Bio-based Hydraulic Fluids

Presented at

STLE Seminar on Environmentally Friendly Tribology

17 April 2008

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

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Report Documentation Page	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
17 APR 2008	**N/A**	**-**

4. TITLE AND SUBTITLE	
Bio-based Hydraulic Fluids	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **Dr. In-Sik Rhee**	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **US Army RDECOM-TARDEC 6501 E 11 Mile Rd Warren, MI 48397-5000**	8. PERFORMING ORGANIZATION REPORT NUMBER **18809**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR’S ACRONYM(S) **TACOM/TARDEC**
	11. SPONSOR/MONITOR’S REPORT NUMBER(S) **18809**

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES

Presented at STLE Seminar on Enivironmentally Friendly Tribology 17 April 2008, The original document contains color images.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**SAR**	**49**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Outline

- Background
- Market Survey
- Evaluation of Bio-based Hydraulic Fluids
- ASTM Biodegradation Tests and Toxicity Test
- Field Performance
- Summary

What is Bio-based Hydraulic Fluid

- Bio-based Hydraulic Fluids (BHFs) are currently formulated with vegetable oils (i.e., rapeseed, sun flower, corn, soybean, canola, coconut, etc.) and synthetic ester, such as polyol ester, and additive packages.
- Their lubrication properties are very similar to mineral oils and readily biodegradable and low toxic fluids.
- Some of fluids have a limited operational capability such as a poor low temperature characteristics and oxidation stability.
- Many oil companies have developed bio-based fluids to eliminate the hazardous pollution caused by accidental oil spillage, which is especially important in environmentally sensitive applications such as construction.
- Another good reason to use bio-based hydraulic fluids is to develop a market for US grown agricultural feedstock and to reduce reliance on overseas petroleum crude oil.

USDA Federal Bio-based Products Preferred Procurement Program

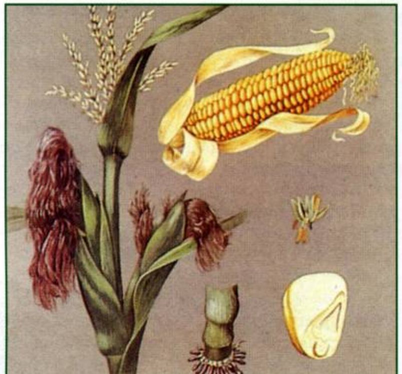
- Implement Section 9002 of Farm Security and Rural Investment Act of 2002.
- Provide information about availability , price, performance, environmental and public health benefits, life cycle costs, and recommended biobased content.
- Require that biobased products must be manufactured with raw materials or wastes from domestic agricultural production or feed stock from trade agreement - farming, ranching, forestry, aquaculture.
- Certify biobased products
- Web site: www. biobased.oce.usda.gov

CRITERIA FOR PRODUCTS TO BE DESIGNATED BIOBASED

- 1. BIOBASED CONTENT
  - Products must be manufactured with raw materials or wastes from domestic agricultural production – farming, ranching, forestry, aquaculture
  - Minimum content
    - By category (item)
    - Verified by ASTM methodology using ^{14}C dating
- 2. PERFORMANCE AND SPECIFICATIONS
- 3. ENVIRONMENTAL PERFORMANCE/LIFE CYCLE
  - National Institute of Standards and Technology “Building for Environmental and Economic Sustainabilty” (BEES) program

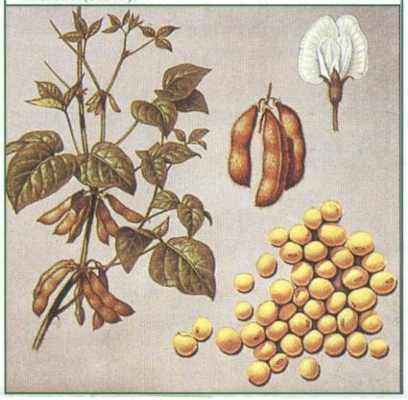
www.bfrl.nist.gov/oae/bees.html

Seed Oils and Their Fatty Acid and Genetic Varieties



Corn: contains 4-5% oil (as compared to soybeans (about 20%). New genetic varieties called high oil corn contains about 8% oil. Fatty acid consumption includes: lauric acid (.1%), myrisitc acid (2.0%), palmitic acid (11.8%) stearic acid (2.0%), oleic acid (24.1%) linoleic acid (61.9%), and linolenic acid (0.7%).

Soybean: (*glycine max*), glycine assurinsis (wild), glycine max (cultivated), and glycine gracillis (intermediate). Chemical composition: protein and oil make up about 60%, about 1/3 consists of carbohydrates including polysaccarides, stachlose. (3-8%), raffinese (1-1%) and sucrose (5.0%).

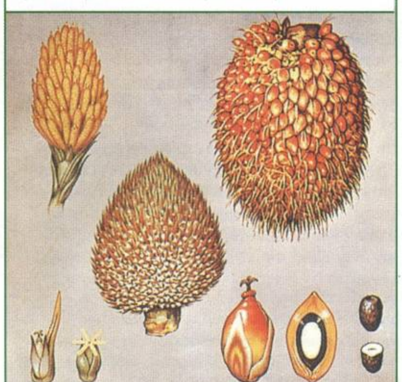


Sunflower: (*Helianthus annuus*) is known in two types = oilseed and nonoil or confectionary. Fatty acid composition is primarily palmitic (7.2%), stearic (4.1%), oleic (16.2%) and a large portion of linoleic (72.5%). High oleic varieties contain 75% or more oleic acid contents.

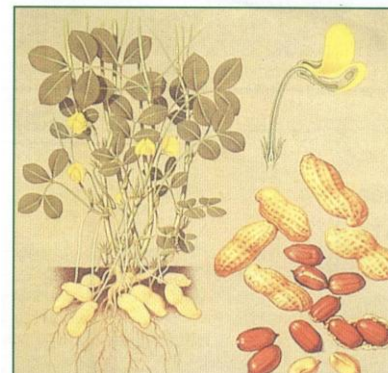
Cotton: (*Gossypiun*) A member of the Malva family. There are 30 different bush-like species of cotton. Around 70% of the harvest consists of seed containing 18-28% fat. Refined and purified cotton oil is odorless, colorless, and high quality cooking oil. It contains linoleic acid content of 35-60%.

Rapeseed: refers to more than one plant species and is often used to denote the seeds derived from oil yielding members of the Brassica family. Brassica napus and B. campestris are the two most important and widely grown species. B. juncea and B. campestris are grown in India and the East.

Oil Palm: consists of mostly monoglycerides (48-55%) and diunsaturated glyceride (30-40%); small quantities of saturated (6-8%) and unsaturated (6-8%) glyceride. The fatty acid composition includes: lauric (46-52%), myristic (15%-17%), palmitic (6-9%), oleic (13-19%), and linolenic (0.5-2.0%).



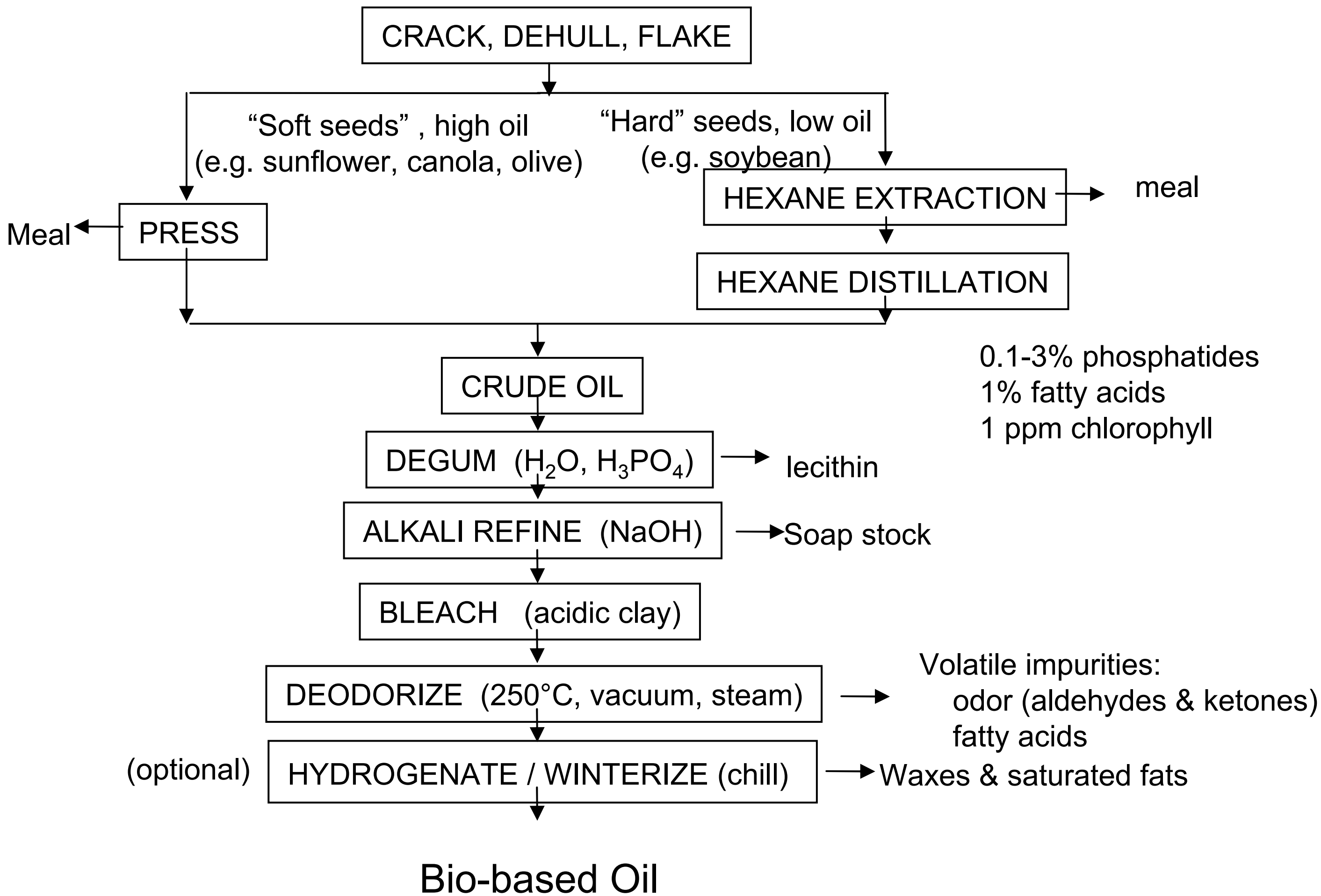
Coconut Palm: growth primarily between the tropics. About 650g of coconut oil can be obtained from 1kg of copra; it has a fat content of 63-70%. The melting point of coconut oil is 20-28% C with a solid fat acid content of 81% at 10º C and 32% at 20º C.

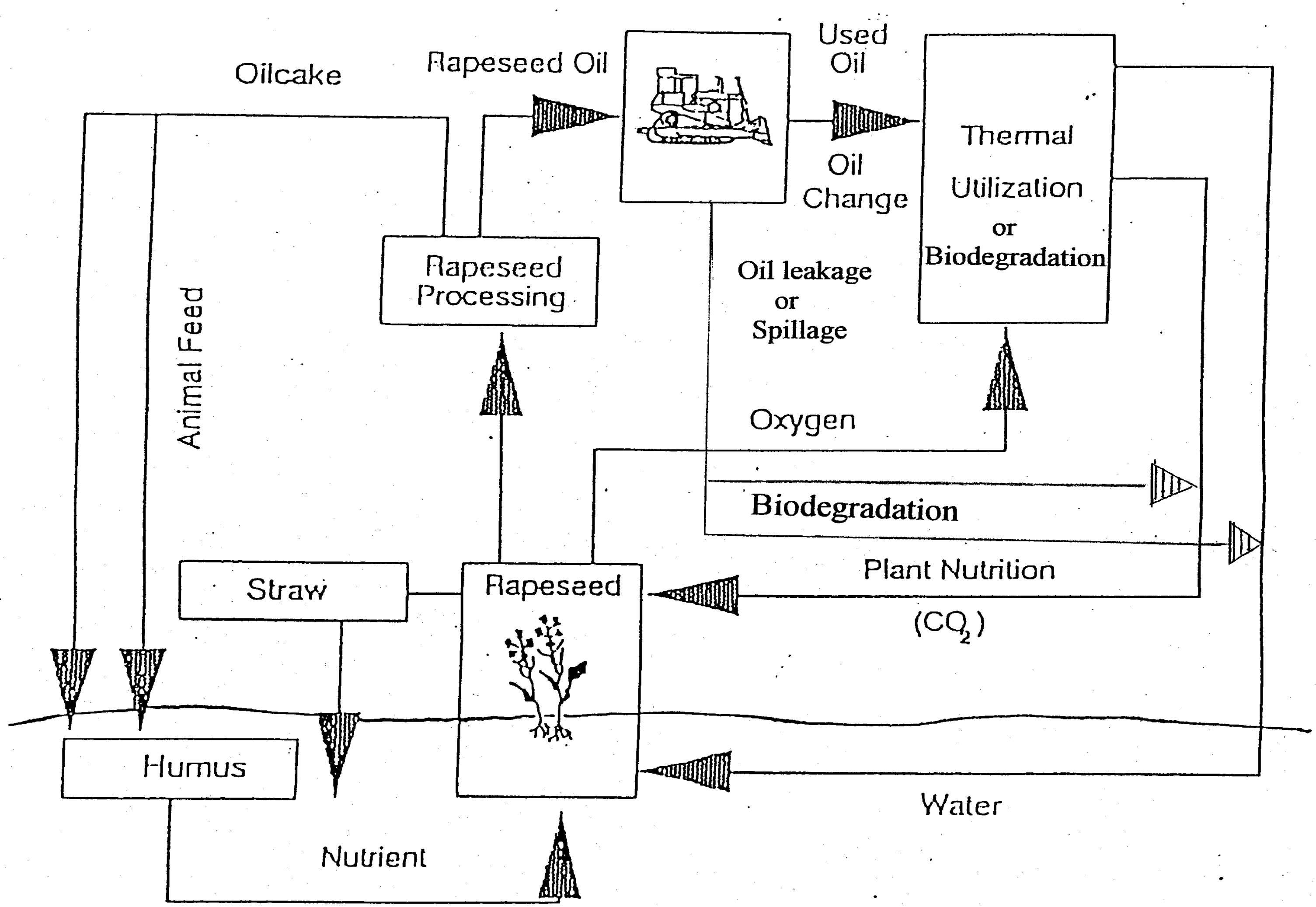


Peanut: (*Arachis hyppogea L.*) Peanut oil is 40-50% fat and 24-35% protein. Low in polyunsaturated fatty acids. Peanut oil is used as cooking oil and in margarine production. Fatty acid composition includes: palmetic (10%), stearic (3%), oleic (42%), linoleic (38%), linolenic (0%).

Source: Leissner, O. et al (1989) Vegetable Oils and Fats, Karlshammn, Sweden

Bio-based Oil Process





Rapeseed life cycle at environmental view point

Projected Benefits for Bio-based Hydraulic Fluids

- Reduce hazardous waste by natural recycling
- Reduce petroleum hydrocarbon contamination in landfill
- Preserve ground water and soil
- Reduce disposal costs of hazardous wastes
- Reduce clean up costs of soil and ground water
- Reduce petroleum consumption
- Alternative lubrication resource
- Others

Market Survey for Bio-based Hydraulic Fluid

- A number of lubricant industries have developed BHFs which are less toxic and more biodegradable than currently used hydraulic fluids.
- Potential market for Bio-based hydraulic fluids is expected to grow with the increase of environmental regulations.
- Two types of Bio-based Hydraulic Fluids are commercially available (I.e., Vegetable based, Synthetic Ester based).
- US Army had evaluated twenty-six (26) Bio-based hydraulic fluids (BHFs) in accordance with Military Requirements. Ref: “Evaluation of Environmentally Acceptable Hydraulic Fluids”, NLGI Spokesman Vol 60,1996.

Vegetable Oil

- Excellent lubrication
- Nontoxic
- Biodegradable
- Derived from renewable resources such as rapeseed, sunflower, corn, canola, soybean, etc.
- Various chemical and physical properties
- Poor low temperature fluidity
- Poor oxidation stability
- Inexpensive

Bio-based Synthetic Ester

- Excellent lubrication
- Excellent fluidity
- Excellent low temperature and aging stability
- Nontoxic (some products are toxic)
- Biodegradable
- Physical and chemical properties varied depend on renewable resource
- Polyol ester, Diester, Trimethylolpropane, Pentaerythritol
- Very expensive

Comparison of Bio-based Fluids

	Mineral Oils	Vegetable Oils	Synthetic Esters
Biodegradability ASTM D5864, %	10-40	40-80	30-80
Viscosity, cSt	15-150	32-68	20 -300
Pour Points, ºC	-54 to -15	-20 to 10	-60 to -20
Compatibility with Mineral Oils	-	Good	Good
Oxidation Stability	Good	Poor to Good	Poor to Good
Service life	2 yrs	6 month to 1 yrs	3 yrs
Relative Cost	1	2 to 3	4-5

Laboratory Chemical and Physical Property Test for Bio-based Hydraulic Fluid

- Viscosity
- Pour point test
- Flash point test
- Oxidation stability test
- Corrosion protection test
- Low temperature stability test
- Elastormer compatibility test
- Wear test
- Water stability test
- Thermal stability test
- Particle contamination test
- Biodegradation test
- Toxicity test
- Others

ASTM Biodegradation Tests

- ASTM D 5864, Determining Aerobic Aquatic Biodegradation of Lubricants or Their Components.
- ASTM 6731, Determining the Aerobic Aquatic Biodegradability of Lubricants or Lubricant Components in a Closed Respirometer.
- ASTM D 7373, Predicting Biodegradability of Lubricants Using a Bio-kinetic Model.
- ASTM D 6139, Determining the Aerobic Biodegradation of Lubricants or Their Components Using the Gledhill Shake Flask.

Inferenced factors on lubricants' biodegradability (1)

- Biodegradability of lubricants generally depend on their molecular structure and material.
- Straight-chain aliphatic compounds are easily degraded.
- Aromatic compounds are usually slowly degradable due to their structures and toxicity.
- Natural bio-based lubricants give higher biodegradability than petroleum based lubricants.

Inferenced factors on lubricants' biodegradability (2)

- High water solubility of lubricants provide higher biodegradability.
- Low viscosity lubricants give good biodegradability due to their smaller molecular size.
- Biodegradability depends on microorganism cultures and types of material used for food.
- Long polymeric material have a low biodegradability.

Chemical Equation for Biodegradation

(Hydrocarbon lubricants) + (oxygen) + (water) + (microorganisms)

→ (carbon dioxide)+ (water) + (more microorganisms)

$$C_nH_mO_p + aO_2 + H_2O \xrightarrow{\text{bacteria cell}} rCO_2 + aH_2O + tC_3H_5O$$

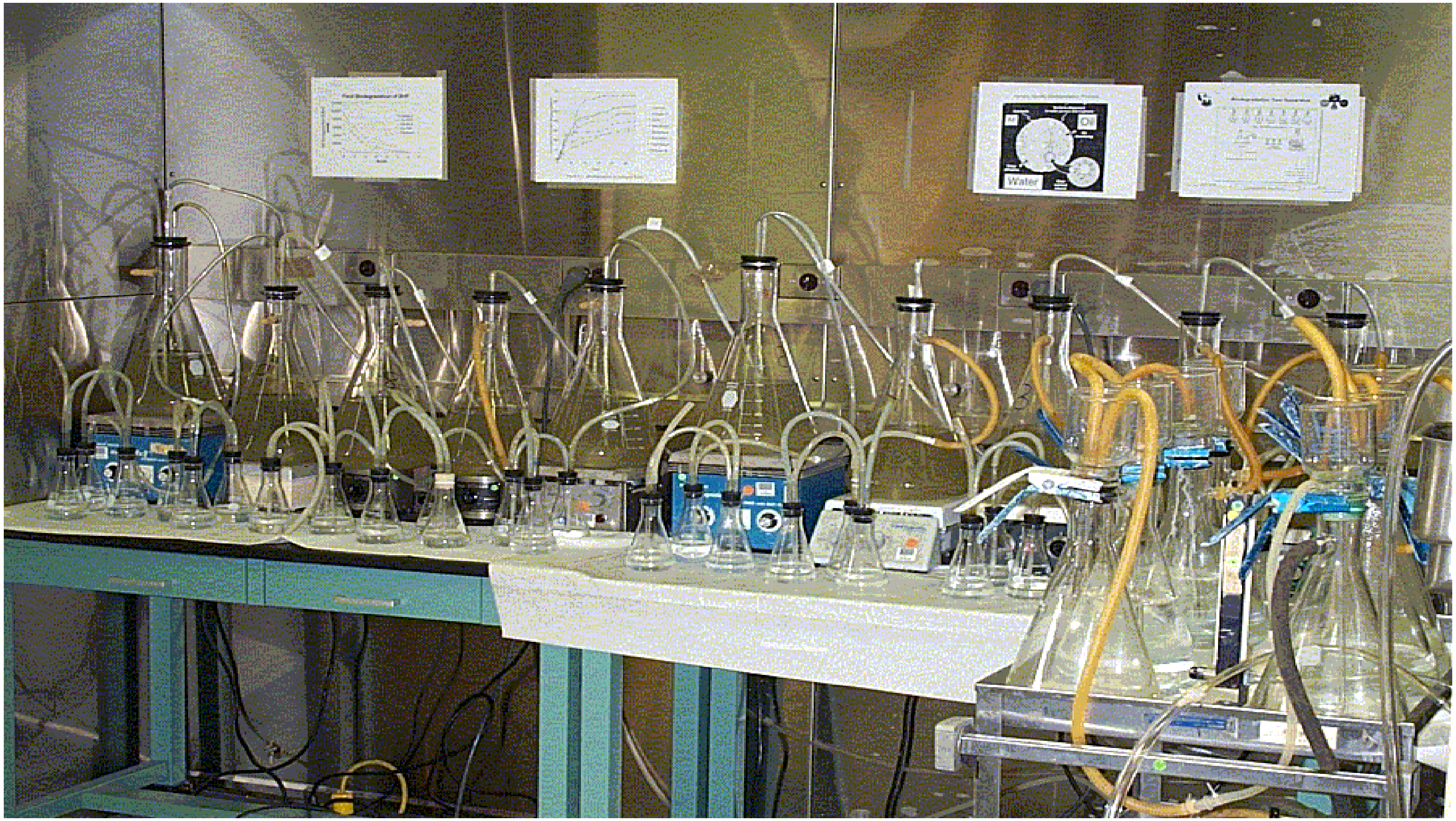
where $C_nH_mO_p$: Ester group in lubricant with
n =14, 20, or 2
m = 2n-1 or 2n-2
p =2 or 4

C_3H_5O: biomass

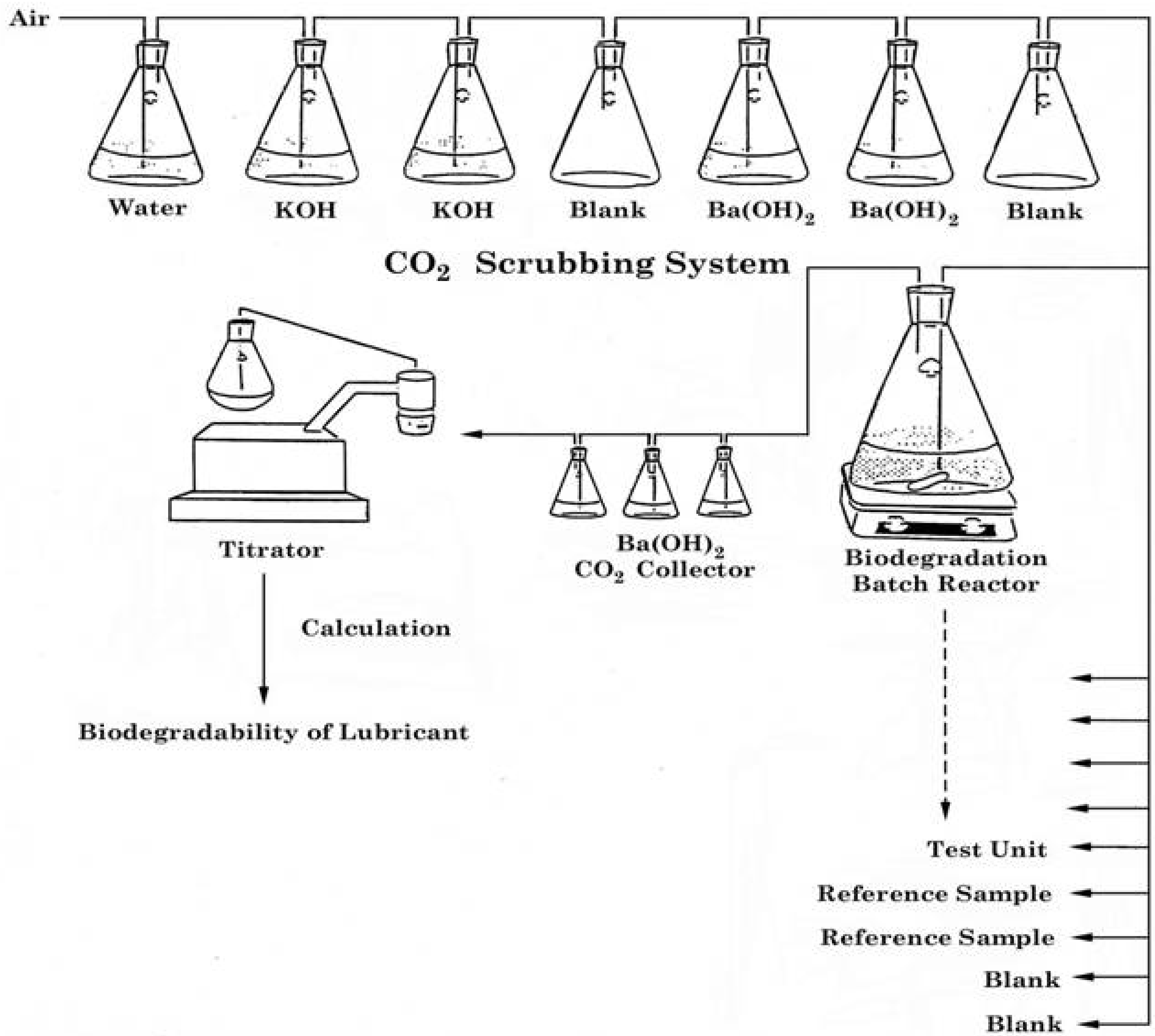
ASTM D 5864 Biodegradation Test (Modified Stun Test)

- ASTM D 5864 biodegradation test is a version of OECD 301B test and is called as Modified sturn test.
- Design to determine degree of aerobic aquatic biodegradation of lubricants on exposure to an inoculum under laboratory conditions.
- Express biodegradability of lubricant as percentage of maximum (theoretical) carbon conversion (or carbon dioxide generation) under well-controlled conditions for 28 days.
- 60 % of biodegradability or above is considered as readily biodegradation.
- Today, this test method is widely used to measure biodegradability of lubricants.

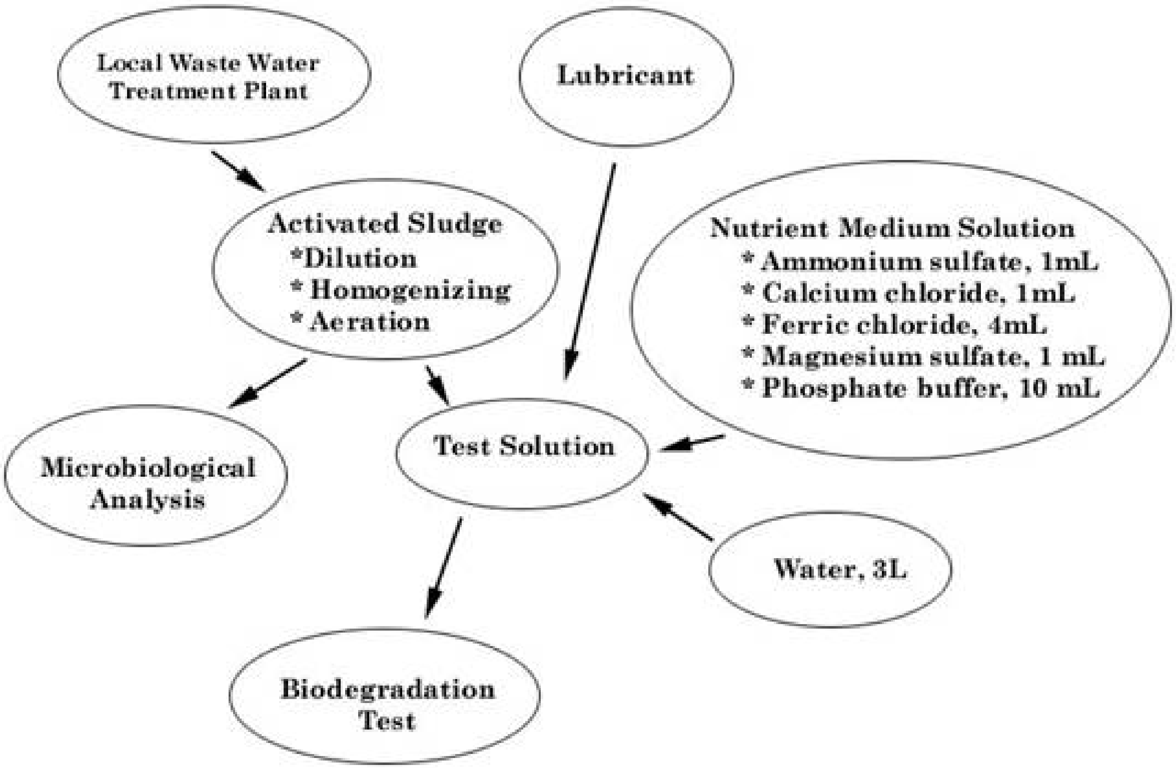
ASTM D 5864 Biodegradation Test Apparatus

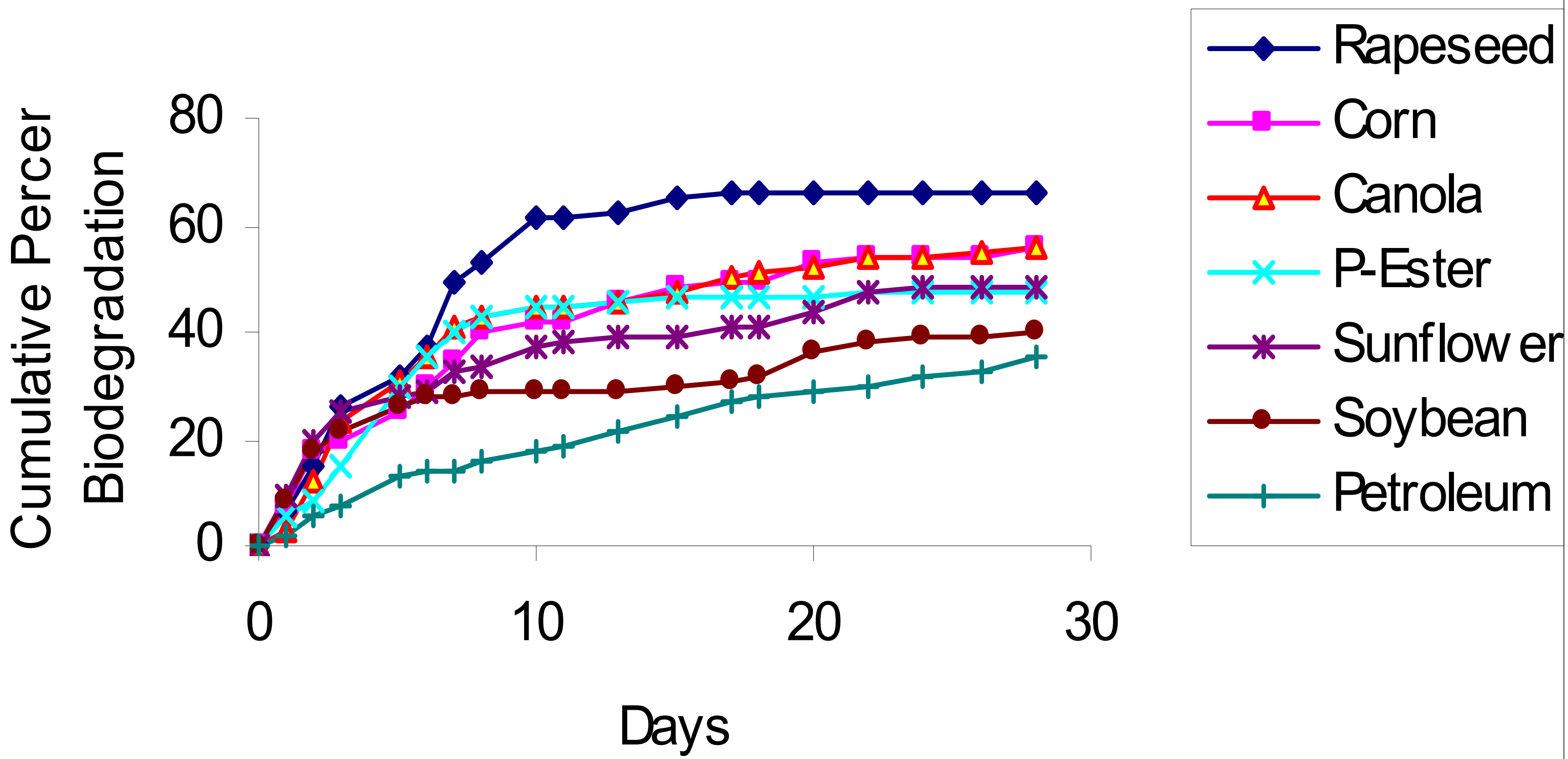


Biodegradation Test Apparatus



Preparation of Test Solution





Biodegradation of Bio-based Hydraulic Fluids

Pro and Con for Modified Stun Test

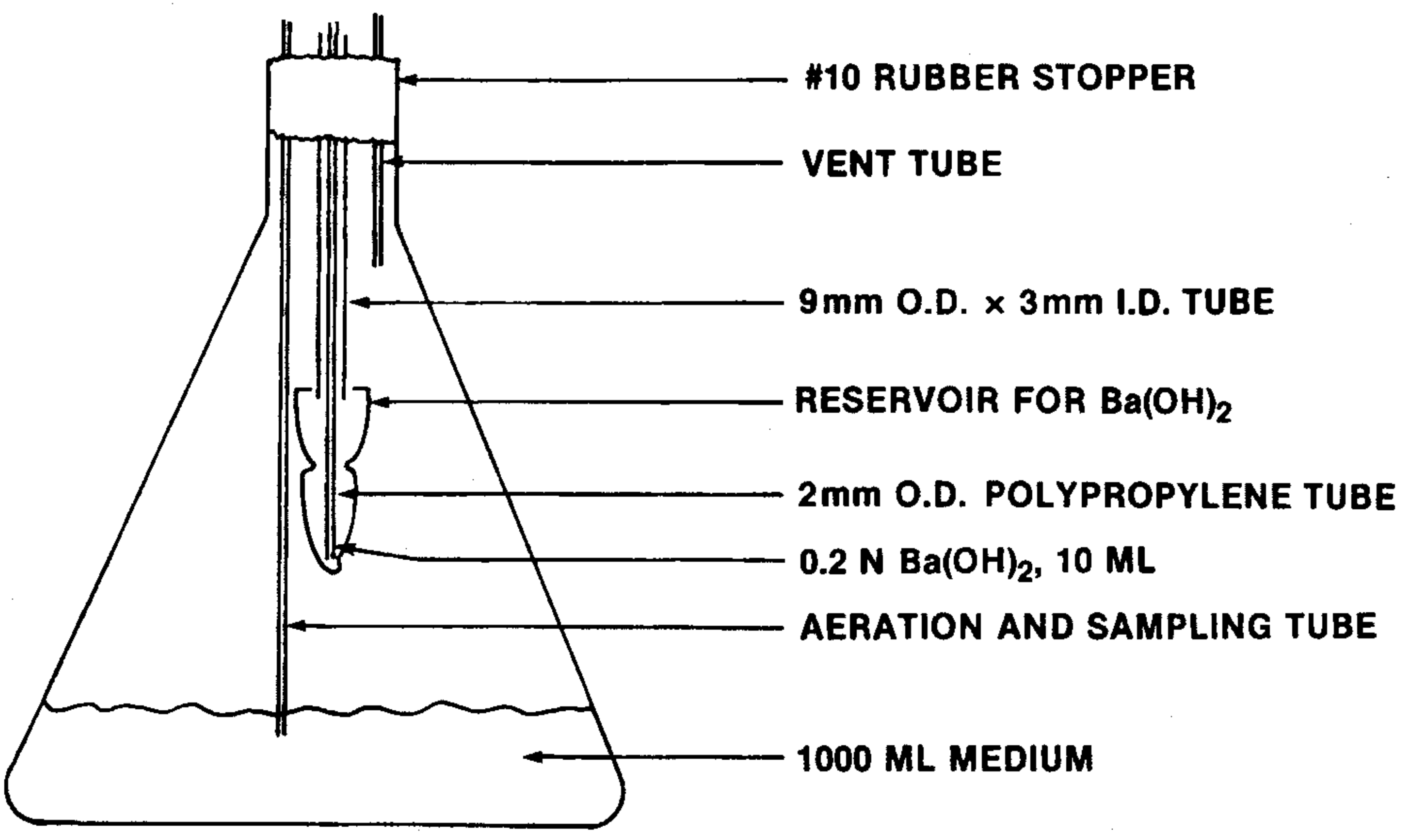
- Pro
  - Widely used in Environmental Laboratories.
  - Many data are available in petroleum community.
  - Provide meaningful data and test results agree with field performance.
  - Test apparatus is inexpensive (glassware test).

- Con
  - Poor test precision.
  - Require manpower due to manual operation (high operation cost).
  - Long testing time.
  - Handling microorganisms.
  - Operational problems (connecting hose leaking, safety problem, etc.).
  - Require large laboratory space.

ASTM 6139 Biodegradation Test Method

- Same as ASTM D 5864 biodegradation test except for agitating test solution and called as EPA Shake Flask Test.
- Design to determine degree of aerobic aquatic biodegradation of lubricants on exposure to an inoculum under laboratory conditions.
- Express biodegradability of lubricant as percentage of maximum (theoretical) carbon conversion (or carbon dioxide generation) under well-controlled conditions for 28 days.
- 60 % of biodegradability or above is considered as readily biodegradation.
- Today, this test method is not widely used to measure biodegradability of lubricants.

EPA Shake Flask Test



ASTM D 6731 Biodegradation Test (Respirometer)

- ASTM D 6731 biodegradation test is a version of OECD 301F test and is called as Respirometer test.
- Design to determine degree of aerobic aquatic biodegradation of lubricants on exposure to an inoculum under laboratory conditions.
- Express biodegradability of lubricant as percentage of maximum (theoretical) oxygen consumption of microorganism under well-controlled conditions for 28 days.
- 67 % of biodegradability or above is considered as readily biodegradation.
- Today, this test method is widely used to measure biodegradability of lubricants.

ASTM D 6731Biodegradation Test Apparatus (Respirometer)

Pro and Con for Respirometer Test

- Pro
  - Widely used in Environmental Laboratories.
  - Many data are available in petroleum community.
  - Provide meaningful data and test results agree with field performance.
  - Test apparatus is expensive.
  - Automatic system

- Con
  - Poor test precision.
  - Long testing time.
  - Handling microorganisms.
  - Some operational problems associated with test apparatus (sensors may not working).
  - Need calibration often

ASTM D 7373 Biodegradation Test

- Biodegradability of Lubricants is calculated using a Bio-kinetic model and Chemical Composition of a lubricant .
- It was developed based on fundamental microbiology theory and composition of lubricants.
- This bio-kinetic model does not require any biodegradation test apparatus and inoculums.
- It can predict biodegradability of lubricant within a day.
- Correlated Conventional ASTM Biodegradation Tests.

Bio-kinetic Model

$$B(t) = B(1) + \frac{0.49}{\ln(6.8 \times ECB^{-2.38})} \ln t$$

$$where:$$

$$ECB = \sum_{a}^{b} (\eta_a C_a + \eta_b C_b)$$

$$B(1): 0.01$$

ECB Calculation

$$ECB = \sum_{a}^{b} (\eta_a C_a + \eta_b C_b)$$

where

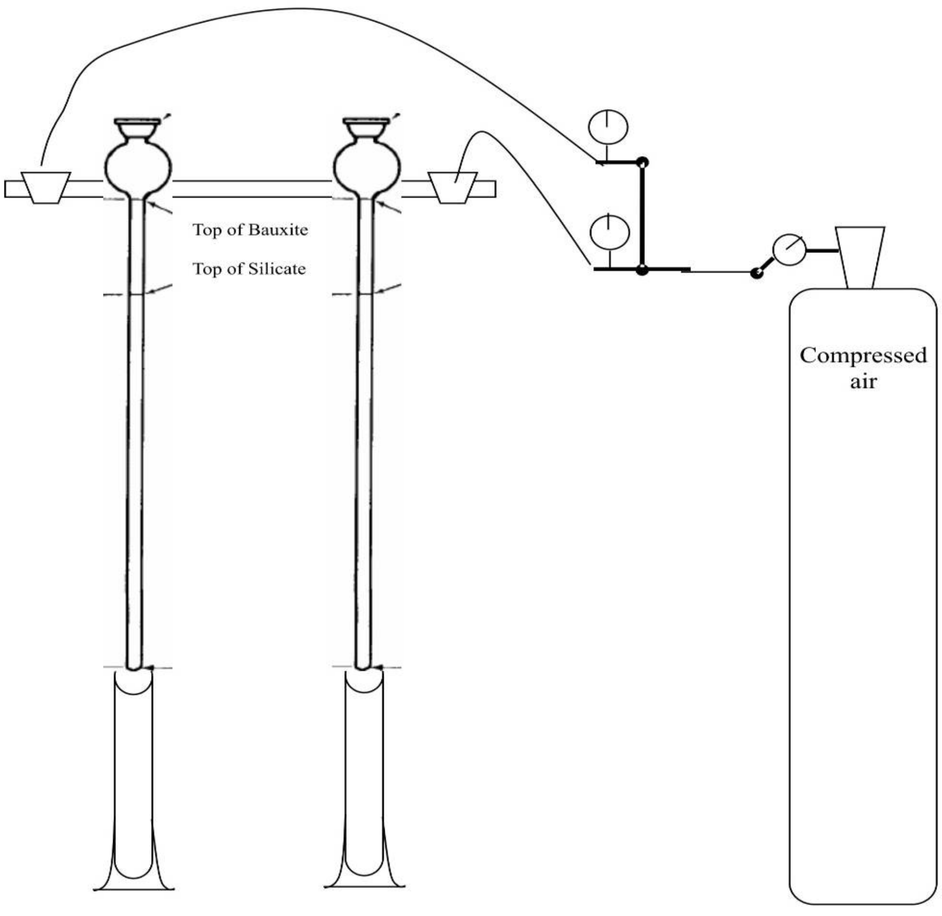
η : ECB coefficient
C_a: Fraction of composition in Step 1 (Pentane)
C_b: Fraction of composition in Step 3 (Diethyl Ether)

ECB: Effective Composition of Biodegradation

ECB Coefficients for Oils

Lubricant	ECB Coefficient (η)
Mineral oil	0.3
PAO 2	0.8
PAO 4	0.6
PAO 6 or above	0.4
Natural esters	1
Renewable based diester or polyol esters	0.8
Petroleum based ester types	0.01

ASTM D 7373 Composition Analysis Test Apparatus



ASTM D 7373 Composition Analysis Procedure

Process	Composition Analysis	
Step 1	Pentane	Non-aromatics (saturate, mineral oil, PAO)
Step 2	50 % pentane+50% toluene	Non-polar based aromatics
Step 3	Diethyl ether	Esters, acid, waxes
Step 4	Chloroform/Ethyl alcohol	Polar based aromatics

Tested Hydraulic Fluids

Code	Type of base oil	ISO classification	Identification
A	Soybean	46	Commercial HF*
B	PAO 4 + diester	22	MIL-PRF-48170[8]
C	Canola	46	MIL-PRF-32073[9] Grade 4
D	Canola	46	MIL-PRF-32073 Grade 4
E	PAO 2	2	Commercial HF
F	Mineral Oil	100	SAE 15W-40
G	Rapeseed	32	Commercial HF
H	Polyol ester	22	MIL-PRF-32073 Grade 2
I	Canola	-	Cooking Oil

*Hydraulic fluid

Composition Analysis of Tested Fluids

Code	Alkanes or Saturate	Non-polar aromatics	Ester, Acid, or Wax	Polar aromatics	ECB*
A	24.5	2.2	67.9	5.4	0.75
B	68.7	2.9	27.7	0.7	0.55
C	3.49	2.57	90.56	3.38	91.6
D	17.53	1.32	77.45	3.69	0.82
E	98.8	0.47	0.05	0.7	0.79
F	82.5	13.5	1.4	1.7	0.26
G	0.07	1.00	92.95	5.98	0.93
H	17.5	1.32	77.5	3.7	0.83
I	0.18	1.6	90.7	7.5	0.91

* Effective composition for biodegradation

Biodegradation Test Results

Code	ASTM D 5864	ASTM 6731	CES CO_2 Evolution Test	Bio-kinetic Model
A	67	63.4	73.7	64.0
B	51.9	51.3	47.8	51.0
C	72.3	75.3	74.1	77.8
D	71.7	75.2	69.7	69.3
E	71.2	78.4	61.3	67.0
F	30.1	36.6	24.1	32.8
G	77.0	84.8	80.2	79.0
H	66	76.6	66.2	70.0
I	73.3	88.0	94.7	77.2

Biodegradation Profile for Canola based BHF

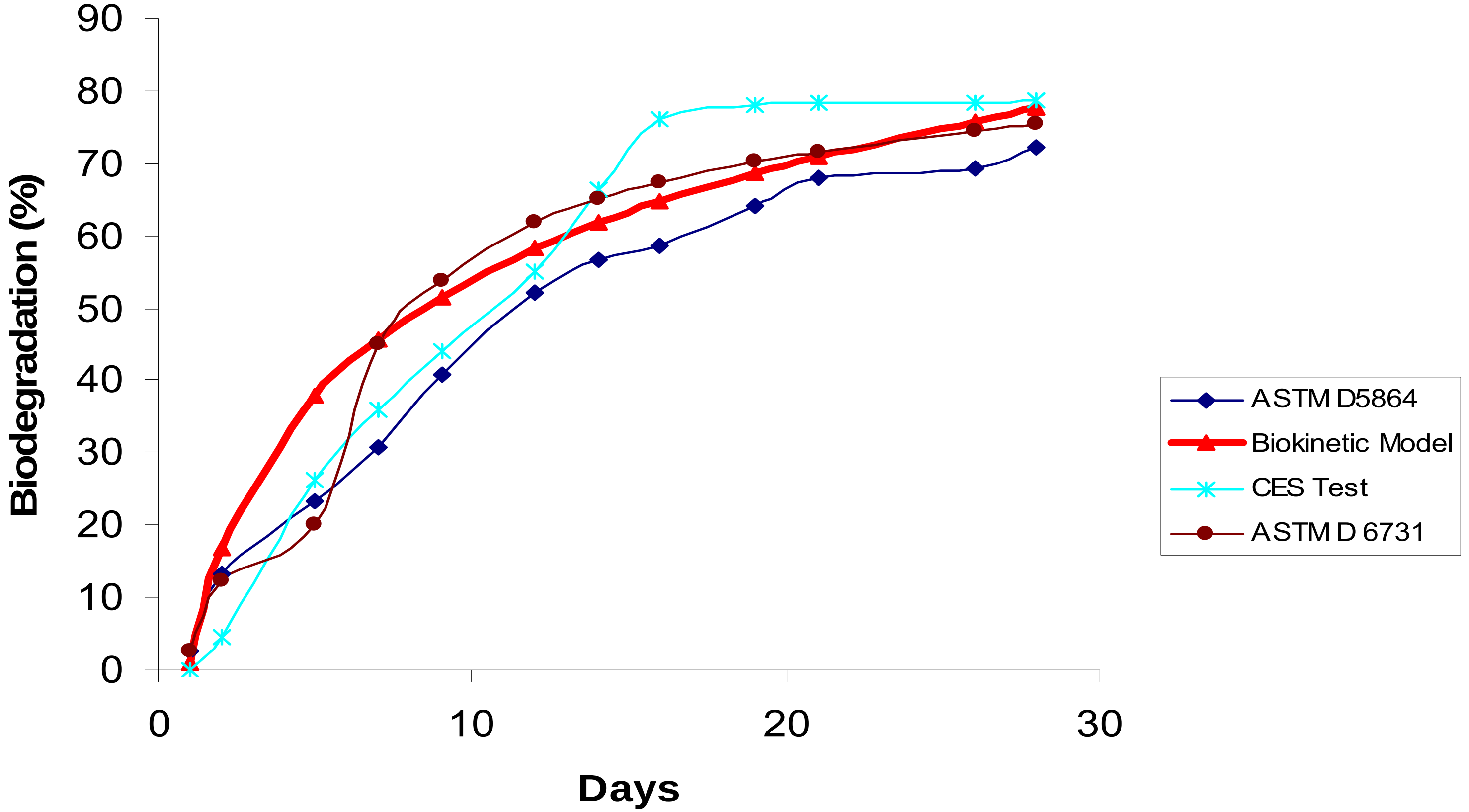
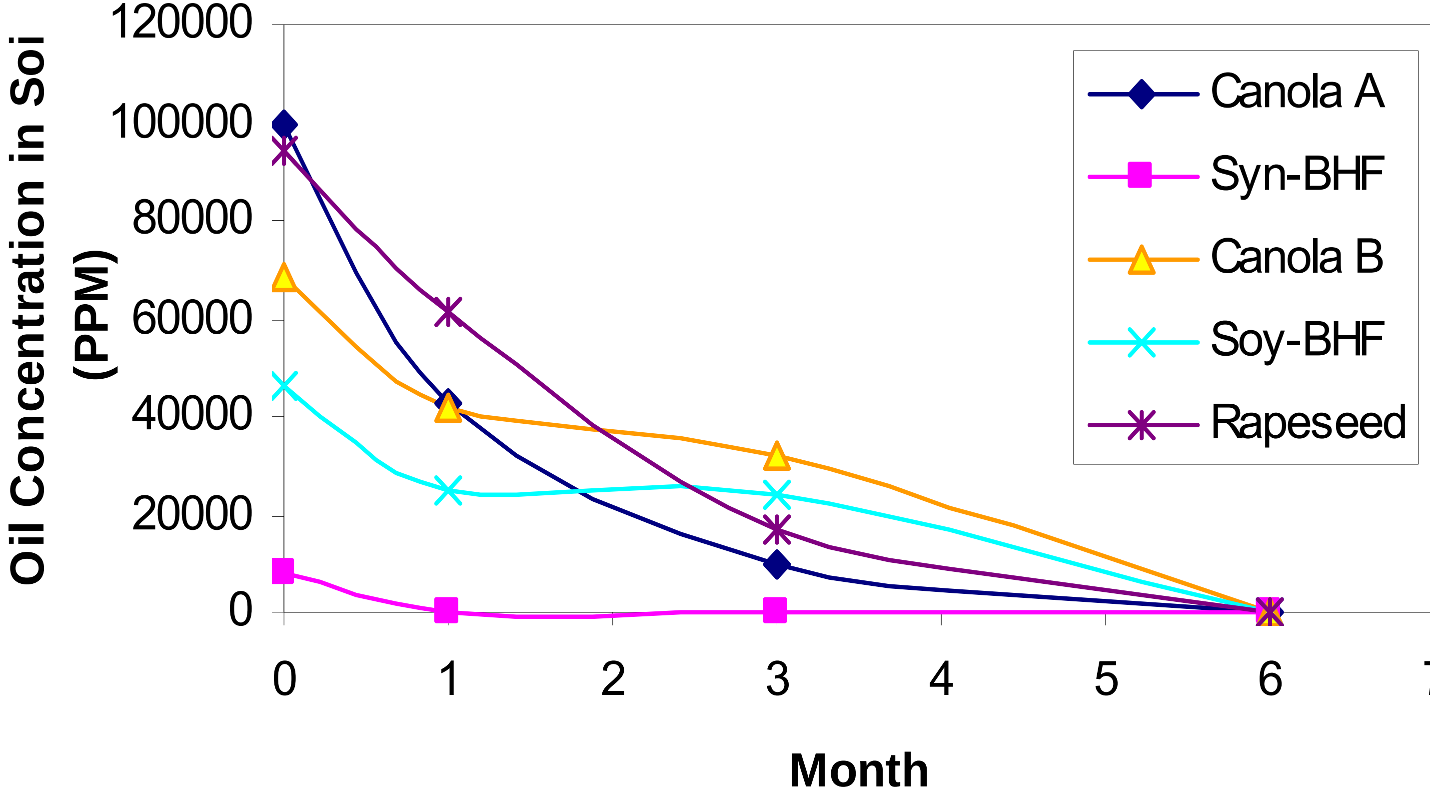


Figure 2. Biodegradation Profile for Canola based BHF

Correlation Coefficients (r^2) Between Biodegradation Tests

	ASTM D 5864	ASTM D 6731	CES CO_2 Evolution Test	ASTM D 7373
ASTM D 5864	1	0.89	0.8	0.95
ASTM D 6731	0.89	1	0.82	0.92
CES CO_2 evolution test	0.8	0.82	1	0.87

Soil Biodegradation Test



Soil Biodegradation Test for BHFs

Toxicity Test

- OECD Guideline 203, Acute Toxicity to Fish, and Good Laboratory Practices.
  – Widely used in Environmental Laboratory
  – Use live fishes (i.e., trout) as a test specimen
  – Toxicity is determined based on the number of dead fish
  – Seven day test
  – Not many laboratory performs this test in U.S.A.

- Draft ASTM Microtoxicity Test, “Assessing the Toxicity of the Water Accomodating Extracts from Lubricants Using Luminescent Marine Bacterium”.
  - Use Marine bacterium, Vibro fisherie.
  - Toxicity is measured based on analysis of light change on Vibro fisherie.
  - Modify ASTM D 5660, Standard Test Method for Assessing the Microbial Detoxification of Chemically Contaminated Water and Soil Using a Toxicity Test with a Luminescent Marine Bacterium,
  - Simple and short test (about one hour)

Field Performance Test for Bio-based Hydraulic Fluids

- US Army conducted two Field tests using ten pieces of construction equipment (i.e., scoop loaders, dump trucks, Bulldozers, etc.) at Military installations.
- Five (5) BHFs (i.e., rapeseed oil, canola oil, soybean oil, polyol ester, and diester) selected as field demonstration samples.
- Evaluation criteria used in this demonstration are their field operational performances and environmental performances (i.e., biodegradability, toxicity).
- Duration of tests was one (1) year.


BIO
OIL

Field Test Results (1)

- No significant viscosity changes observed in any construction Equipment.
- All samples showed some degree of oxidation, but still have good conditions.
- None of fluids had Low Temperature Operational Problem at Midwest Winter Weather (subzero to -30 ºC).
- BHFs had good hydrolytic stability that resists reaction with water.
- Equipment had no leaking problem, seals look good

Field Test Results (2)

- BHFs did not give any volatility problem during demonstration.
- No evidence for incompatibility between BHFs and structural materials used in hydraulic systems.
- No Biodegradation occurred in hydraulic systems.
- Environment property of fluids (i.e., biodegradability) did not change throughout demonstration.
- No incompatibility was observed between bio-based fluids and petroleum based fluids.
- All BHF samples did not give any abnormal behavior during one year of testing and provided excellent service.

Summary

- Numerous Bio-based hydraulic fluids are currently available in domestic market and new products are being developed to meet commercial and military requirements.
- Bio-based hydraulic fluid formulated by renewable resource (i.e., rapeseed, canola, soybean, coconut, etc.)
- This fluid provide a high biodegradability and low toxicity.
- And they provide same quality of performance compared to petroleum based hydraulic fluids.
- Therefore, Bio-based hydraulic fluid can be used in construction or other types of equipment.