATION, AND REPORT FOR PROCEDURES A AND B

13. Calculation

13.1 Observe and record the ambient barometric pressure (see Note 10) at the time of the test. When the pressure differs from 101.3 kPa (760 mm Hg), correct the flash point as follows:

$$\text{Corrected flash point} = C + 0.25\,(101.3 - K) \qquad (1)$$

$$\text{Corrected flash point} = F + 0.06\,(760 - P) \qquad (2)$$

$$\text{Corrected flash point} = C + 0.033\,(760 - P) \qquad (3)$$

where:

C = observed flash point, °C,
F = observed flash point, °F,
P = ambient barometric pressure, mm Hg, and
K = ambient barometric pressure, kPa.

NOTE 10—The barometric pressure used in this calculation is the ambient pressure for the laboratory at the time of the test. Many aneroid barometers, such as those used at weather stations and airports, are precorrected to give sea level readings and would not give the correct reading for this test.

13.2 After correction for barometric pressure, round the temperature to the nearest 0.5°C (1°F) and record.

14. Report

14.1 Report the corrected flash point as the ASTM D 93–IP 34, Procedure A or Procedure B Pensky-Martens Closed Cup Flash Point of the test specimen.

15. Precision and Bias (Procedure A)

15.1 *Precision*—The precision of this procedure as determined by the statistical examination of the interlaboratory test results, is as follows:

15.1.1 *Repeatability*—The difference between successive results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values in 1 case in 20.

$$r = AX, \tag{4}$$

$A = 0.029$,

X = mean result in °C, and

r = repeatability.

15.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in 1 case in 20.

$$R = BX, \tag{5}$$

$B = 0.071$,

X = mean result in °C, and

R = reproducibility.

15.1.3 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in these test methods, bias has not been determined.

15.1.4 *Relative Bias*—Statistical evaluation of the data did not detect any significant difference between the reproducibility variances of manual and automated Pensky-Martens flash point results for the samples studied. Evaluation of the data did not detect any significant difference between averages of manual and automated Pensky-Martens flash point for the samples studied with the exception of cycle oil and fuel oil which showed some bias. In any case of dispute, the manual procedure shall be considered the referee test.

NOTE 11—The precision statements were derived on clear liquids only. Refer to the research report[10] for information regarding relative bias and types of samples. Additional studies are in progress concerning relative bias.

15.1.5 The precision data were developed from a combined 1991 ASTM cooperative test program[10] using 5 samples of fuel and lubricating oils (Twelve laboratories participated with the manual apparatus and 21 laboratories participated with the automated equipment) and a 1994 IP cooperative test program using 12 fuel samples and 4 pure chemicals. (Twenty-six laboratories participated with manual and automated equipment. The apparatus used either a gas test flame or an electric resistance (hot wire) device for the ignition source. Information on the type of samples and their average flash point are in the research report.[10]

16. Precision and Bias (Procedure B)

16.1 *Precision*—The precision of this procedure as determined by the statistical examination of the interlaboratory test results, is as follows:

16.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the following value in 1 case in 20:

Residual fuel oil 2°C (5°F)
Other types 5°C (9°F) (6)

16.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical material would, in the long run, exceed the following value only in 1 case in 20.

Residual fuel oil 6°C (12°F)
Other types 10°C (18°F) (7)

16.1.3 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in these test methods, bias has not been determined.

16.1.4 The precision data for residual fuel oils were developed in a 1996 cooperative test program conducted by the IP using 12 samples of residual fuel and 40 laboratories worldwide using both the manual and automated apparatus. Information on the type of samples and their average flash point are in the research report.

16.1.5 The precision data for other sample types in Procedure B is not known to have been developed in accordance with RR:D02–1007.[11]

NOTE 12—Procedure B was not tested in the 1991 interlaboratory program.

17. Keywords

17.1 automated flash point; automated Pensky-Martens closed cup; flammability; flash point; Pensky-Martens closed cup

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[10] Supporting data (the results of the 1991 interlaboratory cooperative test program) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: S15–1008.

[11] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02–1007.

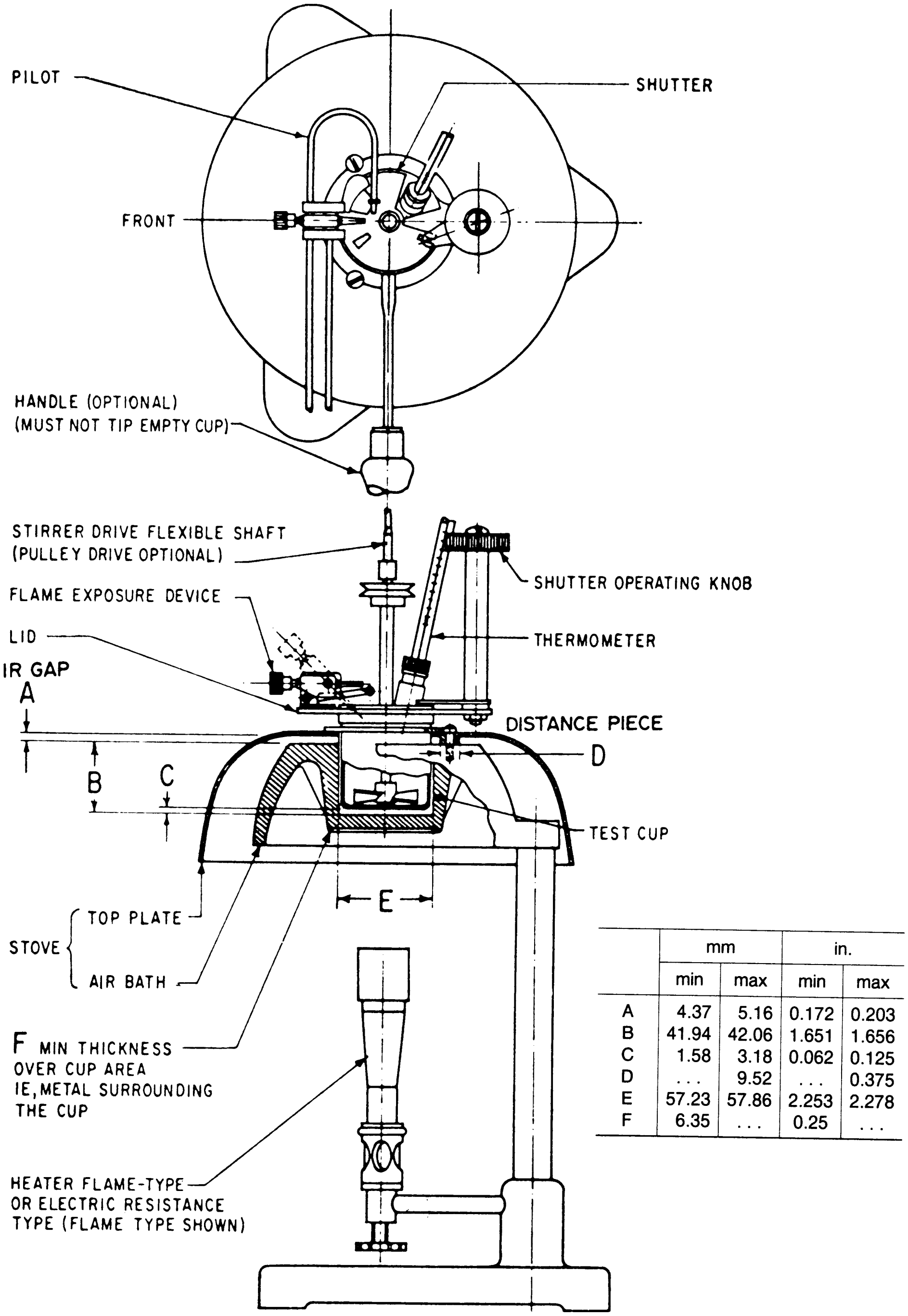
ANNEXES

(Mandatory Information)

A1. APPARATUS SPECIFICATIONS

A1.1 A typical assembly of the apparatus, gas heated, is shown in Fig. A1.1. The apparatus shall consist of a test cup, cover, and stove conforming to the following requirements:

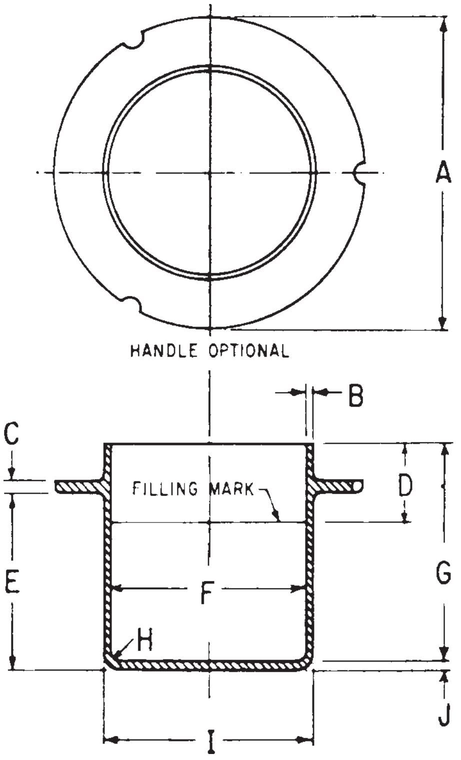
A1.1.1 *Cup*—The cup shall be of brass, or other nonrusting metal of equivalent heat conductivity, and shall conform to the dimensional requirements in Fig. A1.2. The flange shall be



	mm		in.	
	min	max	min	max
A	4.37	5.16	0.172	0.203
B	41.94	42.06	1.651	1.656
C	1.58	3.18	0.062	0.125
D	. . .	9.52	. . .	0.375
E	57.23	57.86	2.253	2.278
F	6.35	. . .	0.25	. . .

NOTE 1—Lid assembly can be positioned either right or left-handed.

FIG. A1.1 Pensky-Martens Closed Flash Tester



	mm		(in.)	
	min	max	(min)	(max)
A	79.0	79.8	(3.11)	(3.14)
B	1.0	...	(0.04)	(...)
C	2.8	3.6	(0.11)	(0.14)
D	21.72	21.84	(0.855)	(0.860)
E	45.47	45.72	(1.790)	(1.800)
F	50.72	50.85	(1.997)	(2.002)
G	55.75	56.00	(2.195)	(2.205)
H	3.8	4.0	(0.15)	(0.16)
I	53.90	54.02	(2.122)	(2.127)
J	2.29	2.54	(0.090)	(0.100)

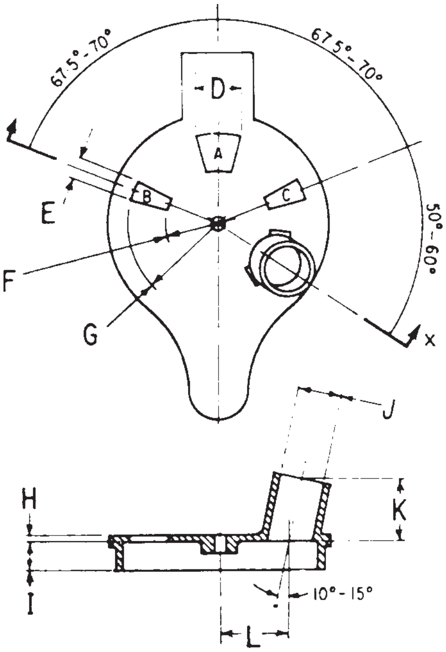
FIG. A1.2 Test Cup

equipped with devices for locating the position of the cup in the stove. A handle attached to the flange of the cup is a desirable accessory. The handle shall not be so heavy as to tip over the empty cup.

A1.1.2 *Cover*:

A1.1.2.1 *Cover Proper*—The cover shown in Fig. A1.3 shall be of brass (A1.1.1) and shall have a rim projecting downward almost to the flange of the cup. The rim shall fit the outside of the cup with a clearance not exceeding 0.36 mm (0.014 in.) on the diameter. There shall be a locating or locking device, or both, engaging with a corresponding device on the cup. The four openings in the cover, *A*, *B*, *C*, and *D*, are shown in Fig. A1.3. The upper edge of the cup shall be in close contact with the inner face of the cover throughout its circumference.

A1.1.2.2 *Shutter*—The cover shall be equipped with a brass shutter (Fig. A1.1 and Fig. A1.4), approximately 2.4 mm (3/32 in.) thick, operating on the plane of the upper surface of the cover. The shutter shall be so shaped and mounted that it rotates on the axis of the horizontal center of the cover between two stops, so placed, that when in one extreme position, the openings *A*, *B*, and *C* in the cover are completely closed, and when in the other extreme position, these openings are completely opened. The mechanism operating the shutter should be of the spring type and constructed so that when at rest the shutter shall exactly close the three openings. When operated to the other extreme, the three cover openings shall be exactly open and the tip of the exposure tube shall be fully depressed.

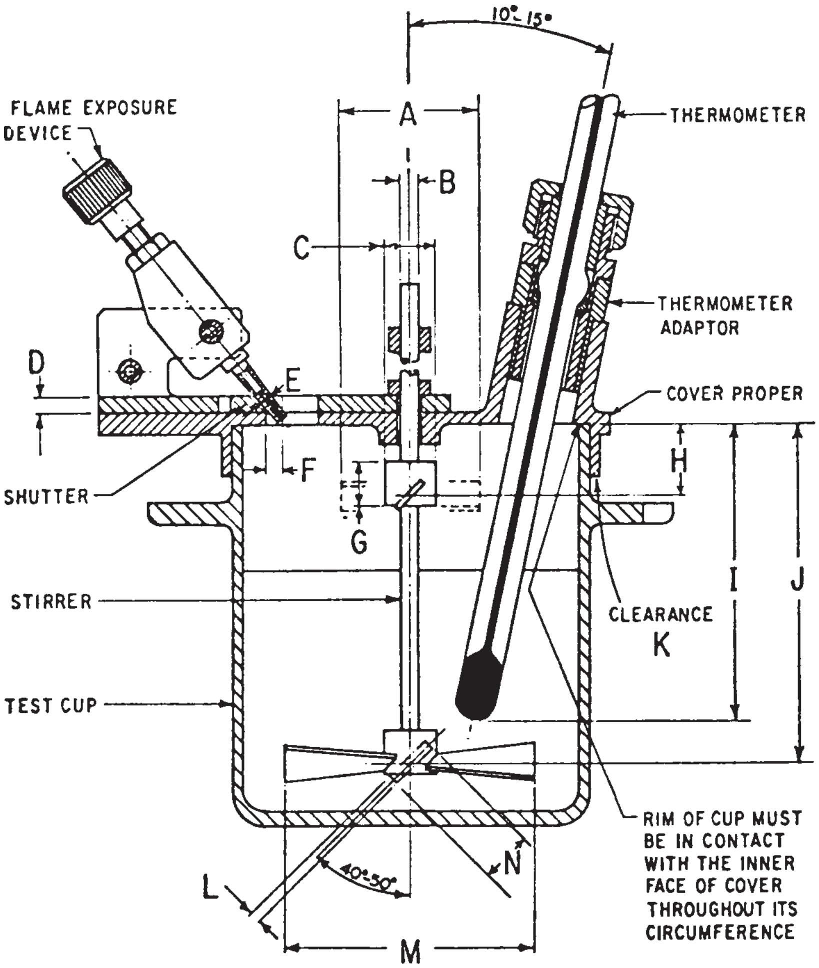


	mm		(in.)	
	min	max	(min)	(max)
D	12.7	13.5	(0.50)	(0.53)
E	4.8	5.6	(0.19)	(0.22)
F	13.5	14.3	(0.53)	(0.56)
G	23.8	24.6	(0.94)	(0.97)
H	1.2	2.0	(0.05)	(0.08)
I	7.9	...	(0.31)	(...)
J	12.00	12.32	(0.472)	(0.485)
K	16.38	17.00	(0.645)	(0.669)
L	18.65	19.45	(0.734)	(0.766)

FIG. A1.3 Cover Proper

A1.1.2.3 *Flame-Ignition Device*—The flame-ignition device (Fig. A1.4) shall have a tip with an opening 0.69 to 0.79 mm (0.027 to 0.031 in.) in diameter. This tip shall be made preferably of stainless steel, although it may be fabricated of other suitable metals. The flame-exposure device shall be equipped with an operating mechanism which, when the shutter is in the open position, depresses the tip so that the center of the orifice is between the planes of the under and upper surfaces of the cover proper at a point on a radius passing through the center of the larger opening *A* (Fig. A1.3). An electric ignitor is also suitable. The electric ignitors shall be of the electric resistance (hot-wire) type and shall position the heated section of the ignitor in the aperture of the test cover in the same manner as the gas flame device.

A1.1.2.4 *Pilot Flame*—A pilot flame shall be provided for automatic relighting of the exposure flame. A bead 4 mm (5/32 in.) in diameter can be mounted on the cover so that the



	mm		(in.)	
	min	max	(min)	(max)
A	18.3	19.8	(0.72)	(0.78)
B	2.38	3.18	(0.094)	(0.125)
C	7.6	8.4	(0.30)	(0.33)
D	2.0	2.8	(0.08)	(0.11)
E	0.69	0.79	(0.027)	(0.031)
F	2.0	2.8	(0.08)	(0.11)
G	6.4	10.4	(0.25)	(0.41)
H	9.6	11.2	(0.38)	(0.44)
I[A]	43.0	46.0	(1.69)	(1.81)
J	50.0	51.6	(1.97)	(2.03)
K	...	0.36	(...)	(0.014)
L	1.22	2.06	(0.048)	(0.08)
M	31.8	44.4	(1.25)	(1.75)
N	7.6	8.4	(0.30)	(0.33)

[A] Includes tolerance for length of thermometer given in Specification E 1.

FIG. A1.4 Test Cup and Cover Assembly

size of the test flame can be regulated by comparison. The tip of the pilot flame shall have an opening the same size as the tip of the flame exposure device (0.69 to 0.79 mm (0.027 to 0.031 in.) in diameter).

A1.1.2.5 *Stirring Device*—The cover shall be equipped with a stirring device (Fig. A1.4) mounted in the center of the cover and carrying two 2-bladed metal propellers. In Fig. A1.4 lower propeller is designated by the letters *L*, *M*, and *N*. This propeller shall measure approximately 38 mm from tip to tip, with each of its two blades 8 mm in width with a pitch of 45°. The upper propeller is designated by the letters *A*, *C*, and *G*. This propeller measures approximately 19 mm, tip to tip, each of its two blades is also 8 mm in width with a pitch of 45°. Both propellers are located on the stirrer shaft in such a manner that, when viewed from the bottom of the stirrer, the blades of one propeller are at 0 and 180° while the blades of the other propeller are at 90 and 270°. A stirrer shaft may be coupled to the motor by a flexible shaft or a suitable arrangement of pulleys.

A1.1.2.6 *Stove*—Heat shall be supplied to the cup by means of a properly designed stove which is equivalent to an air bath. The stove shall consist of an air bath and a top plate on which the flange of the cup rests.

A1.1.2.7 *Air Bath*—The air bath shall have a cylindrical interior and shall conform to the dimensional requirements in Fig. A1.1. The air bath may be either a flame or electrically heated metal casting (A1.1.2.8), or an electric-resistance element (A1.1.2.9). In either case, the air bath must be suitable for use at the temperatures to which it will be subjected without deformation.

A1.1.2.8 *Heater, Flame or Electric*—If the heating element is a flame or an electric heater, it shall be so designed and used that the temperatures of the bottom and the walls are approximately the same. In order that the air bath internal surfaces should be at a uniform temperature, it should not be less than 6.4 mm (¼ in.) in thickness unless the heating element is designed to give equal heat flux densities over all the wall and bottom surfaces.

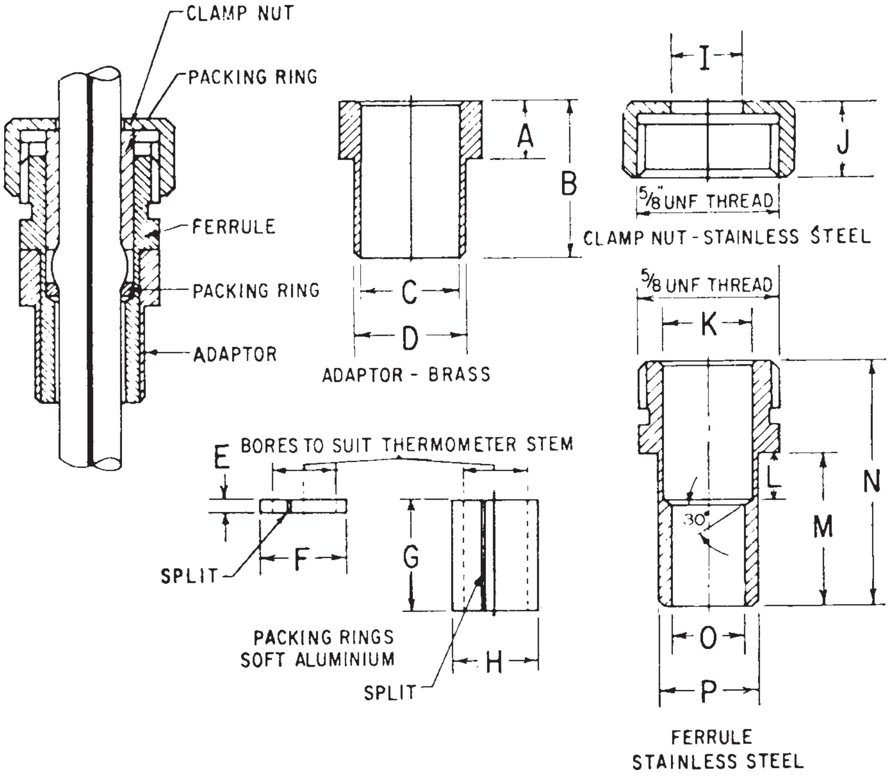
A1.1.2.9 *Heater, Electric Resistance*—If the heater is of the electric resistance type, it shall be constructed so that all parts of the interior surface are heated uniformly. The wall and bottom of the air bath shall not be less than 6.4 mm (¼ in.) in thickness unless the resistance heating elements are distributed over at least 80 % of the wall and all the bottom of the air bath. A heater having such a distribution of the heating elements positioned at least 4.0 mm (5⁄32 in.) away from the internal surface of the heating unit can be used in conjunction with a minimum thickness of 1.58 mm (1⁄16 in.) for the wall and bottom of the air bath.

A1.1.2.10 *Top Plate*—The top plate shall be of metal, and shall be mounted with an air gap between it and the air bath. It may be attached to the air bath by means of three screws and spacing bushings. The bushings should be of proper thickness to define an air gap of 4.8 mm (3⁄16 in.), and they shall be not more than 9.5 mm (⅜ in.) in diameter.

A2. MANUFACTURING STANDARDIZATION OF THERMOMETER AND FERRULE

A2.1 The low-range thermometer, which conforms also to the specification for the cup thermometer in the tag closed tester (Test Method D 56) and which frequently is fitted with a metal ferrule intended to fit the collar on the cover of the tag flash tester, can be supplemented by an adapter (Fig. A2.1) to be used in the larger diameter collar of the Pensky-Martens apparatus. Differences in dimensions of these collars, which do not affect test results, are a source of unnecessary trouble to manufacturers and suppliers of instruments, as well as to users.

A2.2 Dimensional requirements are shown in Fig. A2.1. Conformity to these requirements is not mandatory, but is desirable to users as well as suppliers of Pensky-Martens testers.



	mm		(in.)	
	min	max	(min)	(max)
A	6.20	6.50	(0.244)	(0.256)
B	17.0	18.0	(0.67)	(0.71)
C	9.80	9.85	(0.386)	(0.388)
D	11.92	12.24	(0.469)	(0.482)
E	1.40	1.65	(0.055)	(0.065)
F	8.56	8.61	(0.337)	(0.339)
G	12.4	13.0	(0.49)	(0.57)
H	8.56	8.61	(0.337)	(0.339)
I	8.1	8.6	(0.32)	(0.34)
J	9.9	10.7	(0.39)	(0.42)
K	8.64	8.69	(0.340)	(0.342)
L	5.1	5.6	(0.20)	(0.22)
M	17.0	17.5	(0.67)	(0.69)
N	27.4	28.2	(1.08)	(1.11)
O	7.11	7.16	(0.280)	(0.282)
P	9.73	9.78	(0.383)	(0.385)

FIG. A2.1 Dimensions for Thermometer Adapter, Ferrule, and Packing Ring

A3. THERMOMETER SPECIFICATIONS

A3.1 See Fig. A3.1 and Tables A3.1-A3.4.

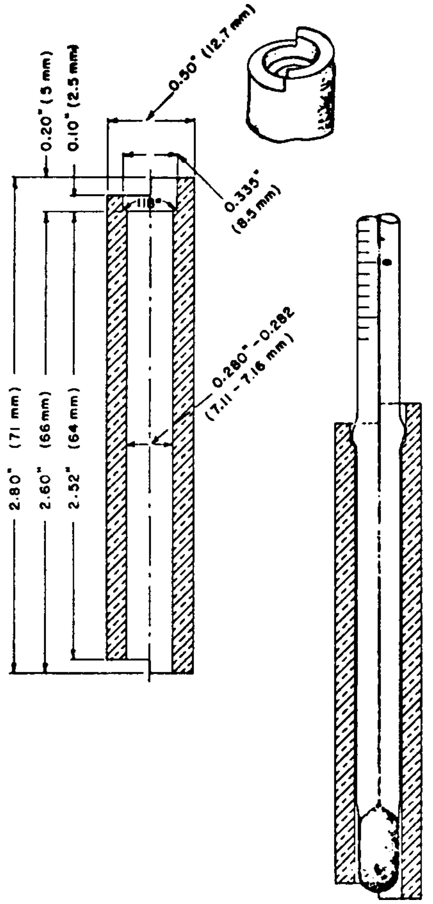


FIG. A3.1 Test Gage for Checking Enlargements on Thermometers

TABLE A3.1 IP Thermometer Specifications

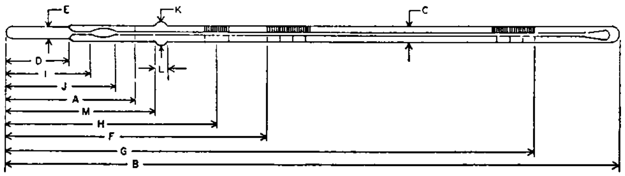
NOTE—The stem shall be made with an enlargement having a diameter of 1.5 to 2.0 mm greater than the stem and a length of 3 to 5 mm, the bottom of the enlargement being 64 to 66 mm from the bottom of the bulb. These dimensions shall be measured with the test gage shown in Fig. A3.1.

Name	IP 15C	IP 16C	IP 101C
	Pensky-Martens Low	Pensky-Martens High	Pensky-Martens Medium
Range	−5 to + 110°C	90 to 370°C	20 to 150°C
Graduation	0.5°C	2°C	1°C
Immersion, mm	57	57	57
Overall length ±5 mm	290	280 ± 10	290
Stem diameter, mm	6.0 to 7.0	6.0 to 7.0	6.0 to 7.0
Bulb shape	cylindrical	cylindrical	cylindrical
Bulb length, mm	9 to 13	7 to 10	9 to 13
Bulb diameter, mm	not less than 5.5 and not greater than stem	not less than 4.5 and not greater than stem	not less than 5.5 and not greater than stem
Length of graduated portion, mm	140 to 175	143 to 180	140 to 175
Distance bottom of bulb to, mm	0°C 85 to 95	90°C 80 to 90	20°C 85 to 95
Longer lines at each	1 and 5°C	10 and 20°C	5°C
Figured at each	5°C	20°C	5°C
Expansion chamber	required	required	required
Top finish	ring	ring	ring
Scale error not to exceed ±	0.5°C	1 to 260°C 2°C above 260°C	1°C
See notes	1 and Table A3.2 for emergent stem temperatures	1 and Table A3.2 for emergent stem temperatures	1 and Table A3.2 for emergent stem temperatures

TABLE A3.2 Specifications for ASTM Thermometers

All dimensions are in millimetres.

See Table A3.3 for Standardization Temperature.



ASTM Number and Name	Range	For Test at	Immersion	Graduations			Scale Error, max	Special Inscription	Expansion Chamber	Total Length ±5	Stem OD	Bulb		Scale Location				Ice Point Scale		Contraction Chamber		Stem Enlargement		
				Subdivisions	Long Lines at Each	Number at Each			Permit Heating to			Length	OD	Bottom of Bulb to Line at	Distance	Bottom of Bulb to Line at	Distance	Range	Bottom of Bulb to Ice Point	Distance to Bottom, min	Distance to Top, max	OD	Length	Distance to Bottom
										B	C	D	E		F		G	H		I	J	K	L	M
9C-62 Pensky-Martens Low-Range Tag Closed Tester 9F-62	–5 to +110°C (20 to 230°F)		57	0.5°C 1°F	1°C 5°F	5°C 10°F	0.5°C 1°F	ASTM 9C or 9F 57 mm IMM	160°C 320°F	287	6.0 to 7.0	9.0 to 13	not greater than stem	0°C 32°F	85 to 98	100°C 212°F	221 to 237					7.5 to 8.5	2.5 to 5.0[A]	64 to 66
10C-62 Pensky-Martens, High-Range 10F-62	90 to 370°C (200 to 700°F)		57	2°C 5°F	10°C 25°F	20°C 50°F	[B] [D]	ASTM 10C or 10F 57 mm IMM	[C]	287	6.0 to 7.0	8.0 to 10.0	4.5 to 6.0	110°C 230°F	86 to 99	360°C 680°F	227 to 245					7.5 to 8.5	2.5 to 5.0[A]	64 to 66

[A] The length of the enlargement, and the distance from the bottom of the enlargement to the bottom of the bulb shall be measured with the test gage shown in Fig. A3.1.

[B] Scale error: 1°C up to 260°C; 2°C over 260°C.

[C] An expansion chamber is provided for relief of gas pressure to avoid distortion of the bulb at higher temperatures. It is not for the purpose of joining mercury separations; and under no circumstances should the thermometer be heated above the highest temperature reading.

[D] Scale error: 2.5°F up to 500°F; 3.5°F over 500°F.

TABLE A3.3 Standardization Temperatures

NOTE—The emergent column temperatures are those attained when using the thermometers in the test equipment for which the thermometers were originally designed. In some cases these temperatures are markedly different from those realized during standardization.

Temperature	Average Temperature of Emergent Column	Temperature	Average Temperature of Emergent Column	Temperature	Average Temperature of Emergent Column	Temperature	Average Temperature of Emergent Column
Thermometer 9C (−5 to + 100°C)		Thermometer 9F (20 to 230°F)		Thermometer 10C (90 to 370°C)		Thermometer 10F (200 to 700°F)	
0°C	19°C	32°F	66°F	100°C	61°C	212°F	141°F
35°C	28°C	100°F	86°F	200°C	71°C	390°F	159°F
70°C	40°C	160°F	106°F	300°C	87°C	570°F	180°F
105°C	50°C	220°F	123°F	370°C	104°C	700°F	220°F
IP 15C (−7 to 110°C)		IP 15F (20 to 230°F)		IP 16C (90 to 370°C)		IP 16F (20 to 700°F)	
0°C	19°C	32°F	66°F	100°C	61°C	200°F	140°F
20°C	20°C	70°F	70°F	150°C	65°C	300°F	149°F
40°C	31°C	100°F	86°F	200°C	71°C	400°F	160°F
70°C	40°C	150°F	104°F	250°C	78°C	500°F	175°F
100°C	48°C	212°F	118°F	300°C	87°C	600°F	195°F
				350°C	99°C	700°F	220°F

TABLE A3.4 Specifications for Medium-Range Pensky-Martens

ASTM No. 88F (88C) Vegetable Oil Flash Thermometer				
Name			Medium-Range Pensky-Martens	
Reference Fig. No.			5	
Range		10–200°C		50–392°F
For test at				
A	Immersion, mm		57	
	Graduations:			
	Subdivisions	0.5°C		1°F
	Long lines at each	1°C and 5°C		5°F
	Numbers at each	5°C		10°F
	Scale error, max	0.5°C		1°F
	Special inscription		ASTM 88F (88C) 57 mm IMM	
	Expansion chamber:			
	Permit heating to	205°C		400°F
B	Total length, mm		285 to 295	
C	Stem OD, mm		6.0 to 7.0	
D	Bulb length, mm		8.0 to 12.0	
E	Bulb OD, mm		>4.5 and <stem[A]	
	Scale location:			
	Bottom of bulb to line at	20°C		68°F
F	Distance, mm		80 to 90	
G	Length of graduated portion, mm		145 to 180	
	Ice-point scale:			
	Range			
H	Bottom of bulb to ice-point, mm			
	Contraction chamber:			
I	Distance to bottom, min, mm			
J	Distance to top, max, mm			
	Stem enlargement:			
K	OD, mm		7.5 to 8.5	
L	Length, mm		2.5 to 5.0[A]	
M	Distance to bottom, mm		64 to 66	

[A] Bulb OD shall be greater than 4.5 mm and less than the outside diameter of the stem (C).

A4. VERIFICATION OF APPARATUS PERFORMANCE

A4.1 *Certified Reference Material (CRM)*—CRM is a stable, pure (99 + mole % purity) hydrocarbon or other stable petroleum product with a method-specific flash point established by a method-specific interlaboratory study following ASTM RR:D02-1007 guidelines[11] or ISO Guide 34 and 35.

A4.1.1 Values of the flash point corrected for barometric pressure for some reference materials and their typical limits are given in Table A4.1[12] (see Note A4.1). Suppliers of CRMs will provide certificates stating the method-specific flash point for each material of the current production batch. Calculation of the limits for these other CRMs can be determined from the reproducibility value of these test methods, reduced by interlaboratory effect and then multiplied by 0.7. See Research Report RR:S15-1008.[10]

TABLE A4.1 D 93 Typical Flash Point Values and Typical Limits for CRM

NOTE—Supporting data for the interlaboratory study to generate the flash point in Table A4.1 can be found in research report RR:S15-1010.[12]

Hydrocarbon	Purity, mole %	Flash Point,°C	Limits, °C
n–decane	99 +	52.8	±2.3
n–undecane	99 +	68.7	±3.0
n–tetradecane	99 +	109.3	±4.8
n–hexadecane	99 +	133.9	±5.9

NOTE A4.1—Materials, purities, flash point values, and limits stated in Table A4.1 were developed in an ASTM interlaboratory program to determine suitability of use for verification fluids in flash point test methods. Other materials, purities, flash point values, and limits can be suitable when produced according to the practices of ASTM RR:D02-1007 or ISO Guides 34 and 35. Certificates of performance of such materials should be consulted before use, as the flashpoint value will vary dependent on the composition of each CRM batch.

A4.2 *Secondary Working Standard (SWS)*—SWS is a stable, pure (99 + mole % purity) hydrocarbon, or other petroleum product whose composition is known to remain appreciably stable.

A4.2.1 Establish the mean flash point and the statistical control limits (3σ) for the SWS using standard statistical techniques. (See ASTM MNL 7).[13]

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[12] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: S15–1010.

[13] *Manual on Presentation of Data and Control Chart Analysis, ASTM MNL*, 6th ed., ASTM International, W. Conshohocken, 1990.

APPENDIXES

(Nonmandatory Information)

X1. FLASH POINT MASKING PHENOMENON

X1.1 A condition during flash point testing can occur with certain mixtures whereby the nonflammable component of the sample tends to inert the vapor space above the liquid, thus preventing a flash. Under this condition, the flash point of the material is masked resulting in the reporting of incorrect high flash point or no flash point.

X1.2 This flash point masking phenomenon most frequently occurs with ignitable liquids that contain certain halogenated hydrocarbons such as dichloromethane (methylene chloride) and trichloroethylene.

X1.3 Under this condition, no distinct flash as defined in 3.1.3 of these test methods is observed. Instead a significant enlargement of the test flame and a change in the color of the test flame from blue to yellow-orange laminar flame is observed.

X1.4 Under this condition, continued heating and testing for flash point at temperatures above ambient temperature, have resulted in significant burning of the ignitable vapor outside the test cup, often above the test flame. This can be a potential fire hazard if not recognized.

X1.5 It is recommended that if this condition is encountered during the flash point testing of these type of materials, testing should be discontinued.

X1.6 Further commentaries regarding flash point test and flammability of mixtures can be found in Test Method E 502.

X2. FLASH POINT TEST AND FLAMMABILITY OF MIXTURES

X2.1 While the flash point can be used to indicate the flammability of liquid materials for certain end uses, flash point does not represent the minimum temperature at which a material can evolve flammable vapors.

X2.2 There are instances with pure materials where the absence of a flash point does not ensure freedom from flammability. Included in this category are materials that require large diameters for flash propagation, such as trichloroethylene. This material will not propagate a flame in apparatus the size of a flash point tester, however, its vapors are flammable and will burn when ignited in apparatus of adequate size.

X2.3 When a liquid contains flammable and nonflammable components, there are cases where this liquid can evolve flammable vapors under certain conditions and yet will not exhibit a close-cup flash point. This phenomenon is noted when a nonflammable component is sufficiently volatile and present in sufficient quantity to inert the vapor space of the closed cup, thus preventing a flash. In addition, there are certain instances where an appreciable quantity of the nonflammable component will be present in the vapor, and the material will exhibit no flash point.

X2.4 Liquids containing a highly volatile nonflammable component or impurity, which exhibit no flash point because of the influence of the nonflammable material, may form flammable mixtures if totally flash vaporized in air in the proper proportions.

SUMMARY OF CHANGES

Subcommittee D02.08 has identified the location of selected changes to this standard since the last issue (D 93–02) that may impact the use of this standard.

(*1*) Added a paragraph to the Introduction about flash point values being dependent on the test procedure used.

(*2*) Deleted Note 2 and renumbered the notes.

Designation: D 97 – 05

An American National Standard

Designation: 15/95

Standard Test Method for Pour Point of Petroleum Products[1]

This standard is issued under the fixed designation D 97; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This test method is intended for use on any petroleum product.[2] A procedure suitable for black specimens, cylinder stock, and nondistillate fuel oil is described in 8.8. A procedure for testing the fluidity of a residual fuel oil at a specified temperature is described in Appendix X1.

1.2 Several ASTM test methods offering alternative procedures for determining pour points using automatic apparatus are available. None of them share the same designation number as Test Method D 97. When an automatic instrument is used, the ASTM test method designation number specific to the technique shall be reported with the results. A procedure for testing the pour point of crude oils is described in Test Method D 5853.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [3]

D 117 Guide for Sampling, Test Methods, and Specifications for Electrical Insulating Oils of Petroleum Origin

D 396 Specification for Fuel Oils

D 1659 Test Method for Maximum Fluidity Temperature of Residual Fuel Oil[4]

D 2500 Test Method for Cloud Point of Petroleum Products

D 3245 Test Method for Pumpability of Industrial Fuel Oils

D 5853 Test Method for Pour Point of Crude Oils

E 1 Specification for ASTM Liquid-in-Glass Thermometers

2.2 *Energy Institute Standards:*

Specifications for IP Standard Thermometers [5]

3. Terminology

3.1 *Definitions:*

3.1.1 *black oil*, *n*—lubricant containing asphaltic materials. Black oils are used in heavy-duty equipment applications, such as mining and quarrying, where extra adhesiveness is desired.

3.1.2 *cylinder stock*, *n*—lubricant for independently lubricated engine cylinders, such as those of steam engines and air compressors. Cylinder stock are also used for lubrication of valves and other elements in the cylinder area.

3.1.3 *pour point*, *n*—*in petroleum products*, the lowest temperature at which movement of the test specimen is observed under prescribed conditions of test.

3.1.4 *residual fuel*, *n*—a liquid fuel containing bottoms remaining from crude distillation or thermal cracking; sometimes referred to as heavy fuel oil.

3.1.4.1 *Discussion*—Residual fuels comprise Grades 4, 5, and 6 fuel oils, as defined in Specification D 396.

4. Summary of Test Method

4.1 After preliminary heating, the sample is cooled at a specified rate and examined at intervals of 3°C for flow characteristics. The lowest temperature at which movement of the specimen is observed is recorded as the pour point.

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.07 on Flow Properties.

Current edition approved June 1, 2005. Published July 2005. Originally approved in 1927, replacing D 47. Last previous edition approved in 2004 as D 97–04.

In the IP, this test method is under the jurisdiction of the Standardization Committee. This test method was adopted as a joint ASTM-IP Standard in 1965.

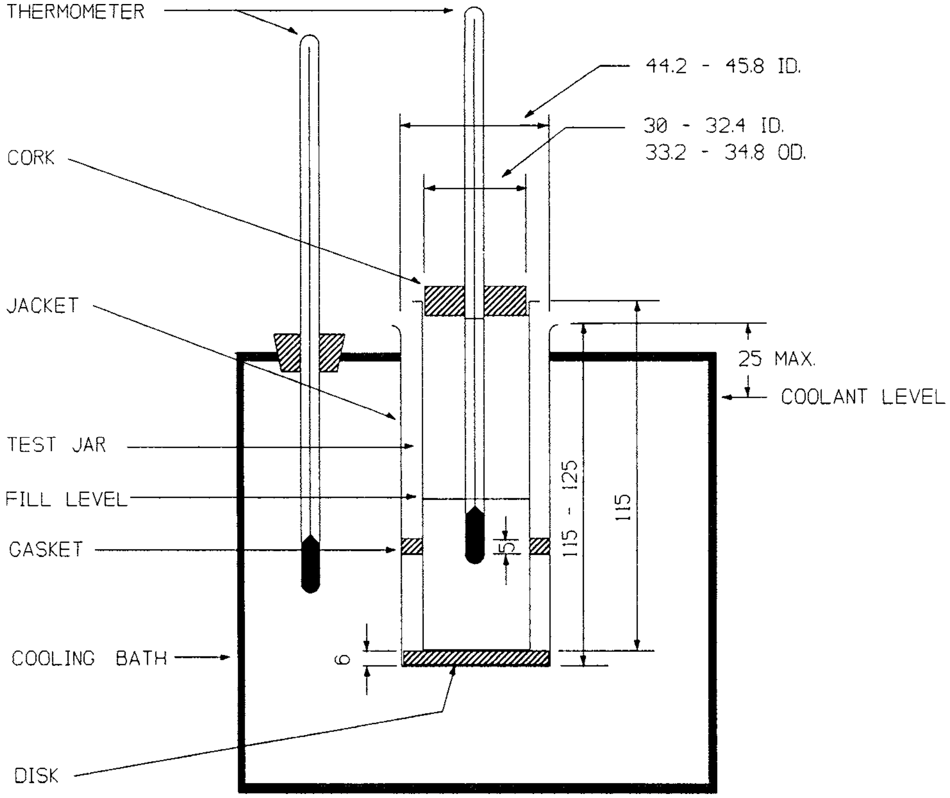
[2] Statements defining this test and its significance when applied to electrical insulating oils of mineral origin will be found in Guide D 117.

[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[4] Withdrawn.

[5] Methods for Analysis and Testing, *IP Standards for Petroleum and its Products*, Part I, Vol 2.

***A Summary of Changes section appears at the end of this standard.**



NOTE—Dimensions are in millimetres (not to scale).

FIG. 1 Apparatus for Pour Point Test

5. Significance and Use

5.1 The pour point of a petroleum specimen is an index of the lowest temperature of its utility for certain applications.

6. Apparatus

6.1 *Test Jar*, cylindrical, of clear glass, flat bottom, 33.2 to 34.8-mm outside diameter, and 115 to 125 mm in height. The inside diameter of the jar can range from 30.0 to 32.4 mm, within the constraint that the wall thickness be no greater than 1.6 mm. The jar shall have a line to indicate a sample height 54 ± 3 mm above the inside bottom. See Fig. 1.

6.2 *Thermometers*, having the following ranges and conforming to the requirements prescribed in Specification E 1 for thermometers:

Thermometer	Temperature Range	Thermometer Number ASTM	IP
High cloud and pour	−38 to +50°C	5C	1C
Low cloud and pour	−80 to +20°C	6C	2C
Melting point	+32 to +127°C	61C	63C

6.2.1 Since separation of liquid column thermometers occasionally occurs and may escape detection, thermometers should be checked immediately prior to the test and used only if they prove accurate within ±1°C (for example ice point).

6.3 *Cork*, to fit the test jar, bored centrally for the test thermometer.

6.4 *Jacket*, watertight, cylindrical, metal, flat-bottomed, 115 ± 3-mm depth, with inside diameter of 44.2 to 45.8 mm. It shall be supported in a vertical position in the cooling bath (see 6.7) so that not more than 25 mm projects out of the cooling medium, and shall be capable of being cleaned.

6.5 *Disk*, cork or felt, 6 mm thick to fit loosely inside the jacket.

6.6 *Gasket*, to fit snugly around the outside of the test jar and loosely inside the jacket. The gasket may be made of rubber, leather, or other material that is elastic enough to cling to the test jar and hard enough to hold its shape. Its purpose is to prevent the test jar from touching the jacket.

6.7 *Bath or Baths*, maintained at prescribed temperatures with a firm support to hold the jacket vertical. The required bath temperatures may be obtained by refrigeration if available, otherwise by suitable freezing mixtures. Freezing mixtures commonly used for temperatures down to those shown are as follows:

	For Temperatures Down
Ice and water	9°C
Crushed ice and sodium chloride crystals	−12°C
Crushed ice and calcium chloride crystals	−27°C
Acetone or petroleum naphtha (see Section 6) chilled in a covered metal beaker with an ice-salt mixture to −12°C then with enough solid carbon dioxide to give the desired temperature.	−57°C

7. Reagents and Materials

7.1 The following solvents of technical grade are appropriate for low-temperature bath media.

7.1.1 *Acetone*, (**Warning**—Extremely flammable).

7.1.2 *Alcohol, Ethanol* (**Warning**—Flammable).

7.1.3 *Alcohol, Methanol* (**Warning**—Flammable. Vapor harmful).

7.1.4 *Petroleum Naphtha*, (**Warning**—Combustible. Vapor harmful).

7.1.5 *Solid Carbon Dioxide*, (**Warning**—Extremely cold −78.5°C).

8. Procedure

8.1 Pour the specimen into the test jar to the level mark. When necessary, heat the specimen in a water bath until it is just sufficiently fluid to pour into the test jar.

NOTE 1—It is known that some materials, when heated to a temperature higher than 45°C during the preceding 24 h, do not yield the same pour point results as when they are kept at room temperature for 24 h prior to testing. Examples of materials which are known to show sensitivity to thermal history are residual fuels, black oils, and cylinder stocks.

8.1.1 Samples of residual fuels, black oils, and cylinder stocks which have been heated to a temperature higher than 45°C during the preceding 24 h, or when the thermal history of these sample types is not known, shall be kept at room temperature for 24 h before testing. Samples which are known by the operator not to be sensitive to thermal history need not be kept at room temperature for 24 h before testing.

8.1.2 Experimental evidence supporting elimination of the 24-h waiting period for some sample types is contained in a research report.[6]

8.2 Close the test jar with the cork carrying the high-pour thermometer (5.2). In the case of pour points above 36°C, use a higher range thermometer such as IP 63C or ASTM 61C. Adjust the position of the cork and thermometer so the cork fits tightly, the thermometer and the jar are coaxial, and the thermometer bulb is immersed so the beginning of the capillary is 3 mm below the surface of the specimen.

8.3 For the measurement of pour point, subject the specimen in the test jar to the following preliminary treatment:

8.3.1 *Specimens Having Pour Points Above −33°C*—Heat the specimen without stirring to 9°C above the expected pour point, but to at least 45°C, in a bath maintained at 12°C above the expected pour point, but at least 48°C. Transfer the test jar to a water bath maintained at 24°C and commence observations for pour point.

8.3.2 *Specimens Having Pour Points of −33°C and Below*—Heat the specimen without stirring to 45°C in a bath maintained at 48°C and cool to 15°C in a water bath maintained at 6°C. Remove the high cloud and pour thermometer, and place the low cloud and pour thermometer in position.

8.4 See that the disk, gasket, and the inside of the jacket are clean and dry. Place the disk in the bottom of the jacket. Place the gasket around the test jar, 25 mm from the bottom. Insert the test jar in the jacket. Never place a jar directly into the cooling medium.

8.5 After the specimen has cooled to allow the formation of paraffin wax crystals, take great care not to disturb the mass of specimen nor permit the thermometer to shift in the specimen; any disturbance of the spongy network of wax crystals will lead to low and erroneous results.

8.6 Pour points are expressed in integers that are positive or negative multiples of 3°C. Begin to examine the appearance of the specimen when the temperature of the specimen is 9°C above the expected pour point (estimated as a multiple of 3°C). At each test thermometer reading that is a multiple of 3°C below the starting temperature remove the test jar from the jacket. To remove condensed moisture that limits visibility wipe the surface with a clean cloth moistened in alcohol (ethanol or methanol). Tilt the jar just enough to ascertain whether there is a movement of the specimen in the test jar. The complete operation of removal, wiping, and replacement shall require not more than 3 s.

8.6.1 If the specimen has not ceased to flow when its temperature has reached 27°C, transfer the test jar to the next lower temperature bath in accordance with the following schedule:

Specimen is at +27°C, move to 0°C bath
Specimen is at +9°C, move to −18°C bath
Specimen is at −6°C, move to −33°C bath
Specimen is at −24°C, move to −51°C bath
Specimen is at −42°C, move to −69°C bath

8.6.2 As soon as the specimen in the jar does not flow when tilted, hold the jar in a horizontal position for 5 s, as noted by an accurate timing device and observe carefully. If the specimen shows any movement, replace the test jar immediately in the jacket and repeat a test for flow at the next temperature, 3°C lower.

8.7 Continue in this manner until a point is reached at which the specimen shows no movement when the test jar is held in a horizontal position for 5 s. Record the observed reading of the test thermometer.

8.8 For black specimen, cylinder stock, and nondistillate fuel specimen, the result obtained by the procedure described in 8.1 through 8.7 is the upper (maximum) pour point. If required, determine the lower (minimum) pour point by heating the sample while stirring, to 105°C, pouring it into the jar, and determining the pour point as described in 8.4 through 8.7.

8.9 Some specifications allow for a pass/fail test or have pour point limits at temperatures not divisible by 3°C. In these cases, it is acceptable practice to conduct the pour point measurement according to the following schedule: Begin to examine the appearance of the specimen when the temperature of the specimen is 9°C above the specification pour point. Continue observations at 3°C intervals as described in 8.6 and 8.7 until the specification temperature is reached. Report the sample as passing or failing the specification limit.

9. Calculation and Report

9.1 Add 3°C to the temperature recorded in 8.7 and report the result as the Pour Point, ASTM D 97. For black oil, and so forth, add 3°C to the temperature recorded in 8.7 and report the

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[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1377.

result as Upper Pour Point, ASTM D 97, or Lower Pour Point, ASTM D 97, as required.

10. Precision and Bias

10.1 *Lubricating Oil and Distillate and Residual Fuel Oil.*[7]

10.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator using the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of this test method, exceed 3°C only in one case in twenty. Differences greater than this should be considered suspect.

10.1.2 *Reproducibility*—The difference between two single and independent test results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of this test method, exceed 6°C only in one case in twenty. Differences greater than this should be considered suspect.

10.2 *Bias*—There being no criteria for measuring bias in these test-product combinations, no statement of bias can be made.

10.3 The precision statements were prepared with data on ten new (unused) mineral oil-based lubricants and sixteen assorted fuel oils tested by twelve cooperators. The mineral oil-based lubricants had pour points ranging from −48 to −6°C while the fuel oils had pour points ranging from −33 to +51°C. The following precision data were obtained:

	Mineral Oil Lubricants	Fuel Oils
95 % Confidence		
Repeatability, °C	2.87	2.52
Reproducibility, °C	6.43	6.59

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[7] The cloud point procedure formerly part of this test method now appears as Test Method D 2500.

APPENDIX

(Nonmandatory Information)

X1. TEST FOR FLUIDITY OF A RESIDUAL FUEL OIL AT A SPECIFIED TEMPERATURE

X1.1 General

X1.1.1 The low-temperature flow properties of a waxy fuel oil depend on handling and storage conditions. Thus, they may not be truly indicated by pour point. The pour point test does not indicate what happens when an oil has a considerable head of pressure behind it, such as when gravitating from a storage tank or being pumped along a pipeline. Failure to flow at the pour point is normally attributed to the separation of wax from the fuel; however, it can also be due to the effect of viscosity in the case of very viscous fuel oils. In addition pour points of residual fuels are influenced by the previous thermal history of the specimens. A loosely knit wax structure built up on cooling of the oil can be normally broken by the application of relatively little pressure.

X1.1.2 The usefulness of the pour point test in relation to residual fuel oils is open to question, and the tendency to regard the pour point as the limiting temperature at which a fuel will flow can be misleading. The problem of accurately specifying the handling behavior of fuel oil is important, and because of the technical limitations of the pour point test, various pumpability tests have been devised to assess the low-temperature flow characteristics of heavy residual fuel oils. Test Method D 3245 is one such method. However, most alternative methods tend to be time-consuming and as such do not find ready acceptance as routine control tests for determining low-temperature flow properties. One method which is relatively quick and easy to perform and has found limited acceptance as a "go-no-go" method is based on the appendix method to the former Test Method D 1659–65. The method is described as follows.

X1.2 Scope

X1.2.1 This method covers the determination of the fluidity of a residual fuel oil at a specified temperature in an as-received condition.

X1.3 Definition

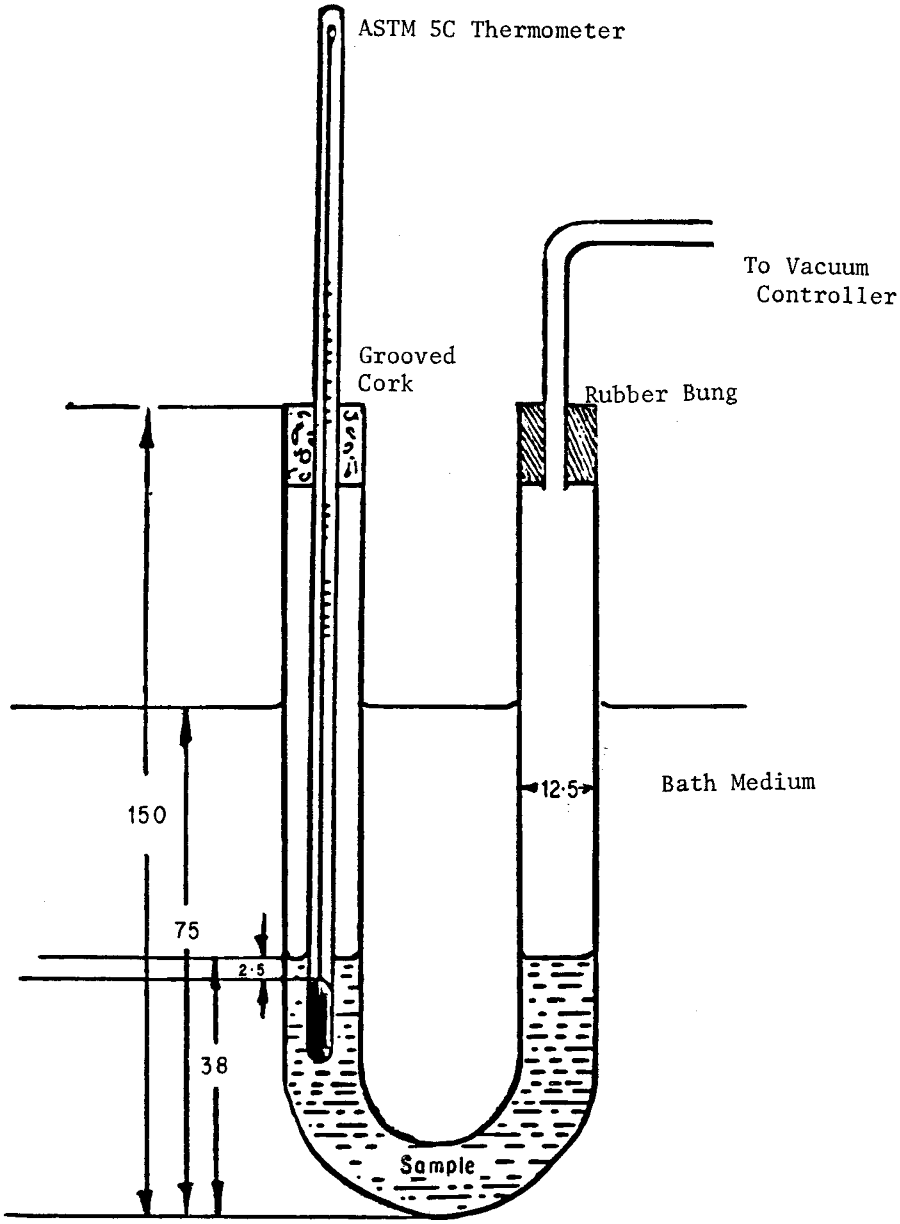
X1.3.1 *fluidity temperature*—the sample when tested in an as-received condition is considered "fluid at the temperature of the test" if it will flow 2 mm in 1 min in a 12.5 mm U-tube under a maximum pressure of 152 mm of mercury.

X1.4 Summary of Test Method

X1.4.1 A sample of fuel in its as-received condition is cooled at the specified temperature for 30 min in the standard U-tube and is tested for movement under prescribed pressure conditions.

X1.5 Significance and Use

X1.5.1 This method may be used as a "go-no-go" procedure for operational situations where it is necessary to ascertain the fluidity of a residual oil under prescribed conditions in an as-received condition. The conditions of this method simulate those of a pumping situation where the oil is expected to flow through a 12-mm pipe under slight pressure at a specified temperature. Fluidity, like Test Method D 97, is used to define cold flow properties. It differs from D 97, however, in that (*1*) it is restricted to residual fuel oil and (*2*) a prescribed pressure is applied to the sample. The latter represents an attempt to overcome the technical limitations of the Pour Point Method where gravity-induced flow is the criterion. Test Method



NOTE—All dimensions are in millimetres

FIG. X1.1 Disposition of U-tube in Fluidity Temperature Test Bath

D 3245, represents another method for predicting field performance in cold flow conditions. Test Method D 3245, however, does have limitations and may not be suitable for use with very waxy fuel oils which solidify so rapidly in the chilling bath that a reading cannot be obtained under the conditions of the test. It is also a time-consuming test and therefore not suitable for routine control testing.

X1.6 Apparatus

X1.6.1 *Glass U-Tubes*, 150 mm high, having a uniform internal diameter of 12.5 ± 1 mm and a radius of curvature, measured to the outside curve of the tube of 35 mm (Fig. X1.1).

X1.6.2 *Thermometers*—Thermometers having a range from −38 to +50°C and conforming to the requirements of Thermometer 5C as prescribed in Specification E 1, shall be used for insertion in the glass U-tubes and for measuring the temperatures of the baths.

X1.6.3 *Fluidity Temperature Test Bath,*[8]

consists of a reservoir, a stirrer, and a motor and pump to circulate coolant through the coils of the tubing placed in the bottom of the test bath and passing through the cold bath. The flow of coolant through these coils can be controlled by a thermostat and a solenoid valve. It is possible that, where justified by the quantity of work, more than one such bath could be utilized to permit concurrent testing at more than one temperature (Fig. X1.2).

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[8] A kinematic viscosity bath is usually satisfactory.

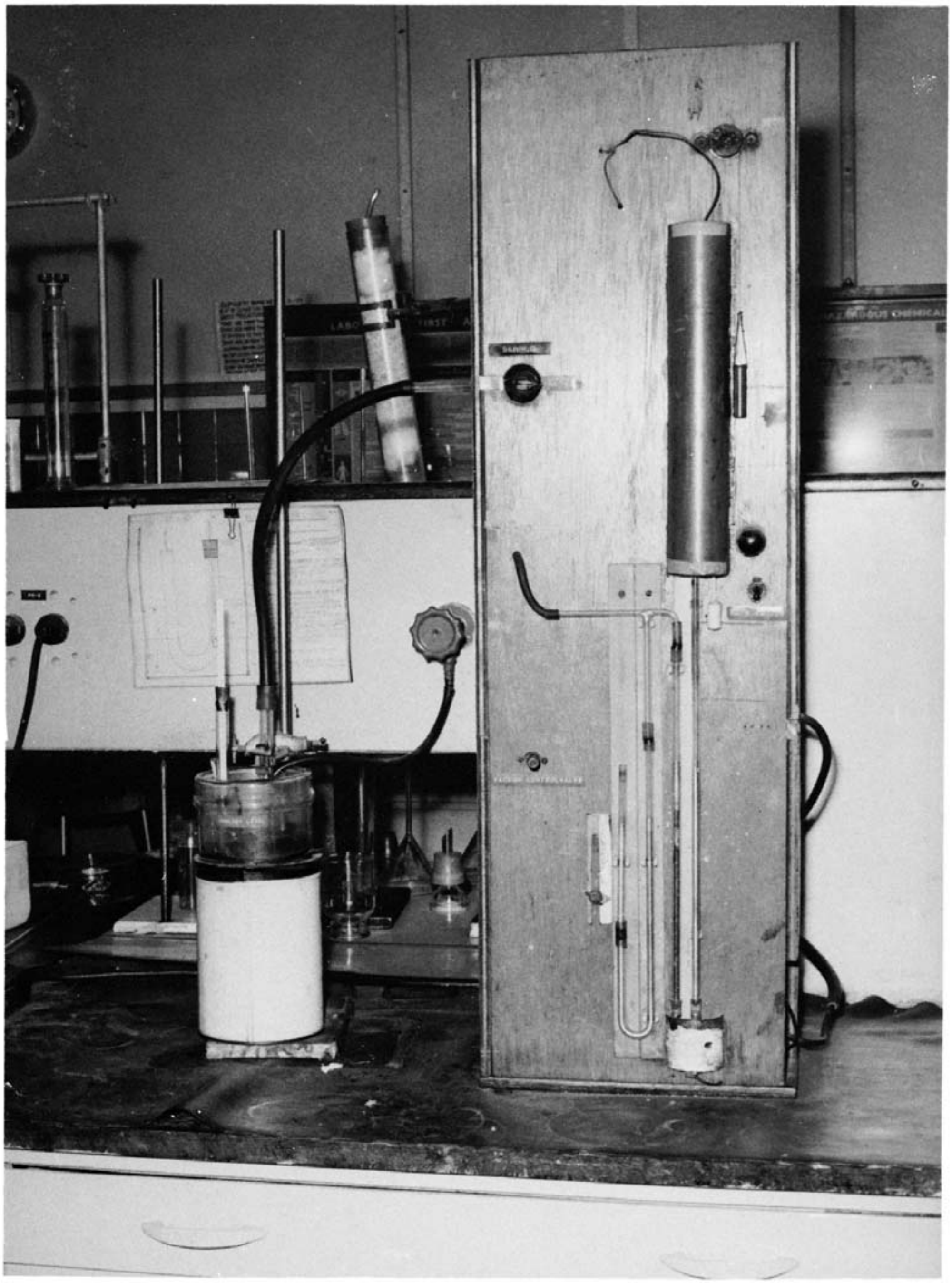

FIG. X1.2 Fluidity Temperature Apparatus

X1.6.4 *Mercury Manometer* calibrated in 10-mm divisions with a distinguishing mark at 152 mm (equivalent to 20.3 kPa).

X1.6.5 *Automatic Vacuum Controller*[9] *(as shown in Fig. X1.3 and Fig. X1.4)*—A device that gradually increased the vacuum applied to one end of the U-tube at the specified rate of 10 mm/4S.

X1.7 Preparation of Apparatus

X1.7.1 Adjust the automatic vacuum controller as follows: close the stopcock on the tube connecting the automatic vacuum controller to the fluidity tester. A pinchcock on the rubber tube will serve as well as a stopcock. Wind the thread attached to the steel rod around the pulley on the synchronous motor until the end of the rod is about 15 mm above the zero level of the mercury in the control manometer. Turn on the power switch. The thread will begin to unwind, lowering the steel rod. When the rod contacts the mercury, the relay will

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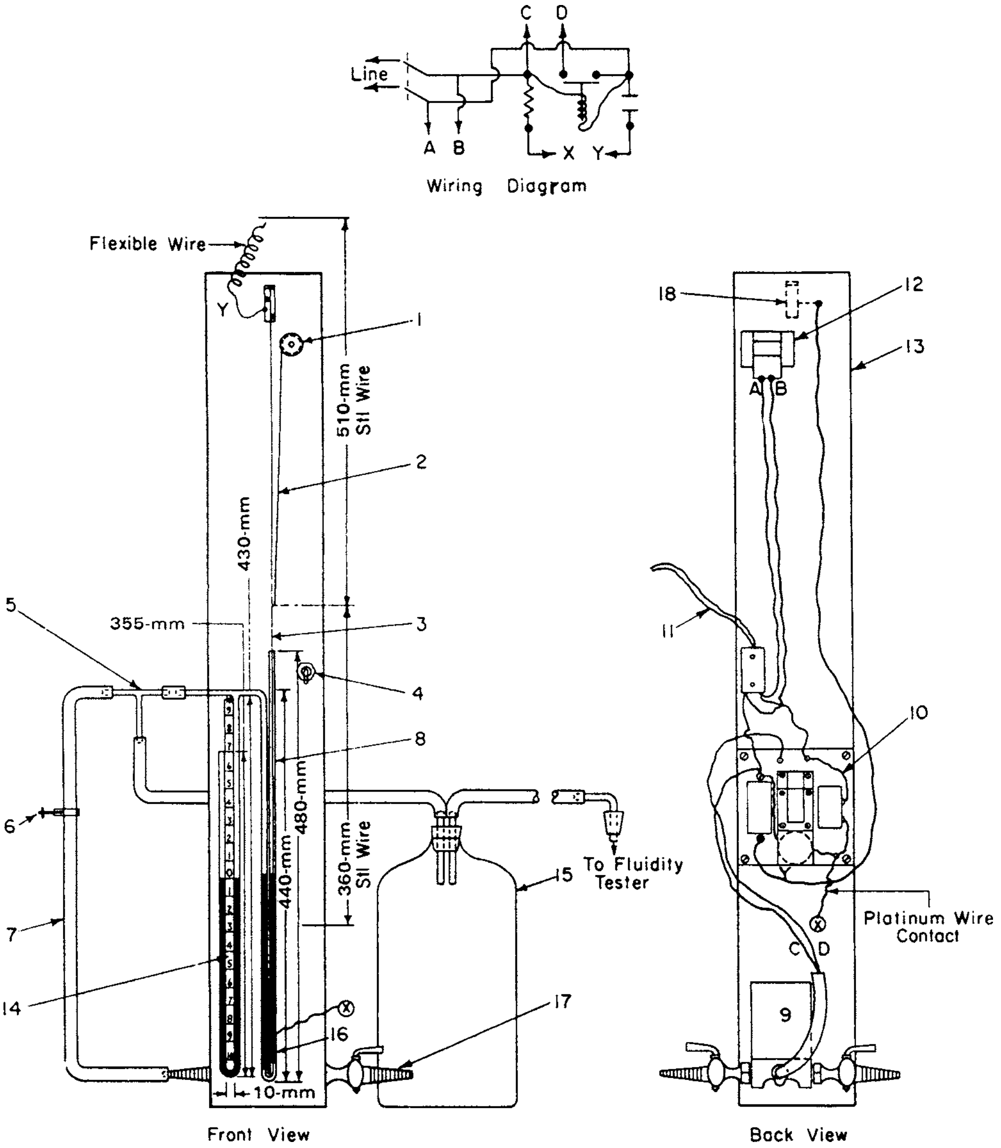
[9] This apparatus may be shop fabricated. Details of special parts are indicated in Figs. X1.3 and X1.4. Alternatively the apparatus can be purchased.



1—26-mm diameter face pulley
2—Thread
3—Steel rod
4—Switch-DPST
5—Tee, 90-mm long
6—Needle valve
7—Rubber or plastic tubing
8—6-mm heat-resistant glass tube
9—Solenoid valve
10—Electric relay
11—Electric cord to outlet
12—Synchronous motor
13—Plywood of approximately 10-mm thickness
14—Millimeter scale
15—4-L bottle
16—0.5-mm heat-resistant glass capillary
17—To vacuum line
18—Rod holder

FIG. X1.3 Assembly Automatic Vacuum Controller Apparatus

open the solenoid valve in the vacuum line and air will be pumped from the system at a rate limited by the needle valve. Adjust this needle valve until the descending mercury in the control manometer just leads the rod, reducing the relay operation to a minimum. When properly adjusted, the pulsations caused by the opening and closing of the solenoid valve should not exceed ±1 mm. In this manner the pressure in the system will be reduced gradually at a rate governed by the descent of the steel rod.

X1.8 Procedure

X1.8.1 Pour the sample as received into a thoroughly cleaned and dry standard fluidity U-tube, without contacting the upper walls of the tube, until the vertical height of the

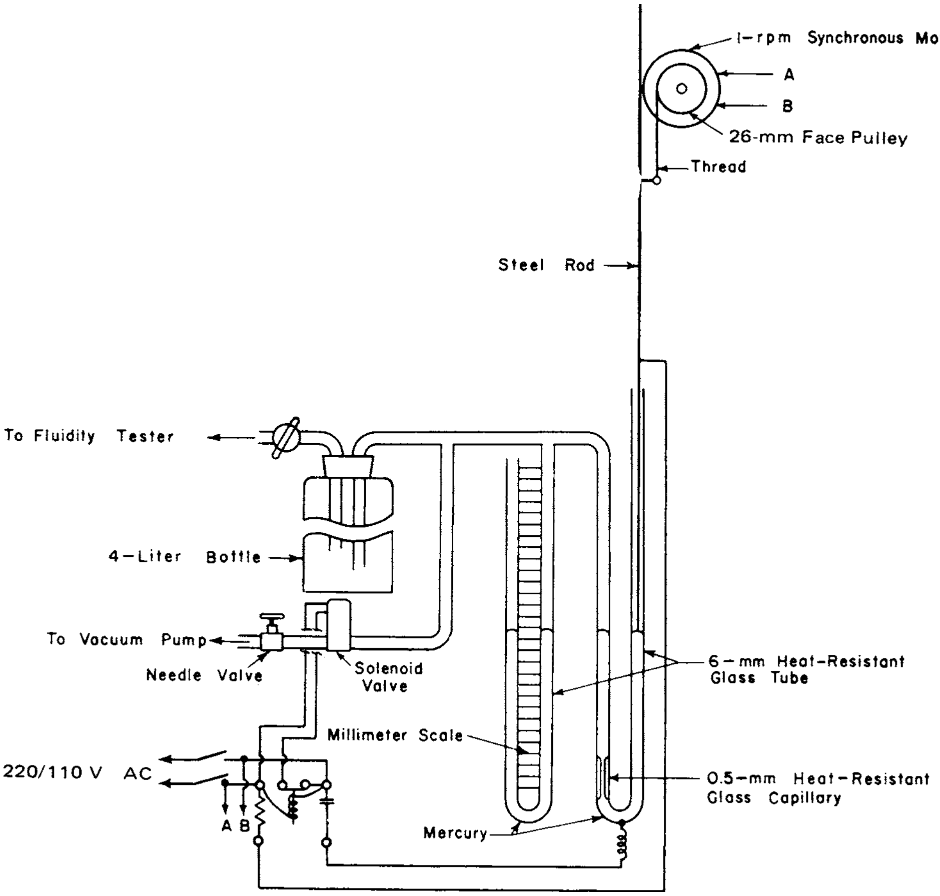


FIG. X1.4 Detail of Automatic Vacuum Controller

sample in the U-tube is 38 mm. Insert in one leg of each U-tube an ASTM Thermometer 5C in a cork that has been grooved to permit the passage of air. The thermometer must be placed in the center of the tube and its bulb immersed so that the beginning of the capillary is 3 mm below the surface of the specimen.

X1.8.2 Fix the tube in the bath set at the specific temperature, immersed to a depth of approximately 75 mm. Control the bath and sample temperatures within ±1°C and ±0.5°C, respectively, of the specified temperature of the test.

X1.8.3 Maintain the sample at the specified temperature for 30 min ± 30 s, with the U-tube connected to the automatic vacuum controller, and the stopcock or pinch-clamp open. Wind the thread on the pulley attached to the synchronous motor. Turn the power switch to the ON position. Apply suction automatically to the U-tube at the prescribed rate. Observe any movement of the specimen during a one-minute interval which is the time required to apply 152-mm Hg vacuum to the specimen in the U-tube. Immediately disconnect the U-tube from the automatic vacuum controller, turn off the power switch and rewind the thread. If the specimen has moved 2 mm or more during the time (1 min) the suction was applied, the specimen is considered fluid at the temperature of the test.

X1.9 Report

X1.9.1 Report the fluidity of the sample at a specified temperature as follows:

X1.9.1.1 If the sample fulfills the conditions of flow, as defined in X1.3.1, report fluidity: "Fluid at (temperature of test)" or fluidity at (temperature of test): "Pass."

X1.9.1.2 If the sample does not fulfill the conditions of flow, as defined in X1.3.1, report fluidity: "Not fluid at (temperature of test)" or fluidity at (temperature of test): "Fail."

X1.10 Precision and Bias

X1.10.1 As in the case of pass-fail data, no statement is made about either the precision or the bias of this method for measuring the fluidity of a residual fuel specimen since the result merely states whether there is conformance to the criteria for success specified in the procedure.

SUMMARY OF CHANGES

Subcommittee D02.07 has identified the location of selected changes to this standard since the last issue (D 97–04) that may impact the use of this standard.

(*1*) Added Test Method D 5853 to the Scope and Referenced Documents sections.

Designation: D 445 – 01

An American National Standard
British Standard 2000: Part 71:1990

Designation: 71/1/97

Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity)[1]

This standard is issued under the fixed designation D 445; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This test method has been approved by the sponsoring committee and accepted by the Cooperating Societies in accordance with established procedures.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method specifies a procedure for the determination of the kinematic viscosity, ν, of liquid petroleum products, both transparent and opaque, by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The dynamic viscosity, η, can be obtained by multiplying the kinematic viscosity, ν, by the density, ρ, of the liquid.

NOTE 1—For the measurement of the kinematic viscosity and viscosity of bitumens, see also Test Methods D 2170 and D 2171.

1.2 The result obtained from this test method is dependent upon the behavior of the sample and is intended for application to liquids for which primarily the shear stress and shear rates are proportional (Newtonian flow behavior). If, however, the viscosity varies significantly with the rate of shear, different results may be obtained from viscometers of different capillary diameters. The procedure and precision values for residual fuel oils, which under some conditions exhibit non-Newtonian behavior, have been included.

1.3 The range of kinematic viscosities covered by this test method is from 0.2 to 300 000 mm^2/s (see Table A1.1) at all temperatures (see 6.3 and 6.4). The precision has only been determined for those materials, kinematic viscosity ranges and temperatures as shown in the footnotes to the precision section.

1.4 The values stated in SI units are to be regarded as the standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 446 Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers[2]
D 1193 Specification for Reagent Water[3]
D 1217 Test Method for Density and Relative Density (Specific Gravity) of Liquids by Bingham Pycnometer[2]
D 1480 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Bingham Pycnometer[2]
D 1481 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Lipkin Bicapillary Pycnometer[2]
D 2170 Test Method for Kinematic Viscosity of Asphalts (Bitumens)[4]
D 2171 Test Method for Viscosity of Asphalts by Vacuum Capillary Viscometer[4]
D 6074 Guide for Characterizing Hydrocarbon Lubricant Base Oils[5]
E 1 Specification for ASTM Thermometers[6]
E 77 Test Method for the Inspection and Verification of Thermometers[6]

2.2 *ISO Standards:*[7]

ISO Guide 25—General Requirements for the Calibration and Testing Laboratories
ISO 3104 Petroleum Products—Transparent and Opaque

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.07 on Flow Properties.

Current edition approved Jan. 10, 2001. Published March 2001. Originally published as D 445 – 37T. Last previous edition D 445 – 97.

In the IP, this test method is under the jurisdiction of the Standardization Committee.

[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 04.03.

[5] *Annual Book of ASTM Standards*, Vol 05.03.

[6] *Annual Book of ASTM Standards*, Vol 14.03.

[7] Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

Liquids—Determination of Kinematic Viscosity and Calculation of Dynamic Viscosity

ISO 3105 Glass Capillary Kinematic Viscometers—Specification and Operating Instructions

ISO 3696 Water for Analytical Laboratory Use—Specification and Test Methods

ISO 9000 Quality Management and Quality Assurance Standards—Guidelines for Selection and Use

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *automated viscometer*, *n*—apparatus which, in part or in whole, has mechanized one or more of the procedural steps indicated in 10 or 11 without changing the principle or technique of the basic manual apparatus. The essential elements of the apparatus in respect to dimensions, design and operational characteristics are not changed. The measured result from the apparatus does not require correction to bring it into correlation with the basic manual apparatus. The precision of the apparatus shall be of statistical equivalence to, or better (has less variability) than the manual apparatus.

3.1.1.1 *Discussion*—Automated viscometers have the capability to mimic some operation of the test method while reducing or removing the need for manual intervention or interpretation. Apparatus which determine kinematic viscosity by physical techniques that are different than those used in this test method are not considered to be Automated Viscometers.

3.1.2 *density*, *n*—the mass per unit volume of a substance at a given temperature.

3.1.3 *dynamic viscosity*, *n*—the ratio between the applied shear stress and rate of shear of a liquid.

3.1.3.1 *Discussion*—It is sometimes called the coefficient of dynamic viscosity or, simply, viscosity. Thus dynamic viscosity is a measure of the resistance to flow or deformation of a liquid.

3.1.3.2 *Discussion*—The term dynamic viscosity can also be used in a different context to denote a frequency-dependent quantity in which shear stress and shear rate have a sinusodial time dependence.

3.1.4 *kinematic viscosity*, *n*—the resistance to flow of a fluid under gravity.

3.1.4.1 *Discussion*—For gravity flow under a given hydrostatic head, the pressure head of a liquid is proportional to its density, ρ. For any particular viscometer, the time of flow of a fixed volume of fluid is directly proportional to its kinematic viscosity, ν, where $\nu = \eta/\rho$, and η is the dynamic viscosity coefficient.

4. Summary of Test Method

4.1 The time is measured for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled and known temperature. The kinematic viscosity is the product of the measured flow time and the calibration constant of the viscometer.

5. Significance and Use

5.1 Many petroleum products, and some non-petroleum materials, are used as lubricants, and the correct operation of the equipment depends upon the appropriate viscosity of the liquid being used. In addition, the viscosity of many petroleum fuels is important for the estimation of optimum storage, handling, and operational conditions. Thus, the accurate determination of viscosity is essential to many product specifications.

6. Apparatus

6.1 *Viscometers*—Use only calibrated viscometers of the glass capillary type, capable of being used to determine kinematic viscosity within the limits of the precision given in the precision section.

6.1.1 Viscometers listed in Table A1.1, whose specifications meet those given in Specifications D 446 and in ISO 3105 meet these requirements. It is not intended to restrict this test method to the use of only those viscometers listed in Table A1.1. Annex A1 gives further guidance.

6.1.2 *Automation Viscometers*—Automated apparatus may be used as long as they mimic the physical conditions, operations or processes of the manual apparatus they replace. Any viscometer, temperature measuring device, temperature control, temperature controlled bath or timing device incorporated in the automated apparatus shall conform to the specification for these components as stated in 6 of this test method. The automated apparatus shall be capable of determining kinematic viscosity of a certified reference material within the limits stated in 8.2.1.

6.2 *Viscometer Holders*—Use viscometer holders to enable all viscometers which have the upper meniscus directly above the lower meniscus to be suspended vertically within 1° in all directions. Those viscometers whose upper meniscus is offset from directly above the lower meniscus shall be suspended vertically within 0.3° in all directions (see Specifications D 446 and ISO 3105).

6.2.1 Viscometers shall be mounted in the constant temperature bath in the same manner as when calibrated and stated on the certificate of calibration. See Specifications D 446, see Operating Instructions in Annex A1, Annex A2, and Annex A3. For those viscometers which have Tube L (see Specifications D 446) held vertical, vertical alignment shall be confirmed by using (*1*) a holder ensured to hold Tube L vertical, or (*2*) a bubble level mounted on a rod designed to fit into Tube L, or (*3*) a plumb line suspended from the center of Tube L, or (*4*) other internal means of support provided in the constant temperature bath.

6.3 *Temperature-Controlled Bath*—Use a transparent liquid bath of sufficient depth such, that at no time during the measurement of flow time, any portion of the sample in the viscometer is less than 20 mm below the surface of the bath liquid or less than 20 mm above the bottom of the bath.

6.3.1 *Temperature Control*—For each series of flow time measurements, the temperature control of the bath liquid shall be such that within the range from 15 to 100°C, the temperature of the bath medium does not vary by more than ±0.02°C of the selected temperature over the length of the viscometer, or between the position of each viscometer, or at the location of the thermometer. For temperatures outside this range, the deviation from the desired temperature must not exceed ± 0.05°C.

6.4 *Temperature Measuring Device in the Range from 0 to 100°C*—Use either calibrated liquid-in-glass thermometers (Annex A2) of an accuracy after correction of ±0.02°C or better, or any other thermometric device of equal or better accuracy.

6.4.1 If calibrated liquid-in-glass thermometers are used, the use of two thermometers is recommended. The two thermometers shall agree within 0.04°C.

6.4.2 Outside the range from 0 to 100°C, use either calibrated liquid-in-glass thermometers of an accuracy after correction of ± 0.05°C or better, or any other thermometric device of equal or better accuracy. When two temperature measuring devices are used in the same bath, they shall agree within ±0.1°C.

6.4.3 When using liquid-in-glass thermometers, such as those in Table A2.2, use a magnifying device to read the thermometer to the nearest ⅕ division (for example, 0.01°C or 0.02°F) to ensure that the required test temperature and temperature control capabilities are met (see 9.1). It is recommended that thermometer readings (and any corrections supplied on the certificates of calibrations for the thermometers) be recorded on a periodic basis to demonstrate compliance with the test method requirements. This information can be quite useful, especially when investigating issues or causes relating to testing accuracy and precision.

6.5 *Timing Device*—Use any timing device that is capable of taking readings with a discrimination of 0.1 s or better, and has an accuracy within ±0.07 % (see Annex A3) of the reading when tested over intervals of 200 and 900 s.

6.5.1 Electrical timing devices may be used if the current frequency is controlled to an accuracy of 0.05 % or better. Alternating currents, as provided by some public power systems, are intermittently rather than continuously controlled. When used to actuate electrical timing devices, such control can cause large errors in kinematic viscosity flow time measurements.

7. Reagents and Materials

7.1 *Chromic Acid Cleaning Solution*, or a nonchromium-containing, strongly oxidizing acid cleaning solution. (**Warning—**Chromic acid is a health hazard. It is toxic, a recognized carcinogen, highly corrosive, and potentially hazardous in contact with organic materials. If used, wear a full face-shield and full-length protective clothing including suitable gloves. Avoid breathing vapor. Dispose of used chromic acid carefully as it remains hazardous. Nonchromium-containing, strongly oxidizing acid cleaning solutions are also highly corrosive and potentially hazardous in contact with organic materials, but do not contain chromium which has special disposal problems.)

7.2 *Sample Solvent*, completely miscible with the sample. Filter before use.

7.2.1 For most samples a volatile petroleum spirit or naphtha is suitable. For residual fuels, a prewash with an aromatic solvent such as toluene or xylene may be necessary to remove asphaltenic material.

7.3 *Drying Solvent*, a volatile solvent miscible with the sample solvent (see 7.2) and water (see 7.4). Filter before use.

7.3.1 Acetone is suitable.

7.4 *Water*, deionized or distilled and conforming to Specification D 1193 or Grade 3 of ISO 3696. Filter before use.

8. Calibration and Verification

8.1 *Viscometers*—Use only calibrated viscometers, thermometers, and timers as described in Section 6.

8.2 *Certified Viscosity Reference Standards*[8] *(Table A1.2)*—These are for use as confirmatory checks on the procedure in the laboratory.

8.2.1 If the determined kinematic viscosity does not agree within ± 0.35 % of the certified value, recheck each step in the procedure, including thermometer and viscometer calibration, to locate the source of error. Annex A1 gives details of standards available.

8.2.2 The most common sources of error are caused by particles of dust lodged in the capillary bore and temperature measurement errors. It must be appreciated that a correct result obtained on a standard oil does not preclude the possibility of a counterbalancing combination of the possible sources of error.

8.3 The calibration constant, C, is dependent upon the gravitational acceleration at the place of calibration and this must, therefore, be supplied by the standardization laboratory together with the instrument constant. Where the acceleration of gravity, g, differs by more that 0.1 %, correct the calibration constant as follows:

$$C_2 = (g_2/g_1) \times C_1 \qquad (1)$$

where the subscripts 1 and 2 indicate, respectively, the standardization laboratory and the testing laboratory.

9. General Procedure for Kinematic Viscosity

9.1 Adjust and maintain the viscometer bath at the required test temperature within the limits given in 6.3.1 taking account of the conditions given in Annex A2 and of the corrections supplied on the certificates of calibration for the thermometers.

9.1.1 Thermometers shall be held in an upright position under the same conditions of immersion as when calibrated.

9.1.2 In order to obtain the most reliable temperature measurement, it is recommended that two thermometers with valid calibration certificates be used (see 6.4).

9.1.3 They should be viewed with a lens assembly giving approximately five times magnification and be arranged to eliminate parallax errors.

9.2 Select a clean, dry, calibrated viscometer having a range covering the estimated kinematic viscosity (that is, a wide capillary for a very viscous liquid and a narrower capillary for a more fluid liquid). The flow time shall not be less than 200 s or the longer time noted in Specifications D 446.

9.2.1 The specific details of operation vary for the different types of viscometers listed in Table A1.1. The operating instructions for the different types of viscometers are given in Specifications D 446.

9.2.2 When the test temperature is below the dew point, fill the viscometer in the normal manner as required in 10.1. To

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[8] The ASTM Viscosity Oil Standards are available in 1-pt (0.47 L) containers. Purchase orders should be addressed to the Cannon Instrument Co., P.O. Box 16, State College, PA 16804. Shipment will be made as specified or by best means.

ensure that moisture does not condense or freeze on the walls of the capillary, draw the test portion into the working capillary and timing bulb, place rubber stoppers into the tubes to hold the test portion in place, and insert the viscometer into the bath. After insertion, allow the viscometer to reach bath temperature, and the remove the stoppers. When performing manual viscosity determinations, do not use those viscometers which cannot be removed from the constant temperature bath for charging the sample portion.

9.2.2.1 The use of loosely packed drying tubes affixed to the open ends of the viscometer is permitted, but not required. If used, the drying tubes shall fit the design of the viscometer and not restrict the flow of the sample by pressures created in the instrument.

9.2.3 Viscometers used for silicone fluids, fluorocarbons, and other liquids which are difficult to remove by the use of a cleaning agent, shall be reserved for the exclusive use of those fluids except during their calibration. Subject such viscometers to calibration checks at frequent intervals. The solvent washings from these viscometers shall not be used for the cleaning of other viscometers.

10. Procedure for Transparent Liquids

10.1 Charge the viscometer in the manner dictated by the design of the instrument, this operation being in conformity with that employed when the instrument was calibrated. If the sample contains solid particles, filter during charging through a (75-µm) filter (see Specifications D 446). If the sample is thought or known to contain fibers or solid particles, filter through a 75 µm screen, either prior to or during charging (see Specifications D 446).

NOTE 2—To minimize the potential of particles passing through the filter from aggregating, it is recommended that the time lapse between filtering and charging be kept to a minimum.

10.1.1 In general, the viscometers used for transparent liquids are of the type listed in Table A1.1, A and B.

10.1.2 With certain products which exhibit *gel-like* behavior, exercise care that flow time measurements are made at sufficiently high temperatures for such materials to flow freely, so that similar kinematic viscosity results are obtained in viscometers of different capillary diameters.

10.1.3 Allow the charged viscometer to remain in the bath long enough to reach the test temperature. Where one bath is used to accommodate several viscometers, never add or withdraw a viscometer while any other viscometer is in use for measuring a flow time.

10.1.4 Because this time will vary for different instruments, for different temperatures, and for different kinematic viscosities, establish a safe equilibrium time by trial.

10.1.4.1 Thirty minutes should be sufficient except for the highest kinematic viscosities.

10.1.5 Where the design of the viscometer requires it, adjust the volume of the sample to the mark after the sample has reached temperature equilibrium.

10.2 Use suction (if the sample contains no volatile constituents) or pressure to adjust the head level of the test sample to a position in the capillary arm of the instrument about 7 mm above the first timing mark, unless any other value is stated in the operating instructions for the viscometer. With the sample flowing freely, measure, in seconds to within 0.1 s, the time required for the meniscus to pass from the first to the second timing mark. If this flow time is less than the specified minimum (see 9.2), select a viscometer with a capillary of smaller diameter and repeat the operation.

10.2.1 Repeat the procedure described in 10.2 to make a second measurement of flow time. Record both measurements.

10.2.2 If the two determinations of kinematic viscosity, calculated from the flow time measurements, agree within the stated determinability figure (see 16.1) for the product, use the average of these determinations to calculate the kinematic viscosity result to be reported. Record the result. If the determinations of kinematic viscosity do not agree within the stated determinability, repeat the measurements of flow times after thorough cleaning and drying of the viscometers and filtering (where required, see 10.1) of the sample. If the material or temperature, or both, is not listed in 16.1, for temperatures between 15 and 100°C use as an estimate of the determinability 0.20 %, and 0.35 % for temperatures outside this range.

11. Procedure for Opaque Liquids

11.1 For steam-refined cylinder oils and black lubricating oils, proceed to 11.3 ensuring a thoroughly representative sample is used. The kinematic viscosity of residual fuel oils and similar waxy products can be affected by the previous thermal history and the following procedure described in 11.1.1-11.2.2 shall be followed to minimize this.

11.1.1 In general, the viscometers used for opaque liquids are of the reverse-flow type listed in Table A1.1, C.

11.1.2 Heat in the original container, in an oven, at 60 ± 2°C for 1 h.

11.1.3 Thoroughly stir the sample with a suitable rod of sufficient length to reach the bottom of the container. Continue stirring until there is no sludge or wax adhering to the rod.

11.1.4 Recap the container tightly and shake vigorously for 1 min to complete the mixing.

11.1.4.1 With samples of a very waxy nature or oils of high kinematic viscosity, it may be necessary to increase the heating temperature above 60°C to achieve proper mixing. The sample should be sufficiently fluid for ease of stirring and shaking.

11.2 Immediately after completing 11.1.4, pour sufficient sample to fill two viscometers into a 100-mL glass flask and loosely stopper.

11.2.1 Immerse the flask in a bath of boiling water for 30 min. (**Warning—**Exercise care as vigorous boil-over can occur when opaque liquids which contain high levels of water are heated to high temperatures.)

11.2.2 Remove the flask from the bath, stopper tightly, and shake for 60 s.

11.3 Charge two viscometers in the manner dictated by the design of the instrument. For example, for the cross-arm or the BS U-tube viscometers for opaque liquids, filter the sample through a 75-µm filter into two viscometers previously placed in the bath. For samples subjected to heat treatment, use a preheated filter to prevent the sample coagulating during the filtration.

11.3.1 Viscometers which are charged before being inserted into the bath may need to be preheated in an oven prior to charging the sample. This is to ensure that the sample will not be cooled below test temperature.

11.3.2 After 10 min, adjust the volume of the sample (where the design of the viscometer requires) to coincide with the filling marks as in the viscometer specifications (see Specifications D 446).

11.3.3 Allow the charged viscometers enough time to reach the test temperature (see 11.3.1). Where one bath is used to accommodate several viscometers, never add or withdraw a viscometer while any other viscometer is in use for measuring flow time.

11.4 With the sample flowing freely, measure in seconds to within 0.1 s, the time required for the advancing ring of contact to pass from the first timing mark to the second. Record the measurement.

11.4.1 In the case of samples requiring heat treatment described in 11.1 through 11.2.1, complete the measurements of flow time within 1 h of completing 11.2.2. Record the measured flow times.

11.5 Calculate kinematic viscosity, ν, in mm ^{2}/s, from each measured flow time.

11.5.1 For residual fuel oils, if the two determinations of kinematic viscosity agree within the stated determinability figure (see 16.1), use the average of these determinations to calculate the kinematic viscosity result to be reported. Record the result. If the calculated kinematic viscosities do not agree, repeat the measurements of flow times after thorough cleaning and drying of the viscometers and filtering of the sample. If the material or temperature, or both, is not listed in 16.1, for temperatures between 15 and 100°C use as an estimate of the determinability 1.0 %, and 1.5 % for temperatures outside this range; it must be realized that these materials can be non-Newtonian, and can contain solids which can come out of solution as the flow time is being measured.

11.5.2 For other opaque liquids, no precision data is available.

12. Cleaning of Viscometer

12.1 Between successive determinations of kinematic viscosity, clean the viscometer thoroughly by several rinsings with the sample solvent, followed by the drying solvent (see 7.3). Dry the tube by passing a slow stream of filtered dry air through the viscometer for 2 min or until the last trace of solvent is removed.

12.2 Periodically clean the viscometer with the cleaning solution (**Warning**—see 7.1), for several hours to remove residual traces of organic deposits, rinse thoroughly with water (7.4) and drying solvent (see 7.3), and dry with filtered dry air or a vacuum line. Remove any inorganic deposits by hydrochloric acid treatment before the use of cleaning acid, particularly if the presence of barium salts is suspected. (**Warning—**It is essential that alkaline cleaning solutions are not used as changes in the viscometer calibration can occur.)

13. Calculation

13.1 Calculate the kinematic viscosity, ν, from the measured flow time, t, and the viscometer constant, C, by means of the following equation:

$$\nu = C \cdot t \tag{2}$$

where:

ν = kinematic viscosity, mm^2/s,
C = calibration constant of the viscometer, (mm^2/s)/s, and
t = mean flow time, s.

13.2 Calculate the dynamic viscosity, η, from the calculated kinematic viscosity, ν, and the density, ρ, by means of the following equation:

$$\eta = \nu \times \rho \times 10^{-3} \tag{3}$$

where:

η = dynamic viscosity, mPa·s,
ρ = density, kg/m^3, at the same temperature used for the determination of the kinematic viscosity, and
ν = kinematic viscosity, mm^2/s.

13.2.1 The density of the sample can be determined at the test temperature of the kinematic viscosity determination by an appropriate method such as Test Methods D 1217, D 1480, or D 1481.

14. Expression of Results

14.1 Report the test results for the kinematic or dynamic viscosity, or both, to four significant figures, together with the test temperature.

15. Report

15.1 Report the following information:

15.1.1 Type and identification of the product tested,

15.1.2 Reference to this test method or a corresponding international standard,

15.1.3 Result of the test (see Section 14),

15.1.4 Any deviation, by agreement or otherwise, from the procedure specified,

15.1.5 Date of the test, and

15.1.6 Name and address of the test laboratory.

16. Precision

16.1 *Determinability (d)*—The difference between successive determinations obtained by the same operator in the same laboratory using the same apparatus for a series of operations leading to a single result, would in the long run, in the normal and correct operation of this test method, exceed the values indicated only in one case in twenty:[9,10,11,12,13,14,15,16]

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[9] These precision values were obtained by statistical examination of interlaboratory results from six mineral oils (base oils without additive package) in the range from 8 to 1005 mm^2/s at 40°C and from 2 to 43 mm ^{2}/s at 100°C, and were first published in 1989. Precision data available from ASTM Headquarters. Request RR:D02-1331 and RR:D02-1132. See Guide D 6074.

[10] These precision values were obtained by statistical examination of interlaboratory results from seven fully formulated engine oils in the range from 36 to 340 mm^2/s at 40°C and from 6 to 25 mm ^{2}/s at 100°C, and were first published in 1991. Precision data available from ASTM Headquarters. Request RR:D02-1332. See Guide D 6071.

Base oils at 40 and 100°C[9]	0.0020 y	(0.20 %)
Formulated oils at 40 and 100°C[10]	0.0013 y	(0.13 %)
Formulated oils at 150°C[11]	0.015 y	(1.5 %)
Petroleum wax at 100°C[12]	0.0080 y	(0.80 %)
Residual fuel oils at 80 and 100°C[13]	0.011 (y + 8)	
Residual fuel oils at 50°C[13]	0.017 y	(1.7 %)
Additives at 100°C[14]	$0.00106\ y^{1.1}$	
Gas oils at 40°C[15]	0.0013 (y+1)	
Jet fuels at –20°C[16]	0.0018 y	(0.18 %)

where: *y* is the average of determinations being compared.

16.2 *Repeatability (r)*—The difference between successive results obtained by the same operator in the same laboratory with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of this test method, exceed the values indicated only in one case in twenty:[9,10,11,12,13,14,15,16]

Base oils at 40 and 100°C[9]	0.0011 x	(0.11 %)
Formulated oils at 40 and 100°C[10]	0.0026 x	(0.26 %)
Formulated oils at 150°C[11]	0.0056 x	(0.56 %)
Petroleum wax at 100°C[12]	$0.0141\ x^{1.2}$	
Residual fuel oils at 80 and 100°C[13]	0.013 (x + 8)	
Residual oils at 50°C[13]	0.015 x	(1.5 %)
Additives at 100°C[14]	$0.00192\ x^{1.1}$	
Gas oils at 40°C[15]	0.0043 (x+1)	
Jet fuels at –20°C[16]	0.007 x	(0.7 %)

where: *x* is the average of results being compared.

16.3 *Reproducibility (R)*—The difference between two single and independent results obtained by different operators working in different laboratories on nominally identical test material would, in the long run, in the normal and correct operation of this test method, exceed the values indicated below only in one case in twenty.[9,10,11,12,13,14,15,16]

Base oils at 40 and 100°C[9]	0.0065 x	(0.65 %)
Formulated oils at 40 and 100°C	0.0076 x	(0.76 %)
Formulated oils at 150°C[11]	0.018 x	(1.8 %)
Petroleum wax at 100°C[12]	$0.0366\ x^{1.2}$	
Residual fuel oils at 80 and 100°C[13]	0.04 (x + 8)	
Residual oils at 50°C[13]	0.074 x	(7.4 %)
Additives at 100°C[14]	$0.00862\ x^{1.1}$	
Gas oils at 40°C[15]	0.0082 (x+1)	
Jet fuels at –20°C[16]	0.019 x	(1.9 %)

where: *x* is the average of results being compared.

16.4 The precision for used oils has not been determined but is expected to be poorer than that for formulated oils. Because of the extreme variability of such used oils, it is not anticipated that the precision of used oils will be determined.

16.5 The precision for specific automated viscometers has not been determined. However, an analysis has been made of a large data set including both automated and manual viscometers over the temperature range of 40 to 100°C. The reproducibility of automated viscometer data is not statistically significantly different than the reproducibility of manual viscometer data. It is also shown that there is no bias of the automated data in comparison to the manual data.[17]

17. Keywords

17.1 dynamic viscosity; kinematic viscosity; viscometer; viscosity

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[11] These precision values were obtained by statistical examination of interlaboratory results for eight fully formulated engine oils in the range from 7 to 19 mm ^{2}/s at 150°C, and first published in 1991. Precision data available from ASTM Headquarters. Request RR:D02-1333. See Guide D 6074.

[12] These precision values were obtained by statistical examination of interlaboratory results from five petroleum waxes in the range from 3 to 16 mm^2/s at 100°C, and were first published in 1988. Precision data available from ASTM Headquarters. Request RR:D02-1334.

[13] These precision values were obtained by statistical examination of interlaboratory results from fourteen residual fuel oils in the range from 30 to 1300 mm ^{2}/s at 50°C and from 5 to 170 mm^2/s at 80 and 100°C, and were first published in 1984. Precision data available from ASTM Headquarters. Request RR:D02-1198.

[14] These precision values were obtained by statistical examination of interlaboratory results from eight additives in the range from 145 to 1500 mm^2/s at 100°C and were first available in 1997. Precision data available from ASTM Headquarters. Request RR:D02-1421.

[15] These precision values were obtained by statistical examination of interlaboratory results from eight gas oils in the range from 1 to 13 mm^2/s at 40°C and were first available in 1997. Precision data available from ASTM Headquarters. Request RR:D02-1422.

[16] These precision values were obtained by statistical examination of interlaboratory results from nine jet fuels in the range from 4.3 to 5.6 mm ^{2}/s at– 20°C and were first available in 1997. Precision data available from ASTM Headquarters. Request RR:D02-1420.

[17] Precision data available from ASTM Headquarters. Request RR: D02–1498.

ANNEXES

(Mandatory Information)

A1. VISCOMETER TYPES, CALIBRATION, AND VERIFICATION

A1.1 Viscometer Types

A1.1.1 Table A1.1 lists capillary viscometers commonly in use for viscosity determinations on petroleum products. For specifications and operating instructions, refer to Specifications D 446.

A1.2 Calibration

A1.2.1 Calibrate working standard viscometers against master viscometers having a certificate of calibration traceable to a national standard. Viscometers used for analysis shall be calibrated in comparison with working standard viscometers or master viscometers, or by the procedures given in Specifications D 446 or ISO 3105. Viscometer constants shall be measured and expressed to the nearest 0.1 % of their value.

A1.3 Verification

A1.3.1 Viscometer constants shall either be verified by a similar procedure to A1.2, or conveniently checked by means of certified viscosity oils.

A1.3.2 These oils can be used for confirmatory checks on the procedure in a laboratory. If the measured viscosity does not agree within ± 0.35 % of the certified value, recheck each step in the procedure including thermometer, timer, and viscometer calibration to locate the source of error. It should be appreciated that a correct result obtained on a certified oil does not preclude the possibility of a counterbalancing combination of the possible sources of error.

A1.3.2.1 A range of viscosity oil standards is commercially available, and each oil carries a certification of the measured value established by multiple testing. Table A1.2 gives the standard range of oils, together with the approximate viscosities over a range of temperatures.

TABLE A1.1 Viscometer Types

Viscometer Identification	Kinematic Viscosity Range,[A] mm^2/s
A. Ostwald Types for Transparent Liquids	
Cannon-Fenske routine[B]	0.5 to 20 000
Zeitfuchs	0.6 to 3 000
BS/U-tube[B]	0.9 to 10 000
BS/U/M miniature	0.2 to 100
SIL[B]	0.6 to 10 000
Cannon-Manning semi-micro	0.4 to 20 000
Pinkevitch[B]	0.6 to 17 000
B. Suspended-level Types for Transparent Liquids	
BS/IP/SL[B]	3.5 to 100 000
BS/IP/SL(S)[B]	1.05 to 10 000
BS/IP/MSL	0.6 to 3 000
Ubbelohde[B]	0.3 to 100 000
FitzSimons	0.6 to 1 200
Atlantic[B]	0.75 to 5 000
Cannon-Ubbelohde(A), Cannon Ubbelohde dilution[B](B)	0.5 to 100 000
Cannon-Ubbelohde semi-micro	0.4 to 20 000
C. Reverse-flow Types for Transparent and Opaque Liquids	
Cannon-Fenske opaque	0.4 to 20 000
Zeitfuchs cross-arm	0.6 to 100 000
BS/IP/RF U-tube reverse-flow	0.6 to 300 000
Lantz-Zeitfuchs type reverse-flow	60 to 100 000

[A] Each range quoted requires a series of viscometers. To avoid the necessity of making a kinetic energy correction, these viscometers are designed for a flow time in excess of 200 s except where noted in Specifications D 446.

[B] In each of these series, the minimum flow time for the viscometers with lowest constants exceeds 200 s.

TABLE A1.2 Viscosity Oil Standards[A]

Designation	Approximate Kinematic Viscosity, mm^2/s					
	−40°C	20°C	25°C	40°C	50°C	100°C
S3	80	4.6	4.0	2.9	...	1.2
S6	...	11	8.9	5.7	...	1.8
S20	...	44	34	18	...	3.9
S60	...	170	120	54	...	7.2
S200	...	640	450	180	...	17
S600	...	2 400	1 600	520	280	32
S2 000	...	8 700	5 600	1 700	...	75
S8 000	...	37 000	23 000	6 700	...	...
S30 000	...	...	81 000	23 000	11 000	...

[A] The actual values for these standards are established and annually reaffirmed by cooperative tests. In 1991, tests were made using 15 different types of viscometers in 28 laboratories located in 14 countries.

[B] Kinematic viscosities may also be supplied at 100°F.

[C] Kinematic viscosities may also be supplied at 210°F.

A2. KINEMATIC VISCOSITY TEST THERMOMETERS

A2.1 Short-Range Specialized Thermometer

A2.1.1 Use a short-range specialized thermometer conforming to the generic specification given in Table A2.1 and Table A2.2 and to one of the designs shown in Fig. A2.1.

A2.1.2 The difference in the designs rests mainly in the position of the ice point scale. In Design A, the ice point is within the scale range, in Design B, the ice point is below the scale range, and in Design C, the ice point is above the scale range.

A2.2 Calibration

A2.2.1 Use liquid-in-glass thermometers with an accuracy after correction of 0.02°C or better, calibrated by a laboratory meeting the requirements of ISO 9000 or ISO 25, and carrying certificates confirming that the calibration is traceable to a national standard. As an alternative, use thermometric devices such as platinum resistance thermometers, of equal or better accuracy, with the same certification requirements.

A2.2.2 The scale correction of liquid-in-glass thermometers can change during storage and use, and therefore regular re-calibration is required. This is most conveniently achieved in a working laboratory by means of a re-calibration of the ice point, and all of the main scale corrections altered for the change seen in the ice point.

A2.2.2.1 It is recommended that the interval for ice-point checking be not greater than six months, but for new thermometers, monthly checking for the first six months is recommended. A complete new re-calibration of the thermometer, while permitted, is not necessary in order to meet the accuracy ascribed to this design thermometer until the ice-point change from the last full calibration amounts to one scale division, or more than five years have elapsed since the last full calibration.

A2.2.2.2 Other thermometric devices, if used, will also require periodic recalibration. Keep records of all re-calibration.

TABLE A2.1 General Specification for Thermometers

NOTE 1—Table A2.2 gives a range of ASTM, IP, and ASTM/IP thermometers that comply with the specification in Table A2.1, together with their designated test temperatures. See Specification E 1 and Test Method E 77.

Immersion		Total
Scale marks:		
Subdivisions	°C	0.05
Long lines at each	°C	0.1 and 0.5
Numbers at each	°C	1
Maximum line width	mm	0.10
Scale error at test temperature, max	°C	0.1
Expansion chamber:		
Permit heating to	°C	105 up to 90, 120 between 90 and 95 130 between 95 and 105, 170 above 105
Total length	mm	300 to 310
Stem outside diameter	mm	6.0 to 8.0
Bulb length	mm	45 to 55
Bulb outside diameter	mm	no greater than stem
Length of scale range	mm	40 to 90

TABLE A2.2 Complying Thermometers

Thermometer No.	Test Temperature		Thermometer No.	Test Temperature	
	°C	°F		°C	°F
ASTM 132C, IP 102C	150		ASTM 128C, F/IP 33C	0	32
ASTM 110C, F/IP 93C	135	275	ASTM 72C, F/IP 67C	−17.8	0
ASTM 121C/IP 32C	98.9,	210,	ASTM 127C/IP 99C	−20	−4
	100	212	ASTM 126C, F/IP 71C	−26.1	−20
ASTM 129C, F/IP 36C	93.3	200	ASTM 73C, F/IP 68C	−40	−40
ASTM 48C, F/IP 90C	82.2	180	ASTM 74C, F/IP 69C	−53.9	−65
IP 100C	80				
ASTM 47C, F/IP 35C	60	140			
ASTM 29C, F/IP 34C	54.4	130			
ASTM 46C F/IP 66C	50	122			
ASTM 120C/IP 92C	40				
ASTM 28C, F/IP 31C	37.8	100			
ASTM 118C, F	30	86			
ASTM 45C, F/IP 30C	25	77			
ASTM 44C, F/IP 29C	20	68			

A2.2.3 *Procedure for Ice-point Re-calibration of Liquid-in-glass Thermometers*.

A2.2.3.1 Unless otherwise listed on the certificate of calibration, the re-calibration of calibrated kinematic viscosity thermometers requires that the ice-point reading shall be taken within 60 min after being at test temperature for not less than 3 min.

A2.2.3.2 Select clear pieces of ice, preferably made from distilled or pure water. Discard any cloudy or unsound portions. Rinse the ice with distilled water and shave or crush into small pieces, avoiding direct contact with the hands or any chemically unclean objects. Fill the Dewar vessel with the crushed ice and add sufficient water to form a slush, but not enough to float the ice. As the ice melts, drain off some of the water and add more crushed ice. Insert the thermometer, and pack the ice gently about the stem, to a depth approximately one scale division below the 0°C graduation.

A2.2.3.3 After at least 3 min have elapsed, tap the thermometer gently and repeatedly at right angles to its axis while making observations. Successive readings taken at least 1 min apart shall agree within 0.005°C.

A2.2.3.4 Record the ice-point readings and determine the thermometer correction at this temperature from the mean reading. If the correction is found to be higher or lower than that corresponding to a previous calibration, change the correction at all other temperatures by the same value.

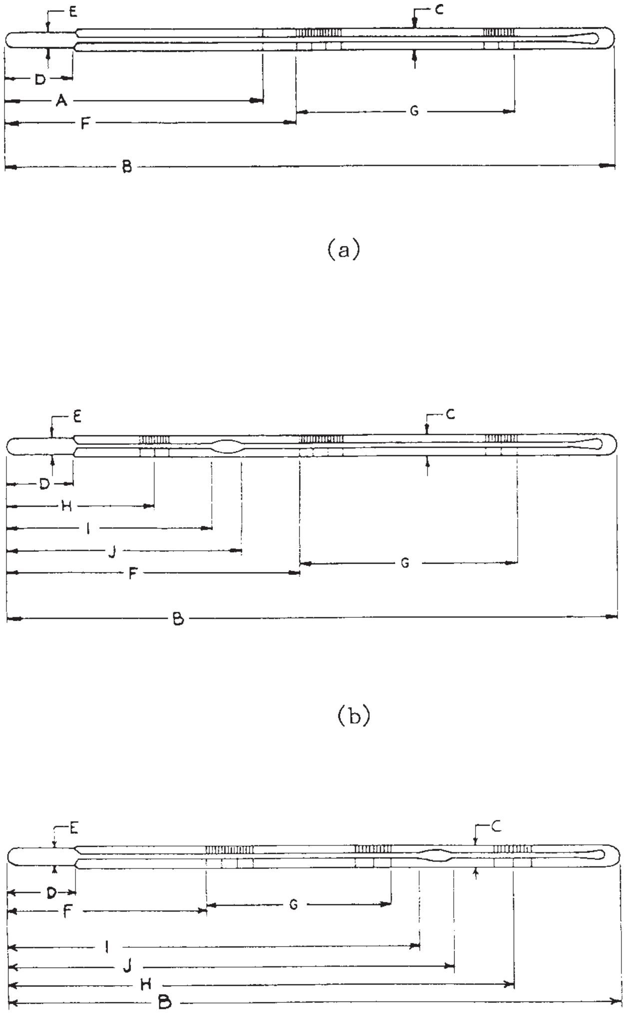
A2.2.3.5 During the procedure, apply the following conditions:

(*a*) The thermometer shall be supported vertically.

(*b*) View the thermometer with an optical aid that gives a magnification of approximately five and also eliminates parallax.

(*c*) Express the ice-point reading to the nearest 0.005°C.

A2.2.4 When in use, immerse the thermometric device to the same depth as when it was fully calibrated. For example, if a liquid-in-glass thermometer was calibrated at the normal total immersion condition, it shall be immersed to the top of the mercury column with the remainder of the stem and the



(a)

(b)

(c)

FIG. A2.1 Thermometer Designs

expansion volume at the uppermost end exposed to room temperature and pressure. In practice, this means that the top of the mercury column shall be within a length equivalent to four scale divisions of the surface of the medium whose temperature is being measured.

A2.2.4.1 If this condition cannot be met, then an extra correction may be necessary.

A3. TIMER ACCURACY

A3.1 Regularly check timers for accuracy and maintain records of such checks.

A3.1.1 Time signals as broadcast by the National Institute of Standards and Technology are a convenient and primary standard reference for calibrating timing devices. The following can be used to an accuracy of 0.1 s:

WWV	Fort Collins, CO	2.5, 5, 10, 15, 20 MHz
WWVH	Kauai, HI	2.5, 5, 10, 15, MHz
CHU	Ottawa, Canada	3.33, 7.335, 14.67 MHz

A3.1.2 Radio broadcast of voice and audio on a telephone line at phone 303-499-7111. Additional time services are available from the National Institute of Standards and Technology.

Designation: D1298 – 12b

Manual of Petroleum Measurement Standards (MPMS), Chapter 9.1

Standard Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method[1]

1. Scope*

1.1 This test method covers the laboratory determination using a glass hydrometer in conjunction with a series of calculations, of the density, relative density, or API gravity of crude petroleum, petroleum products, or mixtures of petroleum and nonpetroleum products normally handled as liquids, and having a Reid vapor pressure of 101.325 kPa (14.696 psi) or less. Values are determined at existing temperatures and corrected to 15°C or 60°F by means of a series of calculations and international standard tables.

1.2 The initial hydrometer readings obtained are uncorrected hydrometer readings and not density measurements. Readings are measured on a hydrometer at either the reference temperature or at another convenient temperature, and readings are corrected for the meniscus effect, the thermal glass expansion effect, alternate calibration temperature effects and to the reference temperature by means of the Petroleum Measurement Tables; values obtained at other than the reference temperature being hydrometer readings and not density measurements.

1.3 Readings determined as density, relative density, or API gravity can be converted to equivalent values in the other units or alternate reference temperatures by means of Interconversion Procedures (API *MPMS* Chapter 11.5), or Adjunct to D1250 Guide for Petroleum Measurement Tables (API *MPMS* Chapter 11.1), or both, or tables, as applicable.

1.4 The initial hydrometer readings determined in the laboratory shall be recorded before performing any calculations. The calculations required in Section 10 shall be applied to the initial hydrometer reading with observations and results reported as required by Section 11 prior to use in a subsequent calculation procedure (ticket calculation, meter factor calculation, or base prover volume determination).

1.5 Annex A1 contains a procedure for verifying or certifying the equipment for this test method.

1.6 The values stated in SI units are to be regarded as standard. The values given in parentheses are provided for information only.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1250 Guide for Use of the Petroleum Measurement Tables
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products
E1 Specification for ASTM Liquid-in-Glass Thermometers
E100 Specification for ASTM Hydrometers

2.2 *API Standards:*[3]

MPMS Chapter 8.1 Manual Sampling of Petroleum and Petroleum Products (ASTM Practice D4057)
MPMS Chapter 8.2 Automatic Sampling of Petroleum and Petroleum Products (ASTM Practice D4177)
MPMS Chapter 8.3 Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products (ASTM Practice D5854)
MPMS Chapter 11.1 Temperature and Pressure Volume Correction Factors for Generalized Crude Oils, Refined Products and Lubricating Oils (Adjunct to ASTM D1250)

***A Summary of Changes section appears at the end of this standard**

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and the API Committee on Petroleum Measurement, and is the direct responsibility of Subcommittee D02.02 /COMQ, the joint ASTM-API Committee on Hydrocarbon Measurement for Custody Transfer (Joint ASTM-API).

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Published as Manual of Petroleum Measurement Standards. Available from the American Petroleum Institute (API), 1220 L St., NW, Washington, DC 20005.

MPMS Chapter 11.5 Density/Weight/Volume Intraconversion

2.3 *Energy Institute Standards:*[4]

IP 389 Determination of wax appearance temperature (WAT) of middle distillate fuels by differential thermal analysis (DTA) or differential scanning calorimetry (DSC)

IP Standard Methods Book, Appendix A, Specifications – IP Standard Thermometers

2.4 *ISO Standards:*[5]

ISO 649-1 Laboratory glassware – Density hydrometers for general purpose – Part 1: Specification

2.5 *ASTM Adjuncts:*

Adjunct to D1250 Guide for Petroleum Measurement Tables (API *MPMS* Chapter 11.1)[6]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *API gravity, n*—a special function of relative density (specific gravity) 60/60°F, represented by:

$$°\text{API} = [141.5/(\text{relative density } 60/60\ °\text{F})] - 131.5 \quad (1)$$

3.1.1.1 *Discussion*—No statement of reference temperature is required, as 60°F is included in the definition.

3.1.2 *cloud point, n*—temperature at which a cloud of wax crystals first appears in a liquid when it is cooled under specific conditions.

3.1.3 *density, n*—the mass of liquid per unit volume at 15°C and 101.325 kPa with the standard unit of measurement being kilograms per cubic metre.

3.1.3.1 *Discussion*—Other reference temperatures, such as 20°C, may be used for some products or in some locations. Less preferred units of measurement (for example, kg/L or g/mL) are still in use.

3.1.4 *hydrometer reading, n*—the point on the hydrometer scale at which the surface of the liquid cuts the scale.

3.1.4.1 *Discussion*—In practice for transparent fluids this can be readily determined by aligning the surface of the liquid on both sides of the hydrometer and reading the Hydrometer scale where these surface readings cut the scale (Hydrometer Reading – Observed). For nontransparent fluids the point at which the liquid surface cuts the Hydrometer scale cannot be determined directly and requires a correction (Meniscus Correction). The value represented by the point (Meniscus Reading) at which the liquid sample rises above the main surface of the liquid subtracted from the value represented by where the main surface of the liquid cuts the Hydrometer scale is the amount of the correction or Meniscus correction. This meniscus correction is documented and then subtracted from the value represented by the Meniscus Reading to yield the Hydrometer Reading corrected for the Meniscus (Hydrometer Reading – Observed, Meniscus Corrected).

3.1.5 *observed values, n*—values observed at temperatures other than the specified reference temperature. These values are only hydrometer readings and not density, relative density (specific gravity), or API gravity at that other temperature.

3.1.6 *pour point, n*—lowest temperature at which a test portion of crude petroleum or petroleum product will continue to flow when it is cooled under specified conditions.

3.1.7 *relative density (specific gravity), n*—the ratio of the mass of a given volume of liquid at a specific temperature to the mass of an equal volume of pure water at the same or different temperature. Both reference temperatures shall be explicitly stated.

3.1.7.1 *Discussion*—Common reference temperatures include 60/60°F, 20/20°C, 20/4°C. The historic deprecated term *specific gravity* may still be found.

3.1.8 *wax appearance temperature (WAT), n*—temperature at which waxy solids form when a crude petroleum or petroleum product is cooled under specified conditions.

4. Summary of Test Method

4.1 The sample is brought to a specified temperature and a test portion is transferred to a hydrometer cylinder that has been brought to approximately the same temperature. The appropriate hydrometer and thermometer, also at a similar temperature, are lowered into the test portion and allowed to settle. After temperature equilibrium has been reached, the hydrometer scale is read, and the temperature of the test portion is taken. The observed hydrometer reading is corrected for the meniscus effect, the thermal glass expansion effect, alternate calibration temperature effects and then reduced to the reference temperature by means of the volume correction factors or tables as applicable by use of the appropriate Adjunct to D1250 Guide for Petroleum Measurement Tables (API *MPMS* Chapter 11.1) and observed temperature from the thermometer.

4.2 If necessary, the hydrometer cylinder and its contents are placed in a constant temperature bath to avoid excessive temperature variation during the test.

5. Significance and Use

5.1 Accurate determination of the density, relative density (specific gravity), or API gravity of petroleum and its products is necessary for the conversion of measured volumes to volumes or masses, or both, at the standard reference temperatures of 15°C or 60°F during custody transfer.

5.2 This procedure is most suitable for determining the density, relative density (specific gravity), or API gravity of low viscosity transparent liquids. This procedure can also be used for viscous liquids by allowing sufficient time for the hydrometer to reach temperature equilibrium, and for opaque liquids by employing a suitable meniscus correction. Additionally for both transparent and opaque fluids the readings shall be corrected for the thermal glass expansion effect and alternate calibration temperature effects before correcting to the reference temperature.

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[4] Available from Energy Institute, 61 New Cavendish St., London, W1M 8AR, UK.

[5] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036.

[6] Available from ASTM International Headquarters. Order Adjunct No. ADJD1250. Original adjunct produced in 1983.

5.3 When used in connection with bulk oil measurements, volume correction errors are minimized by observing the hydrometer reading at a temperature close to that of the bulk oil temperature.

5.4 Density, relative density, or API gravity is a factor governing the quality and pricing of crude petroleum. However, this property of petroleum is an uncertain indication of its quality unless correlated with other properties.

5.5 Density is an important quality indicator for automotive, aviation and marine fuels, where it affects storage, handling and combustion.

6. Apparatus

6.1 *Hydrometers,* of glass, graduated in units of density, relative density, or API gravity as required, conforming to Specification E100 or ISO 649-1, and the requirements given in Table 1.

6.1.1 The user should ascertain that the instruments used for this procedure conform to the requirements set out above with respect to materials, dimensions, and scale errors. In cases where the instrument is provided with a calibration certificate issued by a recognized standardizing body, the instrument is classed as certified and the appropriate corrections for the meniscus effect, the thermal glass expansion effect, and alternative calibration temperature effects shall be applied to the observed readings prior to corrections. Instruments that satisfy the requirements of this test method, but are not provided with a recognized calibration certificate, are classed as uncertified.

6.2 *Thermometers,* having range, graduation intervals and maximum permitted scale error shown in Table 2 and conforming to Specification E1 or IP Appendix A.

6.2.1 Alternate measuring devices or systems may be used, provided that the total uncertainty of the calibrated system is no greater than that specified in 6.2. The stated repeatability and reproducibility values are not applicable if alternate fluids are used in the liquid-in-glass thermometers.

6.3 *Hydrometer Cylinder,* clear glass, or plastic (see 6.3.1). The inside diameter of the cylinder shall be at least 25 mm greater than the outside diameter of the hydrometer and the height shall be such that the appropriate hydrometer floats in the sample test portion with at least 25 mm clearance between the bottom of the hydrometer and the bottom of the cylinder.

6.3.1 Hydrometer cylinders constructed of plastic materials shall be resistant to discoloration or attack by oil samples and shall not affect the material being tested. They shall not become opaque under prolonged exposure to sunlight.

TABLE 1 Recommended Hydrometers

Units	Range		Scale^A		Meniscus
	Total	Each Unit	Interval^A	Error^A	Correction
Density, kg/m^3 at 15°C	600 - 1100	20	0.2	± 0.2	+0.3
	600 - 1100	50	0.5	± 0.3	+0.7
	600 - 1100	50	1.0	± 0.6	+1.4
Relative density, 60/60°F	0.600 - 1.100	0.020	0.0002	± 0.0002	+0.0003
	0.600 - 1.100	0.050	0.0005	± 0.0003	+0.0007
	0.600 - 1.100	0.050	0.001	± 0.0006	+0.0014
Relative density, 60/60°F	0.650 - 1.100	0.050	0.0005	±0.0005	+0.0007
API Gravity	−1 - +101	12	0.1	± 0.1	-0.1

^{A}Interval and Error relate to Scale.

TABLE 2 Recommended Thermometers

Scale	Range	Graduation Interval	Scale Error
°C	−1 - +38	0.1	± 0.1
°C	−20 - +102	0.2	± 0.15
°F	−5 - +215	0.5	± 0.25

6.4 *Constant-Temperature Bath,* if required, of dimensions such that it can accommodate the hydrometer cylinder with the test portion fully immersed below the test portion liquid surface, and a temperature control system capable of maintaining the bath temperature within 0.25°C of the test temperature throughout the duration of the test.

6.5 *Stirring Rod,* optional, of glass or plastic, approximately 400 mm in length.

7. Sampling

7.1 Unless otherwise specified, samples of non-volatile petroleum and petroleum products shall be taken by the procedures described in Practice D4057 (API *MPMS* Chapter 8.1) and D4177 (API *MPMS* Chapter 8.2).

7.2 Samples of volatile crude petroleum or petroleum products are preferably taken by Practice D4177 (API *MPMS* Chapter 8.2), using a variable volume (floating piston) sample receiver to minimize any loss of light components which may affect the accuracy of the density measurement. In the absence of this facility, extreme care shall be taken to minimize these losses, including the transfer of the sample to a chilled container immediately after sampling.

7.3 *Sample Mixing*—May be necessary to obtain a test portion representative of the bulk sample to be tested, but precautions shall be taken to maintain the integrity of the sample during this operation. Mixing of volatile crude petroleum or petroleum products containing water or sediments, or both, or the heating of waxy volatile crude petroleum or petroleum products may result in the loss of light components. The following subsections (7.3.1 to 7.3.4) will give some guidance on sample integrity maintenance.

7.3.1 *Volatile Crude Petroleum and Petroleum Products Having an RVP Greater than 50 kPa*—Mix the sample in its original closed container in order to minimize the loss of light components.

NOTE 1—Mixing volatile samples in open containers will lead to loss of light components and consequently affect the value of the density obtained.

7.3.2 *Waxy Crude Petroleum*—If the petroleum has an expected pour point above 10°C, or a cloud point or WAT above 15°C, warm the sample to a temperature that is sufficient for ensuring the material is fluid enough to provide adequate mixing without excessively heating the material that would otherwise compromise the integrity of the sample. Samples heated to 9°C above its pour point, or 3°C above its cloud point or WAT have been found to be suitable temperatures to warm samples prior to mixing. Whenever possible, mix the sample in its original closed container in order to minimize the loss of light components.

7.3.3 *Waxy Distillate*—Warm the sample to a temperature that is sufficient for ensuring the material is fluid enough to provide adequate mixing without excessively heating the material that would otherwise compromise the integrity of the sample. Samples heated to 3°C above its cloud point or WAT have been found to be suitable temperatures to warm samples prior to mixing.

7.3.4 *Residual Fuel Oils*—Heat the sample to the test temperature prior to mixing (see 9.1.1 and Note 4).

7.4 Additional information on the mixing and handling of liquid samples will be found in Practice D5854 (API *MPMS* Chapter 8.3).

8. Apparatus Verification or Certification

8.1 Hydrometers and thermometers shall be verified in accordance with the procedures in Annex A1.

9. Procedure

9.1 *Temperature of Test:*

9.1.1 Bring the sample to the test temperature which shall be such that the sample is sufficiently fluid but not so high as to cause the loss of light components, nor so low as to result in the appearance of waxy solids in the test portion.

NOTE 2—The density, relative density or API gravity determined by the hydrometer is most accurate at or near the reference temperature.

NOTE 3—The volume and density, the relative density, and the API corrections in the volume correction tables are based on the average expansions of a number of typical materials. Since the same coefficients were used in compiling each set of tables, corrections made over the same temperature interval minimize errors arising from possible differences between the coefficient of the material under test and the standard coefficients. This effect becomes more important as temperatures diverge from the reference temperature.

NOTE 4—The hydrometer reading is obtained at a temperature appropriate to the physico-chemical characteristics of the material under test. This temperature is preferably close to the reference temperature, or when the value is used in conjunction with bulk oil measurements, within 3°C of the bulk temperature (see 5.3).

9.1.2 For crude petroleum, bring the sample close to the reference temperature or, if wax is present, to 9°C above its expected pour point or 3°C above its expected cloud point or WAT, whichever is higher.

NOTE 5—For crude petroleum an indication of the WAT can be found using IP 389, with the modification of using 50 µL ± 5 µL of sample. The precision of WAT for crude petroleum using this technique has not been determined.

9.2 *Density Measurement:*

9.2.1 Bring the hydrometer cylinder and thermometer to within approximately 5°C of the test temperature.

9.2.2 Transfer the sample to the clean, temperature-stabilized hydrometer cylinder without splashing, to avoid the formation of air bubbles, and minimize evaporation of the lower boiling constituents of more volatile samples. (**Warning—**Extremely flammable. Vapors may cause flash fire!)

9.2.3 Transfer highly volatile samples by siphoning or water displacement. (**Warning—**Do not siphon by mouth as it could result in ingestion of sample!)

9.2.3.1 Samples containing alcohol or other water-soluble materials should be placed into the cylinder by siphoning.

9.2.4 Remove any air bubbles formed after they have collected on the surface of the test portion, by touching them with a piece of clean filter paper or other suitable means before inserting the hydrometer.

9.2.5 Place the cylinder containing the test portion in a vertical position in a location free from air currents and where the temperature of the surrounding medium does not change more than 2°C during the time taken to complete the test. When the temperature of the test portion differs by more than 2°C from ambient, use a constant temperature bath to maintain an even temperature throughout the test duration.

9.2.6 Insert the appropriate thermometer or temperature measurement device and stir the test portion with a stirring rod, using a combination of vertical and rotational motions to ensure uniform temperature and density throughout the hydrometer cylinder. Record the temperature of the sample to the nearest 0.1°C and remove the thermometer/temperature measuring device and stirring rod from the hydrometer cylinder.

NOTE 6—If a liquid-in-glass thermometer is used, this is commonly used as the stirring rod.

9.2.7 Lower the appropriate hydrometer into the liquid and release when in a position of equilibrium, taking care to avoid wetting the stem above the level at which it floats freely. For low viscosity transparent or translucent liquids observe the meniscus shape when the hydrometer is pressed below the point of equilibrium about 1 to 2 mm and allowed to return to equilibrium. If the meniscus changes, clean the hydrometer stem and repeat until the meniscus shape remains constant.

9.2.8 For opaque viscous liquids, allow the hydrometer to settle slowly into the liquid.

9.2.9 For low viscosity transparent or translucent liquids depress the hydrometer about two scale divisions into the liquid, and then release it, imparting a slight spin to the hydrometer on release to assist in bringing it to rest floating freely from the walls of the hydrometer cylinder. Ensure that the remainder of the hydrometer stem, which is above the liquid level, is not wetted as liquid on the stem affects the reading obtained.

9.2.10 Allow sufficient time for the hydrometer to come to rest, and for all air bubbles to come to the surface. Remove any air bubbles before taking a reading (see 9.2.12).

9.2.11 If the hydrometer cylinder is made of plastic, dissipate any static charges by wiping the outside with a damp cloth. (Static charges often build up on plastic cylinders and may prevent the hydrometer from floating freely.)

9.2.12 When the hydrometer has come to rest floating freely away from the walls of the cylinder, read the hydrometer scale reading to the nearest one-fifth or one-tenth of a full scale division depending upon the number of subdivisions (that is, 5 or 10, respectively) that exist between a full scale division in accordance with 9.2.12.1 or 9.2.12.2.

9.2.12.1 For transparent liquids, record the hydrometer reading as the point on the hydrometer scale at which the principal surface of the liquid cuts the scale by placing the eye slightly below the level of the liquid and slowly raising it until the surface, first seen as a distorted ellipse, appears to become a straight line cutting the hydrometer scale (see Fig. 1).

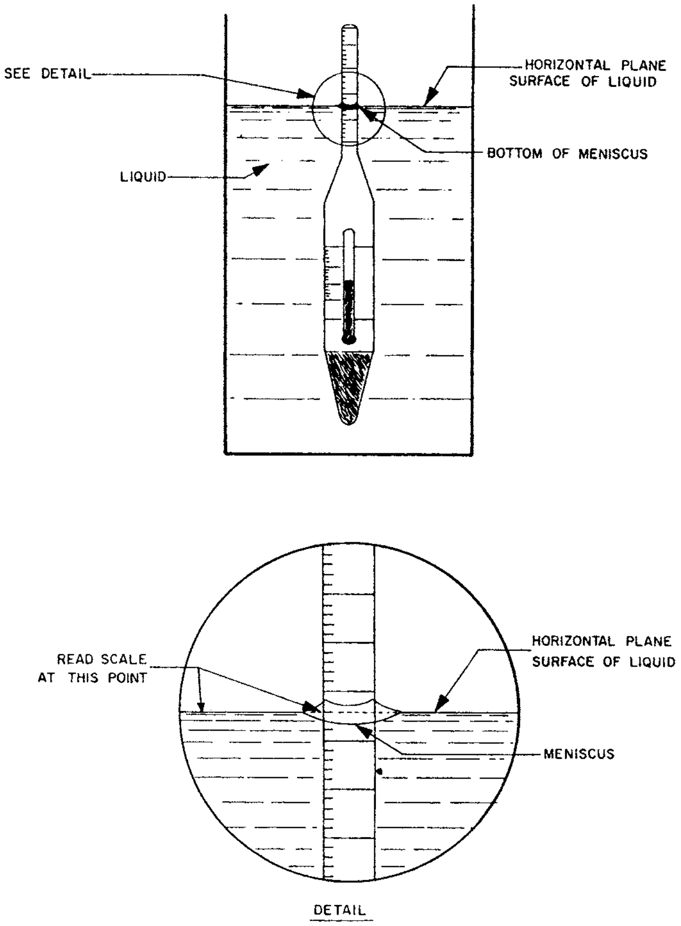

FIG. 1 Hydrometer Scale Reading for Transparent Liquids

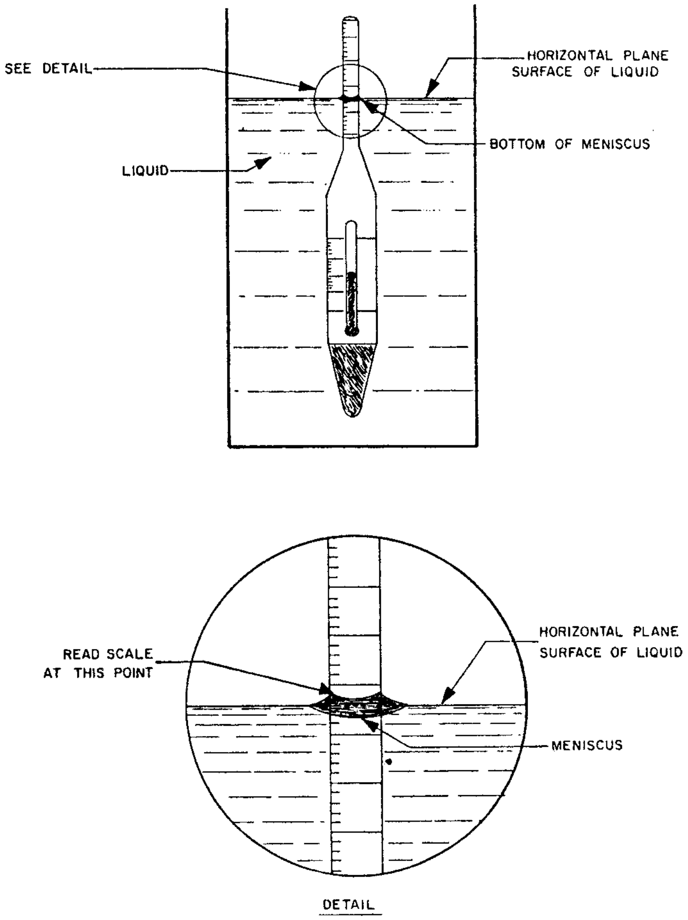

FIG. 2 Hydrometer Scale Reading for Opaque Fluids

9.2.12.2 For opaque liquids record the hydrometer reading at the point on the hydrometer scale to which the sample rises above its main surface, by observing with the eye slightly above the plane of the surface of the liquid (see Fig. 2). This reading requires a meniscus correction. This correction can be determined by one of two methods: 1) observe the height above the main surface of the liquid to which the sample rises on the hydrometer scale when the hydrometer in question is immersed in a transparent liquid having a surface tension similar to that of a sample under test; 2) uses the nominal values shown in Table 1. Document this value as the Meniscus correction.

NOTE 7—When testing opaque liquids using a metal hydrometer cylinder, accurate readings of the hydrometer scale can only be ensured if the liquid surface is within 5 mm of the top of the cylinder.

9.2.13 Immediately after recording the hydrometer scale reading, carefully lift the hydrometer out of the liquid, insert the thermometer or temperature measurement device and stir the test portion vertically with the stirring rod. Record the temperature of the test portion to the nearest 0.1°C. If this temperature differs from the previous reading (9.2.6) by more than 0.05°C, repeat the hydrometer observations and thermometer observations until the temperature becomes stable within 0.05°C. If a stable temperature cannot be obtained, place the hydrometer cylinder in a constant temperature bath and repeat the procedure from 9.1.

9.2.14 If the test temperature is higher than 38°C, allow all hydrometers of the lead shot-in-wax type to drain and cool in a vertical position.

10. Calculation

10.1 Apply any relevant thermometer corrections to the temperature reading observed in 9.2.6 and 9.2.13 and record the average of those two temperatures to the nearest 0.1 °C.

10.2 Record the observed hydrometer scale readings to the nearest 0.1 kg/m^3 in density, 0.0001 g/mL, kg/L or relative density, or 0.1° API for transparent liquids.

10.2.1 For opaque samples, apply the relevant meniscus correction given in Table 1 or determine it as indicated in 9.2.12.2 to the observed hydrometer reading (9.2.12.2) as hydrometers are calibrated to be read at the principal surface of the liquid.

10.3 Apply any hydrometer correction identified in a calibration certificate to the observed reading and record the corrected hydrometer scale reading to the nearest 0.1 kg/m^3 in density, 0.0001 g/mL, kg/L or relative density, or 0.1 °API.

10.4 Application of the glass thermal expansion correction depends upon what version of Adjunct to D1250 Guide for Petroleum Measurement Tables (API *MPMS* Chapter 11.1) will be used to calculate the base density.

(a) The 1980 version of the Adjunct to D1250 Guide for Petroleum Measurement Tables (API *MPMS* Chapter 11.1) has the hydrometer glass thermal expansion correction included. Input into the VCF software requires the Hydrometer Reading – Observed or Hydrometer Reading – Observed, Meniscus Corrected in API, R.D., or kg/m^3 units from 9.2.12.2, observed temperature of the sample, and the built-in hydrometer glass thermal correction switch set to on (0) or off (1). It will return API or R.D. @ 60°F or kg/m^3 @ 15°C.

(b) The 2004 version of the Adjunct to D1250 Guide for Petroleum Measurement Tables (API *MPMS* Chapter 11.1) does not include the hydrometer glass thermal expansion correction, so that correction must be made before entering the software. Depending on the specific end use of the calculation results, the final value may be left rounded or unrounded.

The following steps are required to implement 10.4b:

Step 1. Convert the corrected hydrometer scale reading to density in kg/m^3 if necessary, using either Eq 2 or Eq 3.

Scale Units	Conversion
API gravity	

$$Density\left(kg/m^3\right) = \left(141.5*999.016\right)/\left(131.5+°API\right) \qquad (2)$$

Scale Units	Conversion
Relative density	

$$Density\left(kg/m^3\right) = R.D.*999.016 \qquad (3)$$

Leave the result unrounded.

Step 2. Calculate the hydrometer thermal glass expansion correction factor using the appropriate equation below (t is observed temperature).

Correction for a Base Temperature (T_b) of 60°F:

$$HYC = 1.0 - \left[0.00001278\left(t-60\right)\right] - \left[0.0000000062\left(t-60\right)^2\right] \qquad (4)$$

Correction for a Base Temperature (T_b) of 15°C:

$$HYC = 1.0 - \left[0.000023\left(t-15\right)\right] - \left[0.00000002\left(t-15\right)^2\right] \qquad (5)$$

Correction for a Base Temperature (T_b) of 20°C:

$$HYC = 1.0 - \left[0.000023\left(t-20\right)\right] - \left[0.00000002\left(t-20\right)^2\right] \qquad (6)$$

Leave the result un-rounded.

Step 3. Multiply the density in kg/m^3 from Step 1 by the proper HYC from Step 2 to obtain the glass thermal expansion corrected hydrometer density reading.

$$kg/m^3{}_{HYC} = kg/m^3 * HYC \qquad (7)$$

If the temperature was in degrees Celsius, skip to Step 5.

Step 4a. Convert the densities calculated in Step 3 that started as API Gravity or Relative Density (RD) to RD (Relative Density).

NOTE 8—The current C source code compiled dll and Excel Add-in has an omission and cannot use a kg/m^3 call with degree F.

$$R.D. = kg/m^3{}_{HYC}/999.016 \qquad (8)$$

Step 4b. Input R.D. and degree F into section 11.1.6.2 of the Adjunct to D1250–04 Guide for Petroleum Measurement Tables (API *MPMS* Chapter 11.1–2004), which returns R.D. @ 60 °F.

NOTE 9—Pressure will have to be atmospheric gauge, or 0 psig as the Adjunct to D1250 Guide for Petroleum Measurement Tables (API *MPMS* Chapter 11.1) values are only valid at atmospheric pressure.

Step 4c. Convert the calculated R.D. value @ 60°F to a calculated API Gravity @ 60 °F using Eq 9, if the original input was in API units.

$$\text{API Gravity} = \left(141.5/\text{R.D.}\right) - 131.5 \qquad (9)$$

Step 5. Input the density calculated in Step 3 in kg/m^3 HYC, degree C, base temperature (15°C or 20°C) into Section 11.1.7.2 of the Adjunct to D1250–04 Guide for Petroleum Measurement Tables (API *MPMS* Chapter 11.1–2004), which will return a calculated density in kg/m^3 units at the selected base temperature.

NOTE 10—Pressure will have to be atmospheric gauge, 0 psig, 101.325 kPa or 0 bar as the Adjunct to D1250 Guide for Petroleum Measurement Tables (API *MPMS* Chapter 11.1) values are only valid at atmospheric pressure.

c. Future versions of the Adjunct to D1250 Guide for Petroleum Measurement Tables (API *MPMS* Chapter 11.1) code will be corrected so that it can accept any combination of input units and return any combination of output units. When available, the Adjunct to D1250 Guide for Petroleum Measurement Tables (API *MPMS* Chapter 11.1) code can be accessed directly from Step 3 and return API @ 60 °F, R.D. @ 60 °F, and kg/m^3 at any selected base temperature.

Example 1:

Sample:	Crude Oil	
Observed Temperature:	77°F	
Observed Hydrometer Reading:	33.2 API Gravity	
Base Temperature:	60°F	
Step 1:	858.2924347298...	Eq 2, Eq 3
Step 2:	0.999780948...	Eq 4, Eq 5, Eq 6
Step 3:	858.104424227	Eq 7
Step 4a:	0.858949631...	Eq 8
Step 4b:	0.865678279...	
Step 4c1:	31.955643312...	Eq 9 unrounded
Step 4c2:	32.0°API	Eq 9 rounded

Example 2:

Sample:	Crude Oil	
Observed Temperature:	25.0 °C	
Observed Hydrometer Reading:	858.29 kg/m^3	
Observed Pressure:	0 bar	
Base Temperature:	15°C	
Step 1:	858.290000000...	no conversion necessary
Step 2:	0.999768000...	Eq 4
Step 3:	858.090876720...	Eq 7
Step 5.1:	865.207470082...	unrounded
Step 5.2	865.21 kg/m^3	rounded

Example 3:

Sample:	Crude Oil	
Observed Temperature:	77.0 °F	
Observed Hydrometer Reading (R.D.):	0.859138	
Observed Pressure	0 psig	
Base Temp:	60°F	
Step 1:	858.292608208...	Eq 2, Eq 3
Step 2:	0.999780948...	Eq 4, Eq 5, Eq 6
Step 3:	858.104597667...	Eq 7
Step 4a:	0.858949804...	Eq 8
Step 4b	0.865678451...	unrounded
Step 4c	0.8657...	rounded

10.5 If the hydrometer has been calibrated at a temperature other than the reference temperature, use the equation below to correct the hydrometer scale reading:

$$\rho r = \frac{\rho t}{1 - \left[23\times10^{-6}\ (t-r) - 2\times10^{-8}\ (t-r)^2\right]} \qquad (10)$$

where:

ρ_r = hydrometer reading at the reference temperature, r °C, and

ρ_t = hydrometer reading on the hydrometer scale whose reference temperature is t °C.

11. Report

11.1 Report the final value as density, in kilograms per cubic metre, at the reference temperature, to the nearest 0.1 kg/m^3.

11.2 Report the final value as density, in kilograms per litre or grams per millilitre at the reference temperature, to the nearest 0.0001.

11.3 Report the final value as relative density, with no dimensions, at the two reference temperatures, to the nearest 0.0001.

11.4 Report the final value as API gravity to the nearest 0.1° API.

11.5 The reporting values have no precision or bias determination. It is up to the user to determine whether this test method provides results of sufficient accuracy for the intended purpose.

11.6 Certified hydrometers from a recognized standardizing body, such as NIST, report the output density as 'Density in Vacuo.'

12. Precision and Bias

12.1 *Precision*—The precision of the test method as determined by statistical examination of interlaboratory results is as follows:

12.1.1 *Repeatability*—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values in Table 3 only in 1 case in 20.

12.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in 1 case in 20.

TABLE 3 Precision Values

Product: Transparent Low-viscosity Liquids				
Parameter	Temperature Range, °C (°F)	Units	Repeat-ability	Repro-ducibility
Density	–2 to 24.5	kg/m^3	0.5	1.2
	(29 to 76)	kg/L or g/mL	0.0005	0.0012
Relative Density	–2 to 24.5 (29 to 76)	NONE	0.0005	0.0012
API Gravity	(42 to 78)	°API	0.1	0.3
Product: Opaque Liquids				
Parameter	Temperature Range, °C (°F)	Units	Repeat-ability	Repro-ducibility
Density	–2 to 24.5	kg/m^3	0.6	1.5
	(29 to 76)	kg/L or g/mL	0.0006	0.0015
Relative Density	–2 to 24.5 (29 to 76)	NONE	0.0006	0.0015
API Gravity	(42 to 78)	°API	0.2	0.5

12.1.3 The repeatability and reproducibility values provided in Table 3 are not based on any interlaboratory round robin results. They should be considered historical numbers, the source of which can not be verified by either ASTM or API and have been in this document prior to the current slate of blended crude oils, RFG gasoline's and reformulated distillates. These values do not apply to the current calculation procedures and it is up to the user to determine whether this test method provides results of sufficient accuracy for the intended purpose.

12.2 *Bias*—Bias for this test method has not been determined. However, there should be no bias from absolute measurements, if the calibration of the hydrometer and the thermometer is traceable to International Standards, such as supplied by the National Institute of Standards and Technology.

13. Keywords

13.1 API gravity; crude petroleum; density; hydrometer; Petroleum Measurement Tables; petroleum products; relative density; specific gravity

ANNEX

(Mandatory Information)

A1. APPARATUS

A1.1 Apparatus Verification and Certification

A1.1.1 *Hydrometers,* shall either be certified or verified. Verification shall be either by comparison with a certified hydrometer (see 6.1.1) or by the use of a certified reference material (CRM) specific to the reference temperature used.

A1.1.1.1 The hydrometer scale shall be correctly located within the hydrometer stem by reference to the datum mark. If the scale has moved, reject the hydrometer.

A1.1.2 *Thermometers,* shall be verified at intervals of no more than six months for conformance with specifications. Either comparison with a referenced temperature measurement system traceable to an international standard, or a determination of ice point, is suitable.

SUMMARY OF CHANGES

Subcommittee D02.02 has identified the location of selected changes to this standard since the last issue (D1298–12a) that may impact the use of this standard. (Approved June 1, 2012)

(1) Added 3.1.4.

Subcommittee D02.02 has identified the location of selected changes to this standard since the last issue (D1298–12) that may impact the use of this standard. (Approved May 15, 2012)

(1) Revised 9.2.12.2.

(2) Revised Section 10.

Subcommittee D02.02 has identified the location of selected changes to this standard since the last issue (D1298–99(2005)) that may impact the use of this standard. (Approved April 1, 2012)

(1) Added 10.4 to represent the thermal glass correction now required in this standard.

(2) Made clarifications and corrections in Sections 9, 11, and 12.

Designation: D 2500 – 05

An American National Standard
British Standard 4458

Designation: 219/82

Standard Test Method for Cloud Point of Petroleum Products[1]

This standard is issued under the fixed designation D 2500; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This test method covers only petroleum products and biodiesel fuels that are transparent in layers 40 mm in thickness, and with a cloud point below 49°C.

NOTE 1—The interlaboratory program consisted of petroleum products of Test Method D 1500 color of 3.5 and lower. The precisions stated in this test method may not apply to samples with ASTM color higher than 3.5.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 7.

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 1500 Test Method for ASTM Color of Petroleum Products (ASTM Color Scale)

E 1 Specification for ASTM Liquid-in-Glass Thermometers

2.2 *Energy Institute Standard:*

Specifications for IP Standard Thermometers [3]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *biodiesel*, *n*—a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100.

3.1.1.1 *Discussion*—Biodiesel is typically produced by a reaction of vegetable oil or animal fat with an alcohol such as methanol or ethanol in the presence of a catalyst to yield mono-esters and glycerin. The fuel typically may contain up to 14 different types of fatty acids that are chemically transformed into fatty acid methyl esters (FAME).

3.1.2 *biodiesel blend*, *n*—a blend of biodiesel fuel with petroleum-based diesel fuel designated BXX, where XX is the volume % of biodiesel.

3.1.3 *cloud point*, *n—in petroleum products and biodiesel fuels,* the temperature of a liquid specimen when the smallest observable cluster of hydrocarbon crystals first occurs upon cooling under prescribed conditions.

3.1.3.1 *Discussion*—To many observers, the cluster of wax crystals looks like a patch of whitish or milky cloud, hence the name of the test method. The cloud appears when the temperature of the specimen is low enough to cause wax crystals to form. For many specimens, the crystals first form at the lower circumferential wall of the test jar where the temperature is lowest. The size and position of the cloud or cluster at the cloud point varies depending on the nature of the specimen. Some samples will form large, easily observable, clusters, while others are barely perceptible.

3.1.3.2 *Discussion*—Upon cooling to temperatures lower than the cloud point, clusters of crystals will grow in multiple directions; for example, around the lower circumference of the test jar, towards the center of the jar, or vertically upwards. The crystals can develop into a ring of cloud along the bottom circumference, followed by extensive crystallization across the bottom of the test jar as temperature decreases. Nevertheless, the cloud point is defined as the temperature at which the crystals first appear, not when an entire ring or full layer of wax has been formed at the bottom of the test jar.

3.1.3.3 *Discussion*—In general, it is easier to detect the cloud point of samples with large clusters that form quickly, such as paraffinic samples. The contrast between the opacity of the cluster and the liquid is also sharper. In addition, small brightly-reflective spots can sometimes be observed inside the cluster when the specimen is well illuminated. For other more difficult samples, such as naphthenic, hydrocracked, and those samples whose cold flow behavior have been chemically altered, the appearance of the first cloud can be less distinct. The rate of crystal growth is slow, the opacity contrast is weak,

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.07 on Flow Properties.

Current edition approved July 1, 2005. Published August 2005. Originally approved in 1966. Last previous edition approved in 2002 as D 2500–02$^{\epsilon 1}$.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from Energy Institute, 61 New Cavendish St., London, England WIM 8AR.

***A Summary of Changes section appears at the end of this standard.**

and the boundary of the cluster is more diffuse. As the temperature of these specimens decrease below the cloud point, the diffuse cluster will increase in size and can form a general haze throughout. A slight haze throughout the entire sample, which slowly becomes more apparent as the temperature of the specimen decreases, can also be caused by traces of water in the specimen instead of crystal formation (see Note 4). With these difficult samples, drying the sample prior to testing can eliminate this type of interference.

3.1.3.4 *Discussion*—The purpose of the cloud point method is to detect the presence of the wax crystals in the specimen; however trace amounts of water and inorganic compounds may also be present. The intent of the cloud point method is to capture the temperature at which the liquids in the specimen begin to change from a single liquid phase to a two-phase system containing solid and liquid. It is not the intent of this test method to monitor the phase transition of the trace components, such as water.

4. Summary of Test Method

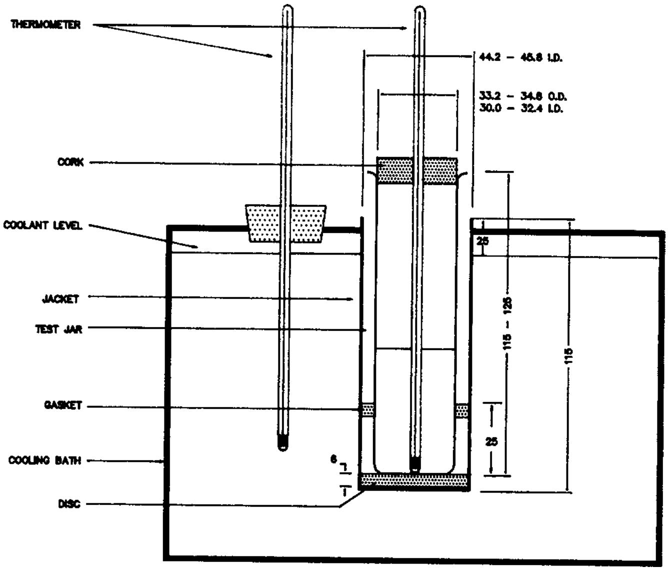
4.1 The specimen is cooled at a specified rate and examined periodically. The temperature at which a cloud is first observed at the bottom of the test jar is recorded as the cloud point.

5. Significance and Use

5.1 For petroleum products and biodiesel fuels, cloud point of a petroleum product is an index of the lowest temperature of their utility for certain applications.

6. Apparatus (see Fig. 1)

6.1 *Test Jar*, clear, cylindrical glass, flat bottom, 33.2 to 34.8-mm outside diameter and 115 and 125-mm height. The inside diameter of the jar may range from 30 to 32.4 mm within the constraint that the wall thickness be no greater than 1.6 mm. The jar should be marked with a line to indicate sample height 54 ± 3 mm above the inside bottom.



NOTE—All dimensions are in milllimetres.

FIG. 1 Apparatus for Cloud Point Test

6.2 *Thermometers*, having ranges shown below and conforming to the requirements as prescribed in Specification E 1 or Specifications for IP Standard Thermometers.

Thermometer	Temperature Range	Thermometer Number ASTM	 IP
High cloud and pour	−38 to +50°C	5C	1C
Low cloud and pour	−80 to +20°C	6C	2C

6.3 *Cork*, to fit the test jar, bored centrally for the test thermometer.

6.4 *Jacket*, metal or glass, watertight, cylindrical, flat bottom, about 115 mm in depth, with an inside diameter of 44.2 to 45.8 mm. It shall be supported free of excessive vibration and firmly in a vertical position in the cooling bath of 6.7 so that not more than 25 mm projects out of the cooling medium.

6.5 *Disk*, cork or felt, 6-mm thick to fit loosely inside the jacket.

6.6 *Gasket*, ring form, about 5 mm in thickness, to fit snugly around the outside of the test jar and loosely inside the jacket. The gasket may be made of rubber, leather, or other material that is elastic enough to cling to the test jar and hard enough to hold its shape. Its purpose is to prevent the test jar from touching the jacket.

6.7 *Bath or Baths*, maintained at prescribed temperatures with a firm support to hold the jacket vertical. The required bath temperatures may be maintained by refrigeration if available, otherwise by suitable freezing mixtures.

NOTE 2—The mixtures commonly used for temperatures down to those shown are as follows:

Ice and water	10°C
Crushed ice and sodium chloride crystals	−12°C
Crushed ice and calcium chloride crystals	−26°C
Acetone, methyl or ethyl alcohol, or petroleum naphtha chilled in a covered metal beaker with an ice-salt mixture to −12°C, then with enough solid carbon dioxide to give the desired temperature	−57°C

7. Reagents and Materials

7.1 *Acetone*—Technical grade acetone is suitable for the cooling bath, provided it does not leave a residue on drying. (**Warning—**Extremely flammable.)

7.2 *Calcium Chloride*—Commercial or technical grade calcium chloride is suitable.

7.3 *Carbon Dioxide (Solid) or Dry Ice*—A commercial grade of dry ice is suitable for use in the cooling bath.

7.4 *Ethanol or Ethyl Alcohol*—A commercial or technical grade of dry ethanol is suitable for the cooling bath. (**Warning—**Flammable. Denatured, cannot be made nontoxic.)

7.5 *Methanol or Methyl Alcohol*—A commercial or technical grade of dry methanol is suitable for the cooling bath. (**Warning—**Flammable. Vapor harmful.)

7.6 *Petroleum Naphtha*—A commercial or technical grade of petroleum naphtha is suitable for the cooling bath. (**Warning—**Combustible. Vapor harmful.)

7.7 *Sodium Chloride Crystals*—Commercial or technical grade sodium chloride is suitable.

7.8 *Sodium Sulfate*—A reagent grade of anhydrous sodium sulfate should be used when required (see Note 4).

8. Procedure

8.1 Bring the sample to be tested to a temperature at least 14°C above the expected cloud point. Remove any moisture present by a method such as filtration through dry lintless filter paper until the oil is perfectly clear, but make such filtration at a temperature of at least 14°C above the approximate cloud point.

8.2 Pour the sample into the test jar to the level mark.

8.3 Close the test jar tightly by the cork carrying the test thermometer. Use the high cloud and pour thermometer if the expected cloud point is above −36°C and the low cloud and pour thermometer if the expected cloud point is below −36°C. Adjust the position of the cork and the thermometer so that the cork fits tightly, the thermometer and the jar are coaxial, and the thermometer bulb is resting on the bottom of the jar.

NOTE 3—Liquid column separation of thermometers occasionally occurs and may escape detection. Thermometers should be checked periodically and used only if their ice points are 0 ± 1°C, when the thermometer is immersed to the immersion line in an ice bath, and when the emergent column temperature does not differ significantly from 21°C. Alternatively, immerse the thermometer to a reading and correct for the resultant cooler stem temperature.

8.4 See that the disk, gasket, and the inside of the jacket are clean and dry. Place the disk in the bottom of the jacket. The disk and jacket shall have been placed in the cooling medium a minimum of 10 min before the test jar is inserted. The use of a jacket cover while the empty jacket is cooling is permitted. Place the gasket around the test jar, 25 mm from the bottom. Insert the test jar in the jacket. Never place a jar directly into the cooling medium.

NOTE 4—Failure to keep the disk, gasket, and the inside of the jacket clean and dry may lead to frost formation, which may cause erroneous results.

8.5 Maintain the temperature of the cooling bath at 0 ± 1.5°C.

8.6 At each test thermometer reading that is a multiple of 1°C, remove the test jar from the jacket quickly but without disturbing the specimen, inspect for cloud, and replace in the jacket. This complete operation shall require not more than 3 s. If the oil does not show a cloud when it has been cooled to 9°C, transfer the test jar to a jacket in a second bath maintained at a temperature of −18 ± 1.5°C (see Table 1). Do not transfer the jacket. If the specimen does not show a cloud when it has been cooled to −6°C, transfer the test jar to a jacket in a third bath maintained at a temperature of −33± 1.5°C. For the determination of very low cloud points, additional baths are required, each bath to be maintained in accordance with Table 1. In each case, transfer the jar to the next bath, if the specimen does not exhibit cloud point and the temperature of the specimen reaches the lowest specimen temperature in the range identified for the current bath in use, based on the ranges stated in Table 1.

TABLE 1 Bath and Sample Temperature Ranges

Bath	Bath Temperature Setting, °C	Sample Temperature Range, °C
1	0 ± 1.5	Start to 9
2	−18 ± 1.5	9 to −6
3	−33 ± 1.5	−6 to −24
4	−51 ± 1.5	−24 to −42
5	−69 ± 1.5	−42 to −60

8.7 Report the cloud point, to the nearest 1°C, at which any cloud is observed at the bottom of the test jar, which is confirmed by continued cooling.

NOTE 5—A wax cloud or haze is always noted first at the bottom of the test jar where the temperature is lowest. A slight haze throughout the entire sample, which slowly becomes more apparent as the temperature is lowered, is usually due to traces of water in the oil. Generally this water haze will not interfere with the determination of the wax cloud point. In most cases of interference, filtration through dry lintless filter papers, such as described in 8.1, is sufficient. In the case of diesel fuels, however, if the haze is very dense, a fresh portion of the sample should be dried by shaking 100 mL with 5 g of anhydrous sodium sulfate for at least 5 min and then filtering through dry lintless filter paper. Given sufficient contact time, this procedure will remove or sufficiently reduce the water haze so that the wax cloud can be readily discerned. Drying and filtering should be done always at a temperature at least 14°C above the approximate cloud point but otherwise not in excess of 49°C.

9. Report

9.1 Report the temperature recorded in 8.7 as the cloud point, Test Method D 2500.

10. Precision and Bias

10.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

10.1.1 *Repeatability*—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of this test method, exceed 2°C only in 1 case in 20.

10.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of this test method, exceed 4°C only in 1 case in 20.

10.1.3 The precision statements were derived from a 1990 interlaboratory cooperative test program.[4] Participants analyzed 13 sample sets comprised of various distillate fuels and lubricating oils with temperature range from -1 to -37°C. Eight laboratories participated with the manual D 2500/IP219 test method. Information on the type of samples and their average cloud points are in the research report.

10.2 *Bias*—The procedure in this test method has no bias, because the value of cloud point can be defined only in terms of a test method.

10.3 *Precision for Biodiesel Products*[5]—The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

10.3.1 *Repeatability for Blends of Biodiesel in Diesel*—The difference between successive test results obtained by the same operator, using the same apparatus, under constant operating

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02–1444.

[5] Supporting data (the results of the 2001 interlaboratory cooperative test program) have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02–1524.

conditions, on identical test material would, in the long run, in the normal and correct operation of this test method, exceed 2°C only in 1 case in 20.

10.3.2 *Reproducibility for Blends of Biodiesel in Diesel*—The difference between two single and independent test results obtained by different operators, working in different laboratories, on identical test material would, in the long run, in the normal and correct operation of this test method, exceed 3°C only in 1 case in 20.

NOTE 6—The precision for blends of biodiesel in diesel samples comprised cloud points from about −2 to +10°C.

10.3.3 The precision statements were derived from a 2001 interlaboratory cooperative test program.[5] Participants analyzed eleven sample sets comprised of different blends of two petroleum distillate fuels, diesel and kerosene, with various biodiesel fuels with temperature range from +10 to −45°C. Ten laboratories participated with the manual D 2500/IP219 test method. Information on the type of samples and their average cloud points are in the research report.

NOTE 7—One of the outcomes of the interlaboratory study was the selection of the sample types, since the ones used in the study contributed to a difficulty in determining the precision statement. Kerosene is a sufficiently different fuel type from biodiesel to cause some slight separation of phases upon cooling when in B20 blends. Also, the particular kerosene sample used was atypical, which complicated the study further. Therefore, data from the blends of kerosene in biodiesel were not used in the precision statement. In addition, the diesel fuel used in the research report was high cloud point material. Due to the cloud point of the base diesel material, this temperature range in the precision statement was limited.

NOTE 8—A future interlaboratory cloud study will be done to include a wider range of base biodiesel fuels with various distillate blend stocks.

10.4 *Bias for Biodiesel Products*[5]—The procedure in this test method has no bias, because the value of cloud point can be defined only in terms of a test method.

11. Keywords

11.1 cloud point; petroleum products; wax crystals

SUMMARY OF CHANGES

Subcommittee D02.07 has identified the location of selected changes to this standard since the last issue, D 2500–02$^{\epsilon 1}$, that may impact the use of this standard.

(*1*) Added a discussion to the definition of cloud point (3.1.3).

BIODATA PENULIS

Penulis mempunyai nama lengkap **Thomas Andherson Sihombing**, lahir di Tebing Tinggi pada tanggal 26 Maret 1995, merupakan anak ke empat dari empat bersaudara. Penulis menempuh pendidikan sekolah dasar di SD Negeri 164522, pendidikan menengah di SMP Negeri 1 Tebing Tinggi, dan melanjutkan pendidikan menengah atas di SMA Negeri 1 Tebing Tinggi yang kemudian dilanjutkan ke ITS Jurusan Teknik Fisika pada tahun 2013 dengan NRP 2413100081. Hingga pada tahun 2017 penulis akhirnya melaksanakan Tugas Akhir sebagai syarat untuk menyelesaikan studi S1 di Jurusan Teknik Fisika dengan judul "**Pengaruh Suhu Dekomposisi dan Konsentrasi Katalis Kalsium Oksida (CaO) dari Cangkang Telur Ayam Terhadap Sintesis Biodiesel dari Minyak Jelantah**". Bagi pembaca yang memiliki saran, kritik, atau ingin berdiskusi lebih lanjut tentang Tugas Akhir ini, maka bisa menghubungi penulis melalui thomasandherson58@gmail.com.