Ph.D Thesis

Study of fuel additives for residual fuel oil applicable to ships

Advisor: Professor Jong-Ho Kim

August, 2016

Graduate School of Korea Maritime and Ocean University

Department of Marine System Engineering
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<국문 초록>

선박용 잔사유 연료 첨가제의 반응메커니즘 연구

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초록

최근 주요 해운회사 들은 연료비 절감을 목적으로, 선박용 연료 첨가제의 본선 적용에 많은 관심을 가지고 있다. 선박은 경제적이면서도 원하는 성능을 발휘할 수 있는 연료유가 에너지원으로 공급되어야 선박의 운항 안정성이나 경제성을 확보할 수 있다. 실제로 연료첨가제를 적용하는 사용자들이 첨가제 적용을 검토하는 배경으로는 유지보수 비용의 감소, 연료 절감 및 유해 배출가스 감소를 가장 대표적인 이유로 들고 있다.

선박에 설치된 대부분의 디젤엔진이 연료유 품질에 대한 민감성이 다소 떨어지긴 하나, 이 또한 초기 개발이나 설계 단계에서부터 매뉴얼에 명시된 최적의 연료유가 공급되는 조건에서 충분히 안정적으로 그리고 효율적으로 운전될 수 있도록 고려되었음은 부정할 수 없다. 기관의 설계 기준과 시장에서 구할 수 있는 연료유의 품질이 완벽히 일치할 수는 없다. 실제로 시장에는 다양한 종류의 연료가 존재하며 이들의 기본 물성이 천차만별 일 뿐 아니라, 화학적 성상도 다양하다. ISO에서 선박 기관에 적용할 수 있는 선박용 연료유의 품질 기준을 정하여 통용하고 있긴 하나, 실제 선박에서 수급 받거나 본선에서 자체 제조하여 사용하는 연료유의 성상은 ISO의 표준치 범위를 벗어나는 경우가 종종 발생하고 있다. 본 연구에서는 고급유로 간주할 수 있는 증류유를 배제하고, 실제 원양항해 선박이 주로 사용하고 있는 잔사유에 연료 첨가제가 미치는 영향에 대해 연구하였다.

잔사유용 연료첨가제를 실제 엔진에서 첨가하여 운전함으로써 객관적인 성능 검증을 시도하였으며, 분산 안정제와 연소 촉매의 반응 메커니즘에 대한 기계공학적인 측면에서의 반응 모델 제안을 시도하였다. 또한, 광학적 분석을 통한 반응 메커니즘 검증에 연구의 촛점을 맞췄다.

잔사유는 상압 증류, 감압 증류, 촉매 분해, 열 분해 등의 정제과정을 통해 고품질의 증류 연료유를 추출해 내고 남은 잔존 연료유를 의미한다. 잔사유의 품질은 아이러니하게도 정제 기술이 고도화 되어감에 따라 악화되어 가고 있다. 이유는 상품적 가치가 높은 연료유를 정제 과정에서 최대한 추출하기 위해 열분해, 촉매 분해 공정이 고도화 되면서 원유가 받게 되는 물리화학적 스트레스가 크게 증대되었기 때문이다. 또한, 촉매 분해의 반응 효율을 높이기 위해 사용한 최대 반응면적의 촉매는 잔사유에 미소 입자로 남아 엔진의 연료 및 연소시스템에 심각한 손상을 야기할 수 있다. 잔사유는 나프텐계 탄화수소 (C_nH_{2n} - 환형구조)로 알려져 있다. 이는, 파라핀계 보다도 더 안정한 구조이다. 주요 구성 물질은 아스팔텐이며, 아스팔텐은 연소시 반응속도가 느리고 연료 분사 시 액적의 크기가 미소화 되기 어려운 특성이 있다. 따라서, 연소 후 카본 누적층이 생성되거나 입자상 물질이 생성되기 쉬운 특성을 가지고 있다.

연료첨가제 기술은 인류가 기관을 개발한 이래로 함께 성장해 온 기술이다. 과거로부터, 옥탄가 향상제, 윤활성 향상제 등 다양한 형태로 활용되어 오고 있다. 다만, 대부분 자동차 산업을 위주로 함께 발전해 왔으며, 잔사유에 적용 가능한 첨가제의 개발이 이뤄진 건 역사가 오래되지 않았음에 주목할 필요가 있다. 현재 선박에 적용 가능한 대표적인 종류의 연료 첨가제로는 분산 안정제, 탄소 적층 방지제, 해유화제, 유동성 향상제, 윤활성 향상제, 연소 촉매, 부식 방지제 및 다기능 첨가제를 들 수 있겠다. 그 중에서도 시장에서 가장 많은 활용을 보이고 있는 첨가제는 분산 안정제가 있으며 그 뒤를 이어 연소 촉매가 또한 많이 사용되고 있다. 본 연구는 분산 안정제의 반응 메커니즘을 문헌 연구를 통하여 확인하고 그 메커니즘을 검증하였다. 또한 연소 촉매의 반응 메커니즘을 문헌 및 실험 결과에 주목하여 도출하고 이 또한 광 분석 기술로 검증하였다.

분산안정제를 잔사유 탱크에 첨가하게 되면, 분산 안정제가 연료유에 침윤하게 되는 과정이 있고, 침윤한 안정제는 응축 경향이 강한 아스팔텐 입자들을 분리시키게 된다. 침윤 과정 및 분리과정이 완료되면, 마지막은 침윤 및 분리 과정을 지속적으로 유지하는 메커니즘이 필요함을 확인 하였다. 분산성을 분석한 결과에 따르자면, 분산제의 3가지 반응 메커니즘 중 침윤 및 분리과정을 유지하는 성능 차이가 존재함이 실험에 의해 밝혀졌으며, 이에 대한 대응이 필요하다.

연소 촉매의 효과를 검증하고 메커니즘을 분석하기 위하여 엔진 연료 소모량 계측, 배출가스 계측, 정적 연소기 계측, 열 계측, 광 계측 등의 분석을 활용하였다.

연료 소모량 계측 결과는 첨가제가 연소 촉매이건 분산성 향상제 이건 간에 무관하게 연료 소모량 저감에 효과를 줄 수 있음을 확인하였다. 이는 잔사유의 특성으로부터 설명할 수 있다. 잔사유 속에 다량 함유된 아스팔텐은 응집성향이 강하나 분산성 향상제가 응집을 방지하였고, 이는 결국 연료유내 가용 에너지 분율이 증가되었기 때문이다. 연소 촉매는 반응성이 좋은 금속이나 전이금속을 주요 구성성분으로 활용하고 있다. 이들은 연소 초기에 활성 래디컬 생성에 기여하여 활발한 연소 화학반응을 조장하게 되어 연소가 촉진되는 것으로 보인다. 또한, 연소 후에도 배출가스 온도가 충분히 높다면 촉매 활성을 유지하여 탄소 적층의 방지, 중질의 탄소분 감소 등의 효과가 있어 보이며, 결국 입자상 물질의 저감에도 효율적으로 작용할 수 있다.

배출가스 관점에서는 연소 활성화로 인하여 질소산화물 배출이 증가함이 관찰되었다. 더불어, 첨가제 불포함 연료에 비해 이산화탄소 배출 농도는 증가하였고 산소 배출 농도는 감소하였다. 이는 분자량이 큰 잔사유의 연소에 산소가 적극 개입할 수 있도록 자유래디컬이 충분히 효과적으로 작용했고, 그 결과로 많은 양의 이산화탄소가 생성되었음이다.

광 계측 결과에서는 연소촉매 첨가제들이 비정질의 탄소 구조를 배출하였고, 첨가제가 포함되어 있지 않거나 효과가 의문시되었던 첨가제에서 흑연(graphite)구조가 계측되었다. 이는 첨가제의 영향으로 인하여 유용한 탄소성분을 엔진의 연소과정 중에 다 소진하였기에 나타난 결과로 보인다.

본 연구를 통해 고찰한 결과를 종합함으로써, 선박 잔사유용 연료 첨가제의 메커니즘을 일부 규명할 수 있었다. 궁극적으로 첨가제가 긍정적으로 작용하고 있으나, 본 연구는 4 행정 사이클(stroke cycle) 디젤엔진에서 수행되었고, 관련 문헌에 의하면 세탄가의 영향이 적거나 전혀 영향을 받지 않는 것으로 알려진 2 행정 사이클 엔진에 연소 활성 목적으로 첨가제 사용은 추가적인 연구가 필요할 것으로 보인다. 다만, 상용 엔진중에서 잔사유를 사용하되 행정이 짧아 평균 피스톤 속도가 상대적으로 높은 일부 4 행정 사이클 엔진에서는 연소 촉매 혹은 분산제가 사용 목적에 부합하게 사용될 수 있다. 미연 탄소의 배출 감소, 입자상 물질 감소 등의 연소 개선으로 인한 효과는 기대할 수 있으나, 질소산화물은 첨가제 제조사가 제시하고 있는 반응 메커니즘으론 저감할 수 없다고 판단된다.

KEY WORDS: Dispersant, 분산제; Combustion catalyst, 연소촉매; Residual fuel, 잔사유; SFOC, 연료 소모율; Emission, 배기배출물

Chapter 1 Introduction

1.1 Marine fuel

Residual fuel oil which is generally used on board of ships is mentioned remained fuel oil after finishing the complex refinery processes which are given hereafter. The process is only one process from various processes because the refinery process can be deviated according to the nationality, region and refinery company.

Gases, naptha, kerosene, gas oil and atmospheric residue can be attained after atmospheric distillation of crude oil. The products after distillation can be used as LPG, jet oil, gasoline and diesel oil except for atmospheric residue. Atmospheric residue can be attained at the lowermost part of the process and vacuum gas oil and vacuum residue can be attained by vacuum distillation of the atmospheric residue. Catalytic cracked distillates can be attained if catalyst decomposition employes and thermally cracked residue is attainable when pyrolyze the vacuum gas oil. Residual fuel after completing refinery process is blended with diesel oil considering purpose of use and quality guidance, blended fuel could be used to diesel engines, thermal power plants and boilers. **Fig.1-1** represents simple refinery process (Monique Vermeire, 2007).

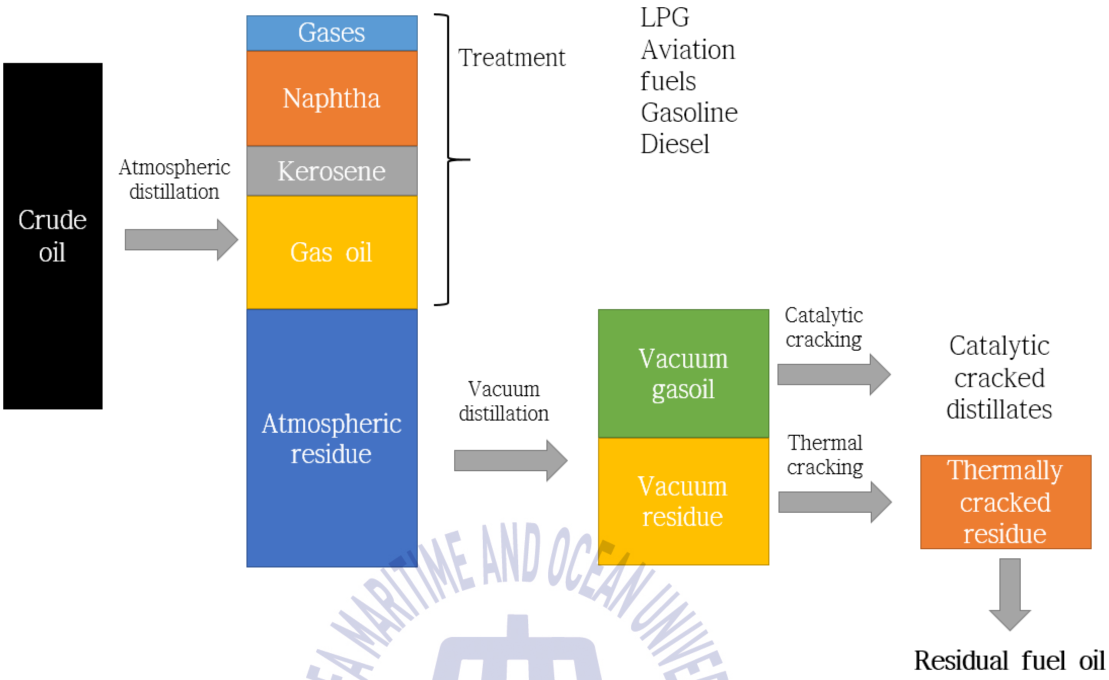


Fig.1-1 Refinery processes to get residual fuel oil

Residual fuel applicable to ships and it passed through complex refinery process is resulted in that less concentration of high quality fuel, changed physical and chemical properties. These fuel can cause long combustion time and decrease flame temperature. Additionally, insufficient combustion speed can be found because of increased molecular weight although internal combustion engine requests high combustion speed.

In this reason, generally carbon deposit creation can be increased or unburned hydrocarbon emission will rise. These phenomena are able to be the reasons of thermal load increase to engine moving parts, increase in fine particulate, increase in fuel consumption and potentially pollutant emission will increase (CIMAC, 2006).

Global economic risk and depressed shipping environment in recent times have forced shipping companies to focus on cost saving (Lee H.K. et al., 2013). According to many reports concerning shipping cost, fuel cost accounts for 30~55%

of the total vessel managing capital depending on the type of ship (V-Ships, 2013).

Ships can consume fuel oils of both different quality levels and different kinds, since the ship's energy can be varied from residual fuel oil to distillate fuel oil (Cho G.H., 2015). Due to high fuel-consuming characteristics of ships, many fuel bound problems have arisen, which normally occurred, while bunkering, storage, supplying and consuming. Filter blocking, fuel starvation, phase separation, and sludge creation are some of the problems caused by poor fuel quality (ABS, 1984).

Shipping companies and managers are interested in minimizing fuel consumption along with safe engine operation. In conjunction with fuel economy, environmental marine regulations also influence shipping and the ship construction industry (Gohary M., 2013). The International Maritime Organization (IMO) is key driver of leading maritime environmental issues. The IMO regulates emissions from ships such as nitrogen oxide (NOx), sulfuric oxide (SOx), particulate matters (PM), volatile organic compound (VOC) and carbon dioxide (CO_2). In case of NOx, the regulation had gradually been introduced. At the early stage of regulation, it was 17.0 g/kWh, Tier 1 stage, based on slow speed marine diesel engine. The regulation became more stringent from 2011 and the limitation was made to 14.4 g/kWh, Tier 2 stage. From the beginning of 2016, it is Tier 3 stage and the regulation only allow the emission of 3.4 g/kWh at emission control area (ECA). **Table 1-1** represents IMO regulated NOx emission.

Table 1-1 IMO MARPOL 73/78 Annex VI Regulation 13

Description	Tier Ⅰ	Tier Ⅱ	Tier Ⅲ
< 130 rpm	17.0 g/kWh	14.4 g/kWh	3.4 g/kWh
130~2000 rpm	45.0 x $n^{(-0.2)}$ g/kWh	44.0 x $n^{(-0.23)}$ g/kWh	9.0 x $n^{(-0.2)}$ g/kWh
> 2000 rpm	9.8 g/kWh	7.7 g/kWh	2.0 g/kWh
Date of entry into force	Vessels keel-laid from January 2000	Vessels keel-laid from January 2011	Vessels keel-laid from January 2016
Effective area	Global	Global	Emission Control Area

The IMO issued environmental regulation is MARPOL and it also contains SOx regulations. The MARPOL considers SOx and PM as a same pollutant. At the initial stage of regulation, sulfur content of fuel oil was limited to 4.5 % (m/m). The currently existing most stringent IMO regulation limits the sulfur content 0.1 % (m/m) from the beginning of 2015. **Table 1-2** describes SOx and PM regulation by IMO marine pollution prevention convention.

Table 1-2 SOx and PM regulation on MARPOL Annex VI

Applicable area	Limitation		
Global	~ 2011.12.31	2012.1.1.~	2020.1.1.~
	4.5% m/m	3.5% m/m	0.5% m/m
SOx emission control area	~ 2010.6.30	2010.7.1.~	2015.1.1.~
	1.5% m/m	1.0% m/m	0.1% m/m

Newly built ships can actively consider adopting new technologies which meet the requirements of maintaining ship stability and emission reduction such as vane wheel, PBCF, duct (Song H.J. et al., 2015) and microbubble system (Paik B.G. et al., 2015). However, ships that have already been put into commercial operation, such as the 110,000 vessels currently in operation, according to statistics from 2013 (Korea Maritime Institute, 2013), cannot aggressively consider such measures due to a lack of capital. Apart from a major conversion of the main and auxiliary engines, using fuel additives is the most realistic course of action. Fuel additives have been recommended to accomplish minimum fuel consumption and reduce emissions (STRATAS Advisors, 2013). However, the performances of most fuel additives supplied to the shipping sector have not been verified. Therefore, questions remain, regarding the performance benefits associated with increased use of fuel additives.

Fuel additive technologies have been derived from lubricant additives and the various kinds of fuel additives available on the market. Many varieties of fuel additives can be found in the market, all of which have various applications and these have been developed with various purposes in mind. Fuel additives are a particularly prominent subject of research in automotive and industrial incinerators due to an increasing interest in bioenergy.

The chemical composition was studied by Grzegorz B. et al.,(2013) to quantify the concentration of additives in diesel oil. Liquid chromatography, followed by gas chromatography, can be used to identify the additives containing aliphatic alcohols, which are common components of diesel fuel cleaning additives. This second staged processes demonstrates the possibility of accurate determination of the additive in diesel fuel. Arianna F. et al.,(2005) studied fuel emulsions and cerium additives. The effects of emulsions were investigated by using a 12% emulsion on a heavy duty (HD) engine and 6% emulsion on a light duty (LD) engine. Emission of particulate matter (PM) was reduced in both cases, by −32% on LD and −59% on HD. The reduction in emission of other pollutants was changeable. Cerium additive was effective in reducing emission in the LD engine but not in HD engine. The possibility of reducing PM emissions was confirmed using a fuel composition change. Zmagoslav P. et al.,(2013) investigated fuel additive effects on a heavy fuel consuming boiler operating in real-time and arrived at the conclusion that fuel additives can have a positive effect on boiler combustion. Aspalan A.(2016) studied the effects of a cetane improver on fuel properties and engine characteristics on blended fuel oil mixed with biofuel. Addition of 2-Ethylhexyl nitrate (EHN) cetane improver to the mixture increased the cetane number without having any effect on density, viscosity, cloud point, cold filter plugging point, and flash point. According to engine test results, EHN decreased the brake specific fuel consumption while increasing the emissions of NOx and CO. Sajjad H. et al.,(2014) illustrated the feasibility of gas to liquid (GTL) fuel in the context of comparative fuel properties between conventional diesel and biodiesel fuels. GTL has lower values in cold flow characteristics, kinematic viscosity and lubricity. However, these characteristics can be improved with the inclusion of an additive. GTL has the potential to reduce emissions and save fuel when blended with conventional diesel.

Kar M.P. et al.,(2016) simulated soot creation in large two stroke marine diesel engine. The simulation used a multi-step soot model derived from laser extinction measurement in an optically accessible constant volume combustion chamber. The model can be applied to identify SOx and sulfuric acid distribution. Guerry et al.,(2016) studied injection timing effects on a diesel methane dual-fuel combustion engine. Such technology is a strategy for future engine, due to the promise of low engine emissions of NOx and PM. The study varied the start of injection timing, and the results confirmed increased fuel conversion efficiency. The effects of fuel additives on engine emissions and efficiency were investigated using an on-road engine (Valentine J. et al., 2000). Teresa A.W. et al.,(2016) summarized recent research on catalytic oxidation and jet fuel reformation. Fe, Co, and Mo are known to increase surface area. Brunauer Emmett Teller (BET) analysis confirmed that Fe had the highest reactivity. The Fe is well-known constituent of the fuel additive as a combustion catalyst. Han W.H. et al.,(2007) investigated the changes in fuel properties when using fuel additives on board a vessel. Robert P.B. (1976) reported that adding manganese-containing fuel additives not only saved fuel oil by reducing excess air but also reduced SO_3 generation by boilers using heavy fuel oil (HFO). Babushokv I.W. et al.(2002) studied the effect of additives on the formation of polycyclic aromatic hydrocarbons. They found that metallic additives suppressed soot formation, and reported the suppression mechanism. Metin G. et al. (2002) studied changes in fuel properties due to additives, and found that Mn lowers fuel freezing point to a greater degree than Cu, Mg, or Ca. Noah I.T. et al. (2009) reported that hydrogenated monoterpenes decrease the cloud point of diesel. Additionally, hydrogenated forms of myrcene and limonene can be used as blending agents in diesel. Fennell P.S. et al. (2002) studied the reaction between NO and Fe at 500~900℃ in terms of reaction rates and possible mechanisms. Rebola et al. (2002) studied emission reduction from heavy fuel oil-fired furnaces, and concluded that simultaneous reduction of nitrogen oxides (NO_x) and PM is extremely difficult. John K.M. et al. (2015) summarized the technical achievements of increased engine efficiency and emission reduction in diesel engines. They suggested that the use of green fuels is effective for increasing engine efficiency and reducing emissions. Bonatesta F. et al. (2016) studied potentials fuel savings of a modern 4-stroke gasoline engine design, focusing on strategies for variable camshaft timing. Engine compression ratio and fuel injection technology have key benefits for fuel economy, and variable camshaft timing can be helpful in achieving additional fuel economy. Vinicius B.P. et al. (2016) studied ethanol dual-fuel combustion at low load condition. The study found increased efficiency by adjusting exhaust gas recirculation, intake air pressure and rail pressure. Following performance optimization, NOx and soot emissions were reduced to 65% and 29%. Zhang Z.H. et al. (2016) studied PM and engine performance using blended fuel oil, consisting of biodiesel and butanol or pentanol. The study found that blended fuel oil could increase brake thermal efficiency and brake specific fuel consumption. The blended fuel oil reduced elemental carbon and diesel particulate matters but water-soluble organic carbon and organic carbon fraction increased. Jinli W. et al. (2015) studied dieseline, a blend of diesel and gasoline, to improve combustion efficiency and emission reduction by reducing ignition delay. Li J. et al. (2015) also simulated dieseline effects, and concluded that while pure diesel could be effective at low loads, dieseline would be efficient at increased engine loads. Matteo I. et al. (2016) studied injection and Miller cycle effect in a large-bore marine engine. IMO Tier 2 compliant marine engines generally employ the Miller cycle. The study investigated split injection effect in conjunction with Miller timing, and concluded that split injection reduced ignition delay. Increased ignition delay can increase fuel economy but has no advantages for reducing emissions.

Unlike the automotive, boiler and bioenergy fields, research or study of additives on heavy fuel oil has been very limited in the maritime sector (Joanna G. et al., 2013). The performance of fuel additives and their effect on the engine has been rarely studied because recently developed additives can be utilized to distillate fuel and additives for residual fuel have just entered the market. Monique V. et al., (2010) studied the combustion characteristics and energy efficacy of marine fuel additives.

Following sections will describe properties of the marine residual fuel oil, kind of additives, history of additives. The purpose of the study is verifying the fuel additive effect to the engine side and fuel storage tank. Therefore, engine test had been done to quantify the fuel additive effect. Various laboratory scale tests were done to understand the additive mechanism. Some literatures will be introduced in this paper regarding fuel additive mechanism. However, these studies are chemical engineers viewpoint. Very rare case of mechanical engineer idea could be found. The study would like to be focused on verifying fuel additive reaction mechanism and would like to suggest guideline to use the additives. The verification is constrained only to combustion improver and stability improvers.

1.2 Basic properties of marine residual fuel oil

Residual fuel oil is created during the refining process and possesses a complex structure of hydrocarbons. The hydrocarbons, which make up residual fuel oils are paraffinic, aromatic, naphthenic, and olefinic in nature. Among these, naphthenic hydrocarbon (C_nH_{2n}-ringtype) is commonly found in heavy marine fuel oils. Naphthenic hydrocarbons are extremely stable cyclical compounds and, in most cases, have greater stability than even paraffinic hydrocarbons. The major constituent of residual fuel oil is asphaltene (ABS, 1984). It can be defined as the portion of crude oil insoluble in n-alkanes such as n-heptane or n-pentane, yet soluble in benzene or toluene. The solubility class definition of asphaltenes generates a broad distribution of molecular structures that can vary greatly from one crude oil to another. In general, asphaltenes are characterized by fused-ring aromaticity, small aliphatic side chains, and polar hetero atom-containing functional groups. It is common to characterize asphaltenes by their average properties as shown in **Table1-3** (Spiecker P.M. et al., 2013).

Table 1-3 Conventional values of elemental composition of asphaltene

Element	Concentration (wt.%)
H/C atomic	1.0 ~ 1.2
Nitrogen	1.0 ~ 1.2
Sulfur	2.0 ~ 6.0
Oxygen	0.8 ~ 2.0
Vanadium (ppm)	100 ~ 300

Asphaltene has a comparably low combustion speed and it also can create bigger droplets when fuel injected. Bigger droplets can create carbon deposits after combustion finishes, thereby contributing to the creation of particulate matter (PM) (Kim D.C. et al., 2008).

Marine residual fuel oil can be classified into following table. **Table 1-4** describes fuel oil quality standard. The definition and explanation of each parameters are given on the following paragraph.

Table 1-4 Specification of marine residual fuel oil

Characteristic	Unit	Limit	Category ISO-F										
			RMA 10	RMB 30	RMD 80	RME 180	RMG 180	RMG 380	RMG 500	RMG 700	RMK 380	RMK 500	RMK 700
Kinematic viscosity at 50℃	mm^2/s	max.	10	30	80	180	180	380	500	700	380	500	700
Density at 15℃	kg/m^3	max.	920	960	975	991	991	991	991	991	1010	1010	1010
CCAI	-	max	850	860	860	860	870	870	870	870	870	870	870
Sulfur	mass %	max.	Statutory requirements										
Flash point	℃	min.	60	60	60	60	60	60	60	60	60	60	60
Hydrogen sulfide	mg/kg	max.	2	2	2	2	2	2	2	2	2	2	2
Acid number	mg $_{KOH/g}$	max.	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Total sediment aged	mass %	max.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Carbon residue, micro	mass %	max.	2.5	10	14	15	18	18	18	18	20	20	20
Pour point													
- Winter	℃	max.	0	0	30	30	30	30	30	30	30	30	30
- Summer	℃	max.	6	6	30	30	30	30	30	30	30	30	30
Water	volume %	max.	0.3	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ash	mass %	max.	0.04	0.07	0.07	0.07	0.1	0.1	0.1	0.1	0.15	0.15	0.15
Vanadium	mg/kg	max.	50	150	150	150	350	350	350	350	450	450	450
Sodium	mg/kg	max.	50	100	100	50	100	100	100	100	100	100	100
Alumium plus silicon	mg/kg	max.	25	40	40	50	60	60	60	60	60	60	60
Used LO			The fuel shall be free of ULO - A fuel shall be considered to contain ULO when either one of the following conditions is met: - Calcium > 30 and zinc > 15 or calcium > 30 and phosphorus > 15										
- Calcium + Zinc	mg/kg	-											
- Calcium + Phosphorus	mg/kg	-											

1.2.1 Viscosity

Complete combustion can take place when the fuel droplet easily atomized. Lower viscosity can be effective to enhance more easier atomization. In the marine sector, viscosity cannot be considered a quality criterion in its own right for fuel oils, and is stated only for handling reasons such as pumping, preheating, and centrifuging for 2-stroke engine.

1.2.2 Density

Density is one of important fuel quality criteria because fuels derived from extensive refinery processing contains higher carbon content which is more aromatic and thus heavier. Therefore, fuels with a high density are also generally considered high in carbon residue and asphaltene.

1.2.3 Flash point

The flash point limit is set as a safeguard against fire. The flash point means vapour of fuel can ignite. However, the ignition will not be resulted in combustion.

1.2.4 Pour point

The pour point indicates the minimum temperature at which the fuel should be pumped and stored. Wax can be formed at temperatures below the pour point. The pour point can be problematic during winter season. Cold flow is related with paraffin which has high melting point. High concentration of asphaltene can lead to high pour point.

1.2.5 Sulfur

Sulfur in the fuel can be transferred to sulfur dioxide (SO_2) via combustion process. Some of gases transfers to the sulfur trioxide (SO_3) and it can be resulted in sufuric acid (H_2SO_4) under exhaust gas temperature of dew point. The sulfuric acid can cause corrosion on metal[$FeSO_4$, $Fe_2(SO_4)_3$]. Dew point can be increased when SO_3 concentration increased and it makes more easier creation of sulfuric acid. The corrosive effect of sulfuric acid during combustion is counteracted by adequate lube oils such as lubricant dosage or alkalinity, and temperature control of the combustion chamber walls.

1.2.6 Carbon residue

The carbon residue is alternatively measured as conradson carbon or micro-carbon. Fuels with a high carbon residue content can cause increased fouling of the gas-ways. More frequent cleaning will be necessary especially of the turbocharger and exhaust gas boiler. Asphaltenes are actually part of the carbon residues. The effect of asphaltenes on the combustion process is similar with the carbon residue. Asphaltenes also affect the fuel oil lubrication properties. Fuels with a high content of asphaltenes may tend to be emulsified with water. The carbon residue of the various petroleum materials serves as an approximation of the tendency of the material to form carbonaceous type deposits under degradation conditions similar to those used in the test method, and can be uselful as a guide in manufacture of certain stocks.

1.2.7 Water

Water in the fuel should be removed by centrifuging the fuel before use. This applies especially to salt water, the sodium content of which can result in deposits on valves and turbochargers. Water can help to create SOx combining with sulfur in the fuel during combustion.

1.2.8 Ash

Ash represents solid contaminants as well as metals bound in the fuel. Ash can be contained in fuel oil maximum 0.1% based on quality guide of ISO and it is consisted with Fe, Si, Al, Ca, Mg, Na, Ni and V. Part of the ash could be catalyst particles from the refining process. Catalyst particles are highly abrasive. Solid ash should be removed to the widest possible extent by centrifuging, and cleaning can be improved by installing a fine filter after the centrifuge.

1.2.9 Vanadium, magnesium and sodium

Vanadium is bound in chemical complexes in the fuel and consequently cannot be removed. Vanadium deposits are normally very hard, and may cause severe damage to the turbocharger more specifically nozzle ring and turbine wheel. Sodium presents in the fuel. Vanadium, in combination with sodium, can cause corrosion of exhaust valve and turbocharger deposits. This can occur when the weight ratio of sodium to vanadium exceeds 1:3 and especially in the case of a high vanadium content.

Magnesium, either present in the fuel, in salt water contamination or introduced via additives can increase the melting point of the vanadium, thus preventing the formation of deposits.

1.2.10 Aluminium and silicon

The limitation of aluminium and silicon contents have been introduced in order to restrict the content of catalytic fines, mainly Al_2O_3 and SiO_2, in the oil. Catalytic fines cause abrasive wear of moving parts, and content of catfines should be reduced as much as possible by centrifuging the fuel oil before it is used on the engine. 80 ppm of catalytic fines before the centrifuge is reduced as much as possible by the fuel centrifuge and, as a guideline, the level should in any case not exceed 15 ppm after the centrifuge.

1.3 Additives

1.3.1 History of additives

A. The pre-additive period - until 1921

In the early 19th century, when the gasoline production be initiated, fuel for spark ignition engines was essentially a waste product. Compression ignition engines did not have demand for fuels. Lighter middle distillate fuels were mainly used for illumination or in cooking stoves. As a consequence, there were no need to develop fuel additive until 20th century. As gasoline engine production increased to be used in automotive sector, the low octane number of the straight run light distillate product used in spark ignition engines were a barrier to engine development

B. 1920s to the present

The growth of use in gasoline additive largely reflects the requirements of engine design and developments in refinery operations. In 1921, lead alkyl antiknock compounds were developed that it has effectiveness increasing octane rating. These additives began to be commercially introduced from 1923 onwards to provide the sufficient octane rating which enable vehicle designers to increase engine compression ratios to levels which gave acceptable efficiency and performance. Increasing demand for gasoline by a rapidly rising vehicle population resulted in the increasing use of cracking operations at refineries. Antioxidants were introduced in the 1930s to prevent the tendency of cracked components to oxidise and form gums. These products became significantly more important in the 1970s when further increased use of catalytic cracking, to satisfy ever higher demand for gasoline and diesel production, raised the levels of unstable olefinic (= unsaturated) compounds in these fuels.

The focus of additive use shifted during the 1950s and 1960s and fixed on automotive fuel systems, when carburettor cleanliness and efficient operation became more important. During the 1980s, deposit control additives were increasingly used to reduce deposit build-up within the engine inlet system and to eliminate the potential performance and emissions problems such deposits can cause.

The elimination of lead alkyl additives from gasoline around the last century resulted in the development of additives to protect exhaust valve from unwanted seat wear in older engines constructed with unsuitable metallurgy.

Deposit control additive packages are now widely used, and recommended in the automotive sector, as a means to maintain optimal engine performance. The blending of bio-fuels, such as ethanol, into the gasoline pool can increase deposit formation potential and, higher additive levels will be required at a consequence. As the current international tendency is carbon reducing to a minimum, additive packages will contain components to minimize fuel consumption, in addition to maintain fuel system cleanliness.

C. Diesel additive developments

Increasing use of diesel additive means growing diesel fuel demand and the changing technology of diesel engines. In the early stage of diesel engine development, cold starting and ignition quality were key issue of development. Ignition improver which was the earliest invention among diesel additives still in use today because it assists in overcoming fuel bound problems. Diesel additives are used for the low specific fuel consumption of the diesel engine, assisted in the widespread adoption of the diesel engine as the power unit for heavy goods vehicles and locomotives.

Demand for diesel fuel rapidly increased and placed heavy burdens on refinery production. The introduction of wax crystal modifiers (cold flow improvers) was critical to increasing diesel fuel availability. Without these additives, the performance of diesel vehicles was not able to be maintained during the winter without additional expense to refineries. Otherwise the diesel car shall develop additional fuel system which is more complex and expensive. The refining pattern has been changed during late 1970s ~ early 1980s. These period affected diesel fuel quality improvement. The need to use a greater proportion of the crude barrel to produce increased volumes of middle distillates resulted in cycle oils from catalytic crackers being blended into diesel fuel. Cracked material has a lower cetane quality than straight-run distillate components. Cetane number is the important parameter for diesel fuel ignition quality, thus the use of cetane number improver additive was needed to meet the specification of cetane number and to provide fuels with the required ignition quality. Diesel engine manufacturers and operators had convinced that the benefits of high cetane quality diesel fuels. Therefore the use of cetane number improver has increased. The tradition of high cetane quality diesel fuels has been maintained in Europe for decades, with the result that cetane improver is a widely used and cost effective product.

The additive packages in the 1980s reflected the growing of the diesel fuel market and, particularly, the greater needs and expectations of the passenger car user. More recently, environmental legislation has reinforced the need for deposit control additives to keep the engine clean and maintain long-term vehicle emissions performance. The introduction of very low sulfur fuels led to a need for lubricity additives, increased the requirement for conductivity improver additives and created a need for revised or novel additives to improve oxidation stability. Conversely, the use of Fatty Acid Methyl Ester (FAME) as a renewable diesel blending component has reversed or reduced the need for lubricity and conductivity improvers whilst making the oxidation stability situation more complex.

1.3.2 Information and technical achievements of diesel additives from bibliography

A. Technical identity of fuel additives

Fuel oil additive technology came from lubricant and refinery processes. Fundamental reaction mechanism is almost same with each other industrial sectors. Therefore, these chapters will briefly introduce technologies applied in lubricant sector. The primary function of the base is to supply energy and act as a carrier of additives. The function of additives is either to enhance an already-existing property of the lubricant or to add a new property. The examples of already-existing properties include viscosity, viscosity index, pour point, and oxidation resistance. The examples of new properties include cleaning and suspending ability, antiwear performance, and corrosion control. The extent of the desirability of various properties differs from lubricant to lubricant and largely depends on the conditions of use. Automotive use, for example, requires with good oxidation resistance, suitable low- and high-temperature viscosities, high-viscosity index (i.e., minimum loss in viscosity with an increase in temperature), and good cleaning and suspending ability. Conversely, the use as nonautomotive lubrication oil, such as industrial and metal-working lubricants, emphasizes oxidation resistance, antiwear performance, corrosion control, and cooling ability.

One of the most critical properties of the automotive lubricants, especially engine oils, is their ability to suspend undesirable products from thermal and oxidative degradation of the lubricant (Leslie R.R., 2003).

B. Deposit control additives and detergents

Deposits are a common problem in diesel injector nozzles, as they are able to reduce the fuel delivery and the torque output of an engine, when every other parameter remains constant. Deposit control additives include various sub-types of additives. Detergents, demulsifier and stabilisers are the major ones, and are commonly used together to control deposit formation. Detergents are used to prevent the formation of deposits by providing a film on the metal surface of the injector and fuel supply pipe, preventing the accumulation of deposits. Detergents also act by forming a protective coating around the developing deposit precursors, to prevent deposits from even forming. In the case of diesel fuels, detergents are predominantly succinimide ($C_4H_5NO_2$) and other ashless polymeric products. The polar head in detergents is derived from oxygen or nitrogen moieties, but is not composed of metals, making them 'ashless', and ideal attribute for diesel combustion where the combustion of metals forms unwanted ash particles. Deposit precursors such as soot or sludge are attracted to this polar head, and are trapped with multiple additive molecules in micelles. The tail of the detergent molecule is a long hydrocarbon chain molecule, which is highly oleophilic. This formulation allows the deposit precursors to be burned, thus avoiding deposition (Adam B. et al., 2014).

Demulsifiers are almost always used in combination with detergents. Detergents can cause the formation of fuel-water emulsion. These effects are countered by demulsifiers. The demulsifier molecule is attracted to the water molecule. It modifies the water emulsion's surface tension to induce coalescence of the water and the fuel. This prevents emulsion of water in fuel, which is unwanted as it is a strong catalyst to corrosion through oxidation. Typical chemistries include alkoxylated polyglycols and aryl sulfonates.

Stabilisers are used intensively in the military industry where fuel may require storage for prolonged periods. Stabilisers ensure that a fuel can be used after long-time storage, using antioxidants to prevent sediment formation, dispersants to make sure the sediments that do form stay suspended and do not accumulate, and metal deactivators to deactivate the catalytic effect of some metals that could produce unstable reactions. Stabilisers are very similar in structure to detergents, where the polar head is a polymeric compound with a variable base or charge depending on what it needs to be attracted to. The tail is an oleophilic hydrocarbon chain. Antioxidants are overbased detergents (the head has a very high base number) that provide the large amount of base required to neutralise acidic components such as mineral and organic acids. It also reduces corrosive wear of the surfaces of metals. Dispersants are detergents that neutralise the charge of specific particles by forming a stabilising layer around the particle. This prevents agglomeration of other particles, which would otherwise create localised high density sediments that would fall to the bottom of the tank. Metal deactivators are additives with a polar head that is attracted to metal surfaces, forming a protecting film around the metal. This prevents corrosion, nullifies the catalytic effect of the metal, and in some cases prevents oxidation of the metal.

Deposit control additives (DCAs) for diesel fuel typically employ succinimide chemistry. There is a general similarity to DCA used in gasoline, with both products consisting of a polar head which has affinity for metal surfaces in the fuel system and a hydrocarbon tail which allows fuel solubility.

DCAs for compression ignition engines are designed to keep the whole fuel system clean, although in diesel engines intake valves do not come into contact with liquid fuel. In diesel engines the most significant focus for cleanliness lies in the fuel injector which atomizes the liquid fuel being delivered into the combustion chamber immediately prior to the onset of combustion during each power stroke. **Fig.1-2** shows magnified image of deposit on injector and its spraying pattern.

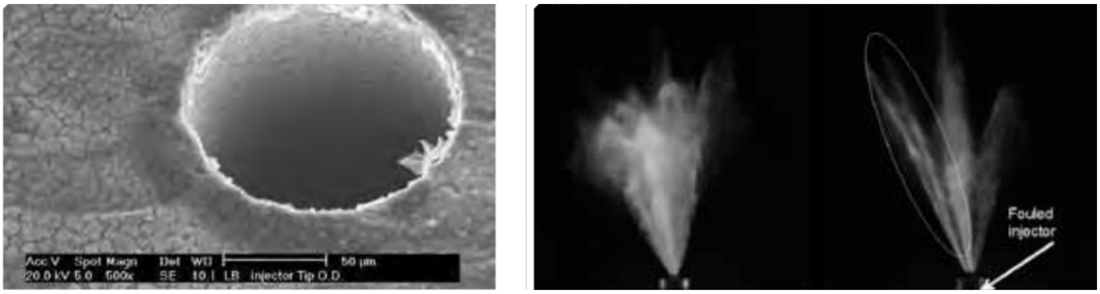


Fig.1-2 Injector deposit images / Fuel spray

Fuel is pumped to high pressures and is forced through very fine orifices during injection. Increasingly strict emissions legislation requires the close control of both the timing of injection and the quantity of fuel injected. Satisfactory engine operation depends very strongly on consistent, long-term control of the drop size distribution and shape of the injected spray inside the combustion chamber. Maintaining injector surfaces in a condition close to the manufactured state is an important factor in maintaining satisfactory long-term emissions, power output and fuel economy performance in the diesel engine.

Diesel DCAs help to prevent the formation of deposits in injector nozzles partly by providing a film on metal surfaces and partly by preventing agglomeration of deposit precursors. Diesel DCA are normally intended to be used on a continuous basis from a new engine condition to avoid deposit build-up, but by changing the equilibrium of accumulation and removal mechanisms, these additives can also provide a deposit removal function. Typical treatment levels for DCAs, which are frequently combined with other components in multi-functional packages, lie in the range 10~200 mg/kg. Treatment levels may be higher to effect removal of existing deposits in engines.

C. Flow improvers

Diesel fuel is used under various weather conditions. When diesel becomes cold (around -10℃ or colder), the long n-paraffins chains (around 15 carbon atoms or more) present in the fuel begin to solidify. The solidified groups of atoms of paraffins agglomerate to form what are called wax crystals. These wax crystals form a rigid matrix which can cause blockage of filters or fuel lines. Although it is possible to refine the fuel to remove such n-paraffins, and thus prevent wax formation, it is generally undesirable to do so as the n-paraffins have good combustion characteristics, and produce low emissions. Thus doing so would be costly and wasteful of the crude oil.

During the solidification process, the n-paraffins first form nuclei, on which other n-paraffin molecules accumulate to form crystals. When crystals are large enough, they start to adhere to each other to form even larger crystals.

Middle Distillate Flow Improvers (MDFI) are the most commonly used wax modifier. They are ashless low molecular weight co-polymers. They co-crystallise with the n-paraffins, which slows down crystal growth by altering the shape of the crystal, and also reducing the crystal’s adhesion. This forces new nuclei to start forming. As a result, multiple small crystals form that have difficulty agglomerating, instead of large agglomerating crystals. The effect, macroscopically, manifests itself as better flow conditions of the fuel, and retarded wax formation.

When the outside ambient temperature is low for a long time, the wax crystals treated with MDFIs will settle at the bottom of the diesel fuel tank in cars due to their increased density. Once settled, the wax crystals bond together over time, forming crystals large enough to be able to block filters. Thus, although the cold filter plugging point (CFPP) of fuel is lowered substantially with MDFIs, their use is limited on their own to a net improvement of about 10℃ because of the uneven properties of the fuel in the tank.

To measure the effectiveness of a cold flow additive, a widely used method known as the CFPP is employed. This method involves letting fuel fall under gravity through a filter. The procedure is repeated, successively cooling the fuel further in 1℃ steps. If the time required to fall through the filter is more than 60 seconds, the fuel has reached the CFPP temperature.

There are other widely varying methods used to determine the waxing point of fuels. A more commonly used alternative method is the cloud point temperature, which is the temperature at which the wax starts becoming visible.

Cold flow improver (CFI) additives (also known as MDFI) for diesel fuels utilize vinyl ester co-polymers. A range of different low molecular weight polymers with a variety of structures is employed to treat fuels from different crude sources with different hydrocarbon compositions. **Fig.1-3** shows image of crystal growth of the fuel and also filter blocking image is given.

Fig.1-3 Example of crystal growth and filter blocking by cold ambient

Middle distillate fuels contain typically 20~40% n-paraffins which have desirable properties in a diesel fuel. However, n-paraffins tend to produce significant volumes of wax crystals in cold weather. As temperatures drop, crystals grow in size and begin to adhere to each other, forming large lattices of crystals. Wax crystallization in diesel fuel can cause vehicle operability problems, blocking fuel filters and feed lines and fuel starvation, ultimately leading to power loss and possible engine shutdown.

Use of cold flow improvers in middle distillates prevents these problems and permits a greater proportion of the crude barrel to be included in the diesel pool, resulting in a smaller output of lower value residual fuel and thereby reducing the overall cost of fuel production.

Preventing the formation of large stable lattices does have a negative aspect, in that the crystals do not remain suspended in the diesel fuel, therefore they begin to sink towards the bottom of the tank. Fuels containing cold flow improver additives, when stored for an extended period in cold weather, can permit fuel quality changes, as fuel in the lower part of the tank becomes wax rich, particularly when the tank fuel level becomes low. Anti-settling additives assist in preventing deposition of wax crystals in treated fuels during tank-storage at refineries and terminals.

Cold flow improver additives function by being only moderately soluble in diesel fuel. As the fuel cools, additive molecules begin to precipitate out of solution as very small nuclei at a temperature close to the cloud point of the fuel. The presence of these nuclei distributed through the fuel encourages the growth of a large number of small wax crystals. Co-precipitation of additive molecules with wax crystals prevents growth of the large plate-like wax crystals seen in untreated fuel. The presence of a large number of small crystals (produced due to the action of a cold flow improver) rather than a small number of large ones, allows the fuel to continue to flow, thus preventing fuel filter and line blockage, and thereby permitting normal engine and vehicle operation at low ambient temperatures. Typical treat levels for CFI additives can range from 50~1,000 mg/kg.

D. Lubricity improvers

Lubricity improvers have been introduced recently to the additives market as a result of the changing regulations on diesel fuels. Lubricity additives are surface active compounds, consisting of an active polar head group which permits the formation of a protective film on moving metal surfaces and a hydrocarbon tail to assist fuel solubility. Typical chemistries used in lubricity improvers include fatty acids, esters and amides. Diesel fuel has natural lubricity properties such as sulfur and other impurities. However, to limit pollutant exhaust emissions, limitation of sulfur content in fuel oil, and other subsequent European emissions standards have drastically lowered the allowed sulfur content to less than 1,000 mg/kg of fuel. The hydro-treating process, which is used to reduce the sulfur content of the fuel, also removes as a by-product the oxygen-containing polar impurities, which are the naturally occurring lubricity compounds in diesel fuel (Antony S. et al., 2010; Danping W. et al., 1986).

The fuel aromatic content has been forced reducing to limit particulate emissions. The decrease of poly-aromatics has severely influenced the natural lubricity of the fuel, as poly-aromatics were another important natural occurring lubricity improver in fuel.

There are two regimes of lubrication: boundary and hydrodynamic lubrication. The former is a type of lubrication that relies on the protective layer that forms on the surfaces of the interacting components by additives or other molecules in the fuel. The latter relies on the properties of the lubricating fluid, notably viscosity and surface tension, to form a film separating the interacting surfaces. Lubricity improvers tend to focus on the boundary lubrication regime, as it is the one that is affected by the recent changes on diesel fuel described above. They can nevertheless be designed to improve the lubrication of either regime.

It is very difficult to alter the viscosity of a fuel without changing its other characteristics, essentially creating a new blend of fuel. The viscosity modifiers, more commonly used with lubricating oils rather than fuels, can be used in very high concentrations (between 5% and 50%) to alter the viscosity of fuel or oil. Viscosity modifiers are high molecular weight polymers whose viscosity is less sensitive to temperature than diesel fuel. The problem with viscosity modifiers is that a large quantity of the additive is required to induce a significant change in viscosity. Furthermore, this change is noticeable at high (over 80℃) or low (under 10℃) temperatures.

Due to the very large quantity of additive required to induce a change in viscosity, viscosity modifiers are rarely used in everyday diesel fuels. Instead, crude oil is refined into component streams and the streams are then blended in order to fit within the viscosity requirements of the World Wide Fuel Charter.

Although hydrodynamic as well as boundary lubrication occur in several components of the fuel delivery system, the lubrication regime that is affected most by the removal of the sulfur and aromatics in diesel fuel is the boundary lubrication regime. Friction modifiers (FMs) are added to the fuel to act on the metal surfaces. FMs have a polar head which is attracted to the metal surfaces, either by adsorption, or by chemically reacting with the metal surface to form oxides. The tail is a long molecular chain, normal to the surface of the metal. The additives coat the metal surface, forming a layer. When the metal surfaces come in contact with one another, the tail molecules slide on one another, reducing metallic contact. sulfur and metal impurities as well as aromatic molecules present in the fuel are attracted to metallic surfaces, and act similarly to natural FMs (Williams J.A., 1994).

The high frequency reciprocating rig (HFRR) was devised to measure the lubricity of a fuel, and is in use in Europe and around the world as the prime lubricity measurement tool. It involves an oscillating ball against a flat piece of metal immersed in fuel. The depth of wear on the metal flat over a large number of reciprocations is a measure of the lubricity figure. This depth needs to be lower than 400 microns with the fuel at 60℃.

Diesel fuel injector relies on the fuel itself to lubricate moving parts. Modern vehicle emission reduction technology demands almost complete elimination of sulfur from diesel fuels, requiring severe refining processes, primarily hydrotreating, to achieve this. These processes also act to reduce the natural lubricating quality of middle distillate blending components. Untreated, very low sulfur fuels can produce extremely rapid wear, and failure, in both automotive and aircraft fuel pumps. Lubricity improver additives are effective in restoring lubricity lost in severe refinery processing, thereby permitting normal pump operation, reliability and service life.

The long chain polar compounds employed in lubricity improver additives permit the establishment of a mono-molecular coating on metal surfaces. This film, or boundary layer, provides a cushion which keeps metal surfaces apart and thus protects against wear. Treat levels, which vary depending on crude source, the level of protection required and the specific additive chemistry employed, lie in the range 25~400 mg/kg. **Fig.1-4** shows HFRR test result on any of metal surface.

Fig.1-4 Industry test wear scar using high frequency reciprocating rig

E. Combustion improvers

Diesel fuel in a compression-ignition engine auto-ignites under high temperature and pressure conditions. It is possible to obtain a measure of the ignition delay of a diesel fuel using its cetane number, a fuel quality either determined experimentally or calculated from knowledge of the fuel composition. A high cetane number is desirable in diesel fuel, so as to reduce the time necessary for the fuel to ignite, and hence prevent violent and noisy combustion. The cetane number of a fuel relates closely to its composition (Yanowitz J. et al., 2004).

The most commonly used cetane improver is 2-ethyl-hexyl nitrate (2-EHN), which is one member of a family of alkyl nitrate improvers. Alkyl nitrates are chain hydrocarbons (n- or iso-paraffins) bonded to the NO_3^- ion. It is assumed that immediately after injection the nitrate ion helps the breaking down of the fuel molecules to provide further free radicals. This allows for some preliminary reactions, which would otherwise be needed when no additive is used, to be skipped and for branching to occur sooner (Daood S.S. et al., 2014). As a result, the ignition delay is shortened. Cetane improvers have also been shown to improve cold starting significantly and to reduce several emissions of particulates, NOx and hydrocarbons (Ickes A.M. et al., 2009). Some results however show that 2-EHN can have a negative effect on NOx emissions, and this is assumed to be caused by the nitrate ion present in all CI additives becoming part of the NOx emissions from the engine. This negative effect on NOx is however very small compared to the benefit on NOx of reducing the ignition delay and the duration of high temperature pre-mixed combustion.

Cetane number improver additives are predominantly alkyl nitrates, of which 2-ethyl hexyl nitrate (2-EHN) is the most common, having been used for over eighty years to increase cetane number of diesel fuels. Peroxides such as tertiary butyl peroxide can also be used but are generally less cost effective than alkyl nitrates.

Cetane number improvers provide a cost effective increase in diesel cetane quality. Combustion in an engine operating on diesel fuel relies on the auto-ignition of fuel injected into the compressed air trapped in the combustion chamber. After fuel injection, onset of combustion is not immediate but subject to a delay, termed ignition delay. Cetane quality of diesel fuel is defined in terms of the ease with which the fuel ignites; increased cetane number corresponds to reduced ignition delay. Operating a diesel engine on inadequate cetane quality fuel results in poor starting characteristics, especially in cold weather, significant white smoke emissions, higher noise levels, increased fuel consumption and higher exhaust emissions. Higher cetane quality is therefore a very desirable feature in diesel fuels.

Cetane number improvers break down during combustion to form free radicals. These radicals increase the rate of decomposition of the fuel, causing it to ignite more readily and so reducing ignition delay. Treat levels vary widely from around 0.015% vol. to 0.2% vol. and above, with the additive employed at the refinery to trim cetane quality during blending operations to meet product specification but also in multifunctional additive packages where a number of enhanced operational benefits can be demonstrated from increased cetane quality fuel.

F. Corrosion inhibitors

Corrosion inhibitors consist typically of a polar head to enable adhesion to the metal surfaces to be protected, and a hydrocarbon tail to ensure fuel solubility. Effective corrosion inhibitors include carboxylic acids, amines and amine salts of carboxylic acids. Corrosion inhibitors are applied either at the refinery, pumping station, terminal or as part of a multifunctional additive package.

Diesel fuel supply arrangements can permit water to enter fuel, with similar potential for surface corrosion of metallic components throughout the fuel storage and delivery system. Corrosion inhibitor additives are very cost effective in preventing such corrosion.

The protective mode of action is that the polar head provides a protective film on the metal surface, while the hydrocarbon tail allows the molecule to be solubilised in the fuel. Treat rates are in the range 5~100 mg/kg.

G. Stability Improvers (including Antioxidants)

Diesel stability improver additives are generally long chain and cyclic amines. Instability leads to fuel darkening and the formation of gums and sediments. Stability improvers, like antioxidants, enhance fuel stability and inhibit its tendency to deteriorate in storage. **Fig.1-5** shows one of test method of fuel stability according to ASTM 2274.

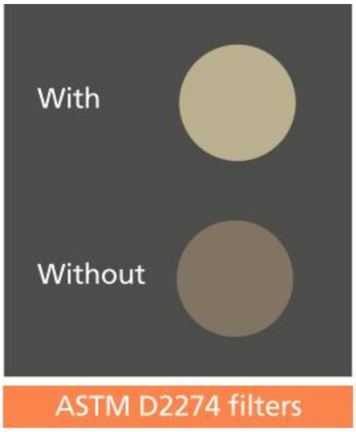


Fig.1-5 Comparison of stable and unstable fuel oil with ASTM D 2274 filter analysis

Diesel fuel may be stored for prolonged periods, particularly for military use, and it is of prime importance that the fuel remains fit for use throughout this time. Refinery processes to increase the proportion of diesel fuel obtained from a barrel of crude oil have utilised cracked material which contains olefins and more nitrogen and sulfur compounds than straight run distillates. Inclusion of unstable species such as olefins can result in polymerisation to form gums, whilst nitrogen and sulfur compounds and organic acids can combine to form sediments. Due to extensive desulphurisation of fuels at the refinery, reactions involving nitrogen and sulfur species have been significantly reduced, although those same refinery processes have resulted in diesel fuel being potentially susceptible to peroxidation, with consequent gum formation and elastomer embrittlement concerns. Gums are generally undesirable and in diesel fuel systems, sediments can result in fuel filter blockage with implications for vehicle operability.

Stability improvers interfere with the acid-base reactions which occur between nitrogen and sulfur compounds and organic acids, reacting preferentially to produce soluble reaction products and preventing sediment formation. Unstable species in diesel fuel produce free radicals which combine with oxygen to produce further free radicals in a chain reaction and react with olefinic compounds to form gums. Antioxidants inhibit chain-branching reactions or intercept free radicals to form stable hindered radicals which do not propagate further. Typical treat rates are in the range 20~200 mg/kg.

H. Multi functional additives

Combined packages of a number of selected additive components can be assembled to provide a bespoke performance-enhancing additive for use by fuel retailers for their products. Such packages enable retailers to differentiate their fuel products at the point of sale to the consumer. They allow increased performance features to be highlighted, and provide a means to sell a higher quality product to the discerning customer at increased margins. They also represent a cost effective and efficient way of delivering multiple benefits conveniently in a single additive treatment at the fuel terminal or pipeline, prior to delivery to the customer sales outlet. Multifunctional gasoline additive packages will often combine a deposit control additive with a corrosion inhibitor and demulsifier additive. Multifunctional diesel additive packages are frequently more complex and may combine deposit control additive with cetane number improver, antifoam additive, corrosion inhibitor and demulsifier (and possibly also cold flow improver additives depending on seasonality).

The composition of multi-functional diesel additives is influenced by national and regional legislation, as well as consumer demands and perception. For example, silicon (Si) based antifoam additives are widely used in European diesel fuel but are not used in the United States due to legislation that prohibits the addition of Si to fuel. Fuel addition can also be influenced by governments who regulate the cost of fuel and provide allowances for a premium to be charged for additised fuels.

I. Nano-sized particles as an additives

Cerium oxide has the ability to promote the combustion reaction by the oxygen atoms arranged in a lattice structure (KEITI, 2013). The catalyst activity is dependent on the surface area. So, among other things nanoparticles may provide a distinct advantage than bulk material or large particles (Paul S. et al., 2014).

Adding the cerium oxide nanoparticles in fuel gives to help the decomposition of the hydrocarbon and soot reducing. The amount of exhausted pollutants and fuel consumption will be reduced. In addition, cerium oxide is able to reduce the pressure of the combustion chamber and it is resulted in reducing the nitrogen oxide and also lead to more efficient combustion reaction.

Cerium oxide nanoparticles can be used as a short-term treatment in the particulate filter for diesel engines. Nanoparticles clean the soot stuck on the filter and significantly increasing performance of the filter.

Fine particles of aluminum and nanoparticles of aluminum can be potentially fuel additives. Aluminum is known to increase the power output of the engine due to the high combustion energy. Nanoparticles allows for more detailed study on the relationship between the properties and performance benefits to the particle size and structure.

Suspension characteristics of nano-aluminum helps to lead micro explosion which will lead more efficient combustion by enhancing air-fuel mixture (Korea Institute of Energy Research, 2009).

Cobalt oxide (Co_3O_4) and magnesium-aluminum (magnalium) will be used as a bio-diesel fuel additive. Oxygen atom of the cobalt oxide particles are suitable for combustion like cerium oxide. Cobalt oxide reduced emissions of carbon monoxide and unburned hydrocarbon by the experiment.

Cobalt nano additives reduces the NOx production particularly on bio-diesel fuel. Bio-diesel fuel is known tend to discharge the high nitrogen oxides compared to normal petrochemical diesel. Nano-particles of magnalium provides a similar effect to the aluminum.

It is shown that Magnalium particles can have a role of heat sink in the combustion chamber. The heat sink reduces overall temperature to avoid hot spot and reducing nitrogen oxide. Although the nano-additive demonstrated the potential to improve the quality of the fuel efficiency, exhaust gas produced by nano-additive can cause environmental problems. Adding the cerium oxide nano-particles in the fuel shows the result of reducing the emissions of particles. Such particles are likely to accumulate in the environment, particularly on the road side.

Chapter 2 Understanding additives and review of relevant literatures

2.1 Combustion with fuel additives

There are many ways to study the diesel combustion process. The combustion process can be investigated via on-board tests, engine bed tests, optical research engine tests and combustion vessel tests.

On-board tests are usually carried out by the manufacturers or end-users on every fuel or additive blend package product to see the behaviour of the vessel in actual running conditions. Usually, this is a final process to determine the effects that the additive blend fuel may have on the engine and vessel performance when the vessel is operating under field conditions.

Engine bed tests are conducted with real engines, under dynamometer distributed load. Engine bed tests can be used to determine the effect that an additive may have in real engine conditions. Engine bed tests usually measure power and emissions, sometimes cylinder gas pressure, but have no optical access. Engine tests are useful to assess the effect of a particular additive on engine running performance, but they are less helpful in studying and understanding the way the additive works.

Engine bed tests and on-board tests do not consider details of the combustion process in detail of additive evaluation. These tests only evaluate output of additives.

Optical research engines are specially designed or modified real engines so as to have windows that allow visualization of the inside of the combustion chamber while engine operating. Optical engines allow the study of the combustion process inside an engine, but are restricted to certain running conditions because the optical access components are fragile.

Combustion vessels are not engines. They are made to study a single combustion event under controlled ambient conditions. They can be helpful for the understanding of the combustion process, as many more parameters such as vessel pressure, temperature and gas composition can be controlled independently in a combustion vessel. Similar control parameters would be difficult to achieve in an engine. Combustion vessels also allow extensive optical access that is not usually possible in an engine. Although combustion vessels are used to characterise combustion, they never fully match engine tests, as those are more complex in nature.

Combustion improvers work by raising the cetane number of a fuel. Cetane improvers have been in use for over 70 years. They work by the additive breaking down during combustion to form free radicals. These free radicals accelerate decomposition of the parent fuel by creating a greater frequency of intermediate reactions. In this way, the improver shortens the pre-combustion period, and reduces the ignition delay (Scott K.B., 2009).

2.2 Chemistry of combustion

In diesel combustion, the fuel reacts with the oxygen in the air that is present in the combustion chamber (Arturo R. et al., 2003). Air is often assumed to be composed of 21 Vol.% oxygen, and 79 Vol.% inert gases, taken as nitrogen. The fuels used in internal combustion engines are blends of many different hydrocarbon compounds which are mostly obtained by refining crude oil. They are typically composed of about 86% carbon and 14% hydrogen atoms by weight

(Wallington T.J. et al., 2005).

There are many molecular structures in which hydrocarbons can be found in nature and most of these can be found in diesel fuels. Some different kinds of molecular structures are described in detail as follows.

Paraffins or alkanes which are single bonded open chain saturated hydrocarbon molecules. They can either be straight-chain molecules (e.g. methane, ethane, propane), which are called normal (n-), or, for bigger molecules, they can also be branched- chained, called isomers (iso- compounds). For example, octane can be n-octane, a single chain of 8 carbon atoms, or iso-octanes, which can be any combinations of 8 atoms of carbon, with branching.

Cycloparaffins which is also called naphthenes or cyclanes are single bonded ring hydrocarbons. They are single-bonded so the ring can be easily broken. Examples include cyclopropane, cyclobutane, and cyclopentane.

Olefins or alkenes are unsaturated open-chain hydrocarbons containing a double bond between two carbon atoms. Both straight and branch-chain structures can exist. Olefins include one, two, or more double bonds. Ethene, propene, butene are olefins and these are also called ethylene, propylene, and butylene.

Acetylenes or alkynes are unsaturated open-chain hydrocarbons containing one triple bond of carbon-carbon.

Aromatics are very stable ring structure hydrocarbons containing six carbon atoms and three single and three double bonds. The simplest of the aromatics is benzene, which can accommodate additional groups in side chains. Examples include toluene, xylene. Several benzene rings can be bonded together to make poly-aromatics with two, three and more rings.

Alcohols are organic compounds where a hydroxyl group (-OH) replaces a hydrogen atom. Methanol and ethanol are common examples of alcohols, the first having one carbon atom and the second two.

Fatty acids esters are present in modern fuels as they are used in the making of bio-diesels refined from vegetable oil or animal fat. They are composed of a long saturated or unsaturated open chain bonded with a carboxyl group (-COOH) or a carboxylic ester (-COOR), where R can be a methyl, ethyl or propyl group. They are not found in crude oil, but can be added in various quantities up to 100% to crude oil (Luciano S. et al., 2010).

Diesel fuel is composed of about 25% aromatics and 75% saturated hydrocarbons, which are primarily paraffins, including cycloparaffins. Unsaturated hydrocarbons are found in very low concentrations in both diesel and gasoline fuels. Diesel fuel also contains sulfur, although modern diesel fuels for road vehicle applications use diesel fuels with sulfur contents of ~10mg/kg of fuel. Modern diesel fuels have a reduced aromatic content that can be as low as 15%, to reduce the content of poly-aromatics which are carcinogenic.

Diesel fuel is not sufficiently volatile to form sufficient combustible vapour under atmospheric pressure and temperature. In an engine, a high pressure and temperature environment causes diesel fuel to auto-ignite. The diesel fuel reaction with air is therefore spontaneous, and cannot occur unless the conditions of pressure and temperature are correct in an engine, that is around 15bar pressure, 400℃. However, diesel fuel will auto-ignite under atmospheric conditions as long as the fuel temperature is elevated enough circa 400℃. The high pressure is simply a consequence of the way air temperature is raised in a compression-ignition engine, but is not a requirement for spontaneous combustion (Carmen C.B. et al., 2014).

The combustion reactions are complicated. The various hydrocarbons break down first to form radicals, which are needed for further reactions. Chain reactions then occur using the newly formed radicals, until a process known as branching occurs leading to a large release in chemical energy known as combustion. The time between injection and start of combustion is known as the ignition delay, and varies depending on how quickly the fuel breakdown reactions occur and branching reactions are reached.

It is impossible to determine all the chemical reactions that occur during a combustion process. Not all diesel fuels are the same, and the temperature and pressure conditions are such that certain reactions may occur more quickly than others. The auto-ignition process has been studied in detail as a function of the type of hydrocarbon, because the auto-ignition capabilities of fuels are important for diesel fuel.

Alkane length has an effect on compression-ignition. As alkane length increases, the ignition is easier and ignition delay shortens. Long chains are sought, so branching is unwanted. Double bonds and aromatic molecules are difficult to auto-ignite, so their maximum proportion in diesel fuel is controlled.

Long olefins with two or three double bonds are generally unwanted, but olefins with a single bond have a fairly small effect on fuel ignitability.

Naphthenes, being single bonded, are better in auto-ignition than the corresponding ring-size aromatics. Increasing the side chain of both naphthenes and aromatics improves auto-ignition of diesel fuel (Lovell W.G. et al., 1948).

2.3 Additive effect on ignition delay

The addition of combustion improver additives in diesel fuel has become a very common and effective way of lowering ignition delay. Addition of combustion improver will increase the cetane number by up to about 10, even with a small quantity of additive of 250mg/kg to 2,500mg/kg. The addition of combustion improver can also help reduce emissions. Some reactions cannot occur straight away as they require the radicals provided by earlier reactions. Combustion improver additives provide free radicals early in the breaking down chemical reactions of the diesel fuel, thus accelerating the chain reaction process that occurs during pre-ignition (ATC, 2004).

The effect of other additives on ignition delay is not available in the literature as very few additives are tested for effects, such as ignition delay, that they have not been specifically developed for. It is however possible that other additives, which are composed of hydrocarbon chains, provide free radicals too when the breaking down of fuel occurs, or conversely, increase ignition delay by absorbing radicals (e.g. anti-knock additives).

2.4 Additive effects on emissions

Additives are chemical compounds added in very small quantities to a fuel. For this reason, it is expected that all additives, as they break down during combustion, will have some effect on emissions (Lee B.H., et al., 1998). This effect is, however, insignificant for most additives (ATC,2004) compared to the effect of combustion and fuel properties. The additives may have an effect on a particular aspect of combustion, which in turn, may have a positive or negative effect on emissions. This is the case for combustion improvers, which reduce ignition delay, and thus improve NOx and other emissions (Kim D.C. et al., 2010).

2.4.1 Reduction of NO to N_2 by reaction with particles of Fe

Iron has been proposed as a possible catalyst for reacting the toxic gases NO and CO using the overall reactions (Fennell P.S. et al., 2002; Hayhurst A.N. et al., 1997).

$$3NO + 2Fe \rightarrow Fe_2O_3 + 3/2N_2 \tag{2-1}$$

$$3CO + Fe_2O_3 \rightarrow 2Fe + 3CO_2 \tag{2-2}$$

whose net effect is

$$CO + NO \rightarrow CO_2 + 1/2N_2 \tag{2-3}$$

The reaction (2-1) already has been proposed from a study (Randall et al., 1998). The advantages of using iron, rather than another catalyst, are that it is cheap and readily available. A study was mainly concerned with the reversible chemisorption of NO on Fe and found appreciable concentrations of N_2O when CO and NO were reacted over Fe_2O_3, although it disappeared entirely from their reactor outlet at temperatures above 350℃. This might mean that N_2O is an intermediate between NO and N_2 in reaction (2-1) even at temperatures higher than 350℃. The initial stage of the reaction of NO with CO was a partial reduction of NO to N_2O.

2.4.2 Additive effects to the creation of Polycyclic Aromatic Hydrocarbon (PAH)

Soot formation is a complicated multistep process. It is generally recognized that reactions involving the formation of PAH represent the most likely pathway to soot formation. Metal additives (e.g., containing iron and/or manganese) are usually considered good soot suppressants in combustion processes. On the other hand, there are experimental studies conducted in well-characterized environments which demonstrate that the same metal-containing additives increase PAH and soot yields in hydrocarbon flames (William P. et al., 1993). **Table 2-1** contains information on effects of some metals on soot and PAH formation from several publications. Ferrocene and manganese additives under all conditions increase soot formation in a premixed ethylene flame. The additives do not change C_1-C_4 species concentrations. The iron on the surface of growing soot particles catalyzes PAH formation from acetylene. An increase in soot formation is observed upon the addition of iron pentacarbonyl to premixed propane flame. In practical combustors, iron addition may catalyze carbon oxidation through Fe_2O_3 formation (soot burn-out). Variations in additive concentration can change the mode of action from smoke suppression effect to enhancement for diffusion flames. The introduction of metal additives at different heights of a diffusion flame can lead to different consequences. The lower heights of additive delivery correspond to decreased levels of soot production. Introduction at higher levels changed additive influence from inhibition to enhancement of soot formation. The available experimental data demonstrate that pro-soot effects of metallic additives were observed in premixed and diffusion flames as stated on **Table 2-1**. It was concluded that fine-scale incorporation of iron compounds within the soot matrix is a primary factor for the soot suppression. Ferrocene was identified as a soot burnout catalyst rather than a soot suppressant in oxygen-rich conditions. Manganese added to a sooting flame is incorporated into the soot particles and subsequently accelerates their rates of oxidation.

Table 2-1 Metal containing agent influence on PAH and soot formation

Additive	Fuel	Process	Effect	Reference
NaCl, KCl	C_2H_4	Laminar co-flowing diffusion flame	Sodium-no effect; K-reduction of soot volume fraction; no effect on the number density.	Tappe M. et al., 1993
Na, K, Cs, Ca, Sr, Ba	C_2H_4/air	Premixed flame	Significant increase of particle number density by Na, K, Cs (<1 ppm) and Slight reduction of soot yield.	Haynes B.S. et al., 1980
Ferrocene, $(C_5H_5)Mn(CO)_3$	$C_2H_4/O_2/N_2$	Premixed flame	Increase of produced soot. No effect on soot inception point and C_1-C_4 species.	Feitelberg A. et al., 1993
Ferrocene, Ferrocene derivatives; organometalic compounds of iron, zinc, titanium	Crude oil	Pool fire	Ferrocene and derivatives reduce soot production. Other organometalic compounds of Fe, Ti, Zn, did not have effect.	Mitchell J.B.A., 1991
$Fe(CO)_5$	Propane	Premixed flame	Increase of soot volume fraction.	Hahn D.W., et al., 1992
Ferrocene	C_2H_4/air	Co-flowing diffusion flame	Enhanced soot formation; Fe encapsulation into soot particles reduces soot by oxidation	Zhang J. et al., 1996
Ferrocene	Methane,	Laminar	C_2H_2 flame-no effect on	Kasper M.

	acetylene	co-flowing diffusion flame	PAH; methane flame-decreased PAH.	et al., 1998
As (cacodylic acid)	C_2H_4, mixture H_2/N_2	Coflowing laminar diffusion flame	No effect on soot formation and oxidation. Arcenic was not incorporated into soot particles.	Chesworth S. et al., 1994
Potassium hydroxide	Toluene	Liquid injection incinerator	Increase of solid-phase PAH for lean flames; increase of PAH concentration was not observed for fuel-rich combustion.	Wei Y.-L. et al., 1998
Li, Na, Ba, K, Cs, Mn, Co, Ni, Cu, Zn, Al, S, Fe, Pb, Cr (salts)	C_2H_2, C_3H_8	Diffusion flame	K and Cs have soot suppression behavior at high concentrations but promotion effect at low concentrations, Cr was a soot promoter at all concentrations.	Bulewicz E.M. et al., 1974
Ba, Cs, K, Na, Li, Sr, Ca, Mg (metals, metal compounds)	C_2H_4	Diffusion flame	Pro-and antismoke effects are observed depending on additive introduction point in a flame.	Salooja K.C., 1972
$Fe(CO)_5$	C_2H_4	Pyrolysis behind shock waves	Promotion effect	Tanke D., et al., 1998

Soot formation is believed to proceed through several overall reaction steps: formation of simple aromatic compounds, PAH growth, particle inception, chemical surface growing, and coagulation. Additives to flames may affect each growth stage differently.

The effect of radical scavenger additives such as iron carbonyl and hydrogen bromide is to increase PAH concentrations under near-stoichiometric conditions. This is a consequence of the increases in the precursor concentrations (C_2H_2,C_3H_3,C_6H_6) during combustion in the jet-stirred reactor and in premixed flames. Absolute concentrations of precursors under such conditions are, however, very low. An increase of the equivalence ratio decreases the relative importance of additives. For a relatively large equivalence ratio, the gas-phase influence of additives practically disappears. Under such conditions precursor concentrations are at a maximum. The qualitative effect arising from the reduction in the concentration of the radical pool is to increase the precursor concentration leading to the corresponding increase of PAH concentrations and to decreased rates of their consumption. It is clear that a gas-phase mechanism for the effects of flame inhibitor additives in the early stages of PAH and soot formation in combustion systems is not compatible with decreases of PAH concentrations. Note that such decrease of soot formation will be more pronounced in diffusion flames where the decreased level of additive effects on the PAH and soot formation in the fuel-rich side of flame is combined with heterogeneous soot oxidation increased by additives in the oxygen-rich side of flame (Babushokv I.W. et al., 2002).

2.4.3 Additive effects to the emission reduction

Fazliakmetov R.G. et al. (1997) reported that particulate matter (PM) emission is reduced when Fe, Mn, Ce content additives are used for diesel engines. 0.2%~0.5% Mn content peroxides reduces smoke 22%~25% (Hinkova M. et al., 1997). It is essential that reducing aromatics in the fuel reduces HC emissions. Yang H.H. et al. (1998) tested Mn based additives to diesel fuel and observed a 50% reduction of aromatic HC in the fuel. If the fuel contains Ca, P, K, Zn or Pb, it is not possible to avoid pollutants. It can be seen in many studies that some additives change the cetane number and affect combustion and emissions. As a result of the experiments, it was observed that Mn has the stronger effect in reducing the fuel freezing point, and the optimum dosage of Mn was determined. Organic compounds of Cu, Mg and Ca are less effective on the fuel properties in comparison with Mn. Temperatures from the solid phase to liquid are measured for the fuel with the Mn organic compound, and the optimum dose is found for the best reduction of freezing point. By optimum additive dosage, the cetane number is increased from 46.22 to 48.24. Exhaust emission measurements for the fuel with additive showed that O_2 is reduced 0.2%, CO 14.3% and CO_2 was increased. SO_2 was reduced, while the net efficiency was increased by 0.8%. It is possible to reduce NOx and SO_2 emissions by 20% when the cetane number is increased from 46 to 54. The flash point is reduced 3℃ compared with the non-additive fuel, and combustion will occur at a lower temperature. Among the compounds of organic based metals, Mn is the best to improve the diesel fuel properties. Since Mn is not a pollutant (Angove D.E. et al., 1996), this additive can be applied effectively (Metin G. et al., 2001).

2.4.4 Effects of an ignition-enhancing, diesel-fuel additive on diesel-spray evaporation, mixing, ignition, and combustion

The primary effect of the 2-ethyl hexyl nitrate additive is to accelerate the pre-ignition radical pool formation, thus shortening the auto-ignition period. Research has shown that improvements in the compression ignition quality of diesel fuels with ignition enhancers such as 2-ethyl hexyl nitrate can not only improve diesel engine performance but also reduce emissions (Ullman T.L. et al., 1995; Gairing M. et al., 1995; Li X. et al., 1997). In addition, a decrease in NOx emission has been shown to correlate well with ignition quality improvement, whether the ignition improvement was achieved by fuel blending or by the addition of 2-ethyl hexyl nitrate. This effect, however, is not uniform. It is strongest at the lowest gas temperature-density conditions and weakest at the highest temperature–density conditions. Finally, the effect of this ignition improver on parameters such as flame liftoff, maximum liquid-phase fuel penetration, and spray dispersion were negligible, indicating that neither the high-temperature combustion chemistry nor the mixing-controlled processes are affected by the additive (Ziman W. et al., 2015). Primary effect of the additive is to shorten the auto-ignition period. This effect, however, is not the same for all ambient gas temperatures and densities and, therefore, cannot be accurately characterized by a rating based on a single engine operating condition, such as the cetane number. The effects of the 2-ethyl hexyl nitrate are more significant at low temperature and low density conditions than the cetane number indicates. These results also suggest that the 2-ethyl hexyl nitrate enhances the radical pool formation early in the injection process, but once the radical pool is initiated, the parent fuel chemistry determines the further evolution of the ignition process.

The flame liftoff results indicate that the primary effect of the additive is through the initial auto-ignition chemistry. Once combustion is initiated, the kinetics are dominated by high temperature radical reactions, and any post ignition increases in radical concentrations due to the additive are insignificant. The results indicate that the primary effect of the additive is to increase the radical pool formation very early in the auto ignition period, leading to a shorter overall auto ignition period for a diesel spray. This effect is greatest at lower temperature and density conditions, corresponding to low load and start-up conditions in a diesel engine, and becomes negligible at the highest temperature-density conditions examined. The additive does not affect physical processes in the spray or combustion processes once the ignition phase is complete. This result is in agreement with the mixing limited nature of diesel combustion after ignition and recent research showing that fuel vaporization is also mixing limited (Siebers D.L., 1998). The results support the hypothesis that the primary effect of the additive is to initiate early formation of a radical pool by providing an efficient mechanism for OH production. Specifically, unimolecular decomposition of 2-ethyl hexyl nitrate creates NO_2, which then further reacts with available H atoms to produce OH radicals. Once ignition begins, 2-ethyl hexyl nitrate appears to have an insignificant effect on the radical pool development, since further development follows that of the parent fuel. After auto-ignition, additional radical species formed by dissociation of 2-ethyl hexyl nitrate are negligible compared with those generated by the high temperature kinetics of combustion (Higgins B. et al., 1998).

Chapter 3 Experimental setup and analyzers

This study aims to investigate the combustion characteristics and fuel oil stability of marine residual fuel blended with additives. A well-known method was adopted to analyze the combustion of the given sample. The details of the fuel sample, fuel combustion characteristics, and experimental conditions are given below.

3.1 Fuel oil samples

Table 3-1 summarizes the fuel additive types and dosages which were applied to the experiment. One of them is normal heavy fuel oil with no fuel additives. The other three samples were blended with heavy fuel oil strictly following blending ratios of maker recommendation. Samples were precisely produced at the laboratory and test shop. Samples that were produced at a laboratory were sent to a third party to analyze their combustion characteristics and stabilities. Samples blended at an engine shop were used for the engine test.

Table 3-1 Fuel additive types and dosage for the samples

	Blank	Sample A	Sample B	Sample C
Type	Heavy fuel oil	Dispersant	Dispersant Cetane number improver	Dispersant Combustion improver
Dosage	N/A	1:80,000	1:20,000	1:20,000
Major constituent	N/A	Fatty acid/Soap	Ferrocene	Nano particle of oxidized iron
Content (wt.%)	N/A	52.2	4.8	25~30

The exact specifications of the additives applied to this study cannot be revealed as they are within the scope of marketing secrets.

Blank refers to the residual fuel oil, which can be obtained on board the ship. Sample A is specified as a dispersant and its manufacturer's recommended dosage is in the ratio of 1:80,000. Samples B and C are hybrid-type fuel oil additives. The term "hybrid-type" means that a single additive can serve two or more functions to the fuel oil. In this case, the additives act as dispersant and combustion improvers. Sample B is a ferrocene-based combustion improver with a concentration of about 4.8%. Sample C is an iron based combustion improver and its composition is about 25%~30%. The base material of samples B and C may be similar (i.e. iron), but the difference between them is in their concentration and their effect on improving combustion characteristics. These combustion properties will be discussed later in the study.

Table 3-2 describes the specifications of blank fuel oil, i.e. fuel oil with no additives. The fuel oil is called 'Bunker C', a widely used term on board of the ship as energy. The blank has viscosity of 357.4 ㎟/s and density of 989.5kg/m^3. Sulfur content of the fuel oil is 3.2% by mass.

Table 3-2 Specifications of blank fuel

Parameters	Values
Kinematic viscosity at 50℃	357.4㎟/s
Density at 15℃	989.5kg/m^3
Flash point (at 100.2 kPa)	85.5℃
Water content	0.1% (V/V)
Carbon content	85.4%
Hydrogen content	10.5%
Sulfur content	3.2%
Nitrogen content	0.2%
Oxygen content	1%

3.2 Fuel dispersability analysis

The study analyzed fuel dispersibility to evaluate the stability performance of each fuel additive. Dispersants are widely used but the performance of each fuel additive is varied. Therefore, the study analyzed the dispersibility performance of each sample.

Fuel dispersibility can be analyzed through the so called TURBISCAN method. The analyzer is compliant with the ASTM D7061-12 standard and records transparency by irradiate light on the treated fuel sample. Transparency will be constant over the entire measuring cylinder if the fuel sample has good dispersibility, otherwise the deviation in transparency will increase. Standard deviation of the measured transparency is the analysis criterion. The dispersibility of the fuel is calculated according to the equation (3-1).

$$S = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_T)}{n-1}} \tag{3-1}$$

X_i: Average transparency recorded every 60s

X_T: Average of X_i, $X_T = (X_1+X_2+\cdots.+X_{16}) / 16$

n: Number of repeated measurements (16 times)

The **Fig.3-1** represents analysis concept of dispersibility. The fuel oil diluted with heptane 23 mL. Again the diluted fuel oil blended with toluene of 2 mL. The **Fig.3-2** shows optical scanning way in a dispersibility analyzer.

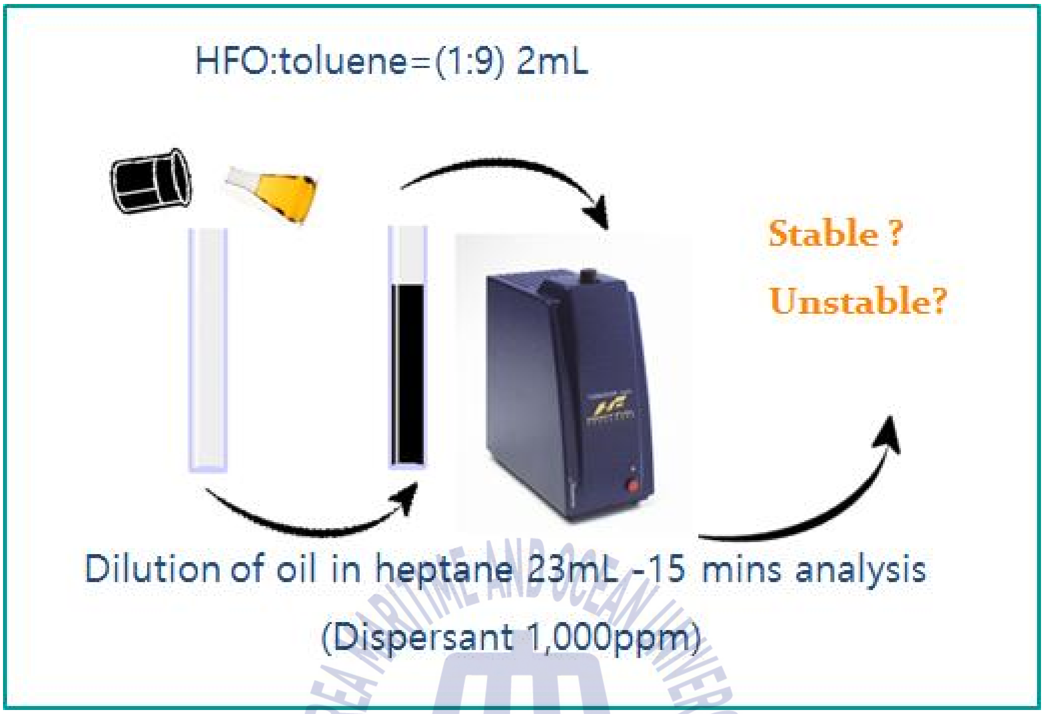


Fig.3-1 Measurement concept of heavy fuel oil dispersability

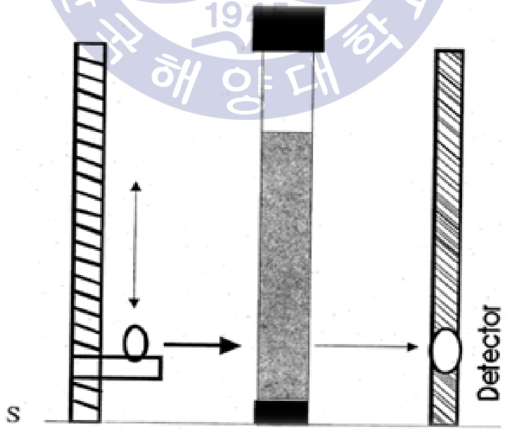


Fig.3-2 Schematic representation of a typical measurement using an optical scanning device.

3.3 Fuel Ignition/Combustion Analysis (FIA/FCA)

The combustion characteristics have been investigated through the IP541/06 standard that specifies a procedure for the quantitative determination of ignition and combustion characteristics of residual fuels used in compression ignition engines. The standard is applicable to residual fuels of petroleum origin with viscosity up to 2000 ㎟/s at 50℃. However, precision has only been determined for residual fuels with viscosity in the range 25~800 ㎟/s at 50℃ (IP 541/06, 2009).

For the analysis, the organized fuel is injected into a constant-volume chamber. The chamber is initially heated to 500℃ and pressurized to 4.5 MPa for the test condition. The blended fuel sample is injected into a constant volume combustion chamber (CVCC), which has been set to 500℃ temperature and 4.5 MPa pressure, before commencing analysis. The change in pressure during ignition and combustion is recorded within a differentiated time frame, and the data is transferred to a data acquisition system for additional calculation and reporting. The data in the present study is the average value calculated after 25 iterations of this process, and the FIA-100/FCA apparatus in this study was taken from FUELTECH (www.fueltechsolutions.com). The schematic diagram of the FIA-100/FCA is given on **Fig.3-3** and actual photo of analyzer is given on **Fig.3-4**.

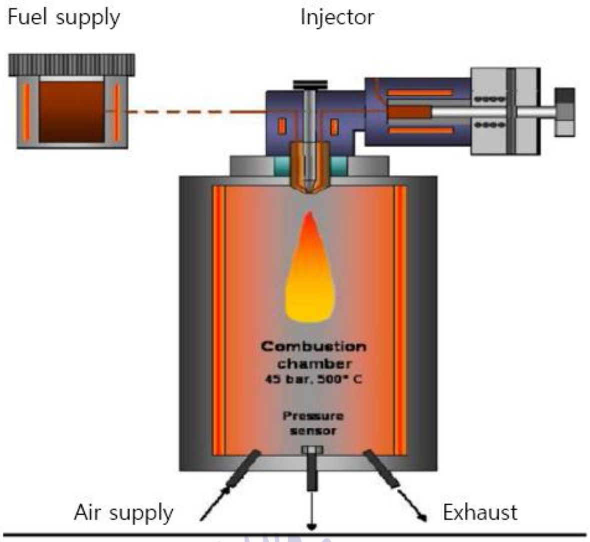


Fig.3-3 Schematic diagram of FIA-100/FCA analyzer

Fig.3-4 Actual image of FIA-100/FCA analyzer which was used in this study

Fuel combustion analysis (FCA) provides the information of pressure trace and heat release rate. **Fig.3-5** and **Fig.3-6** represent normal combustion characteristics of the standard fuel via FCA. **Fig.3-5** describes parameters available via FCA analysis. FCA data are useful to analyze combustion characteristics of different kinds of fuel and/or fuel additives.

Among the many different parameters measured in this study, the most important ones are injection delay (ID), end of combustion (EC), and after burning period (ABP).

Fig.3-6 describes the heat-release rate curve and the parameters on the curve and these parameters are defined as follows.

●PMR: Position of maximum rate of heat release; time between injection needle and maximum pressure change during a unit hour.

●AR: Accumulated ROHR; surface area of the pressure trace curve

●M. ROHR: Maximum pressure change during combustion period

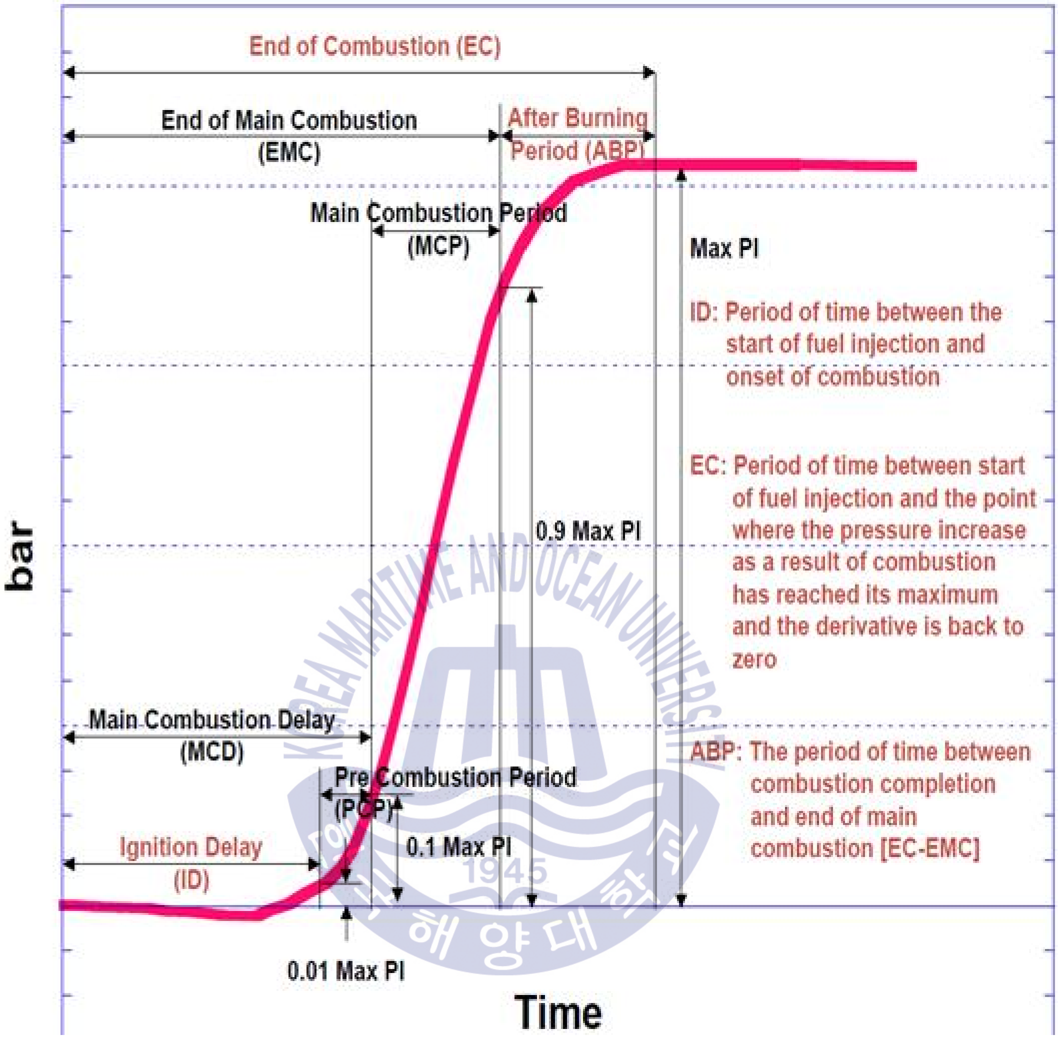


Fig.3-5 Pressure trace curve which is able to be obtained via FCA analysis

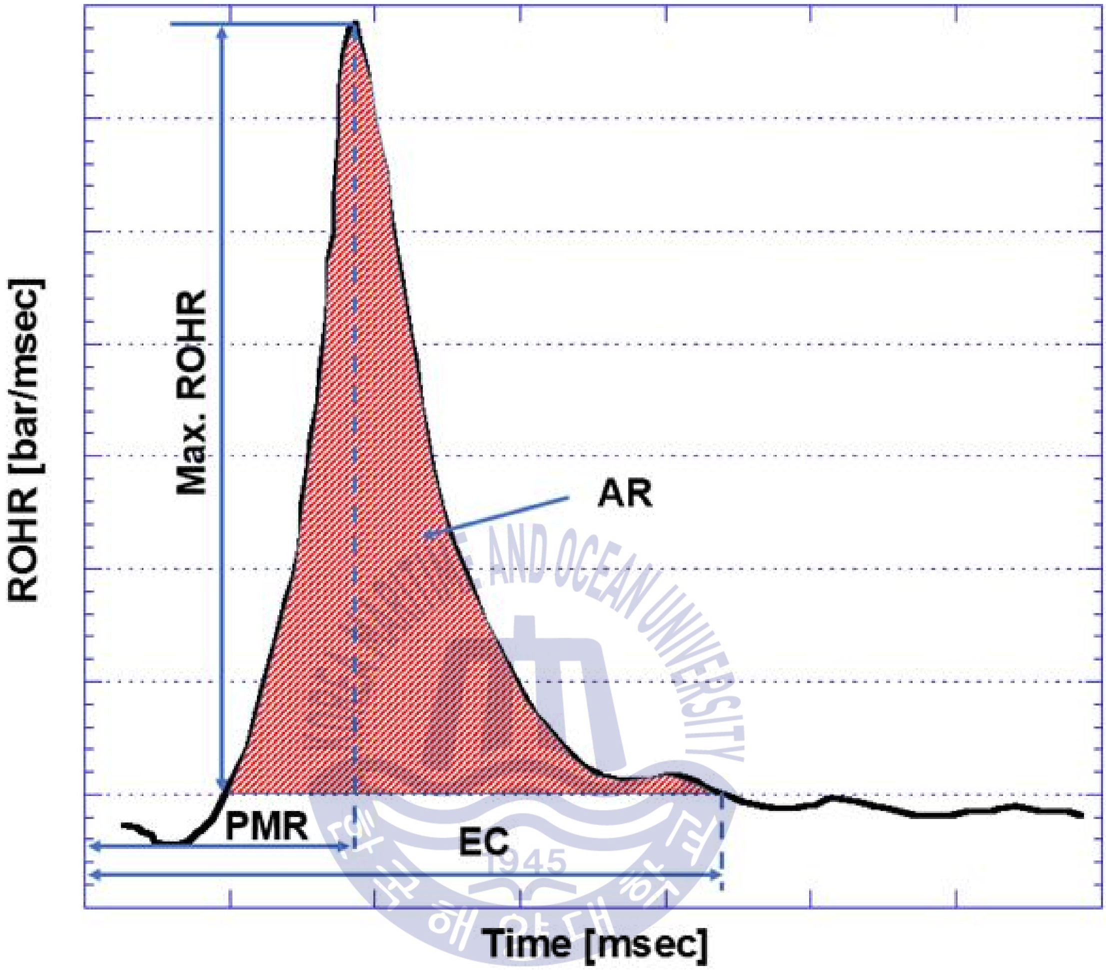


Fig.3-6 Curve of rate of heat release via FCA analysis

Detailed definition of the parameters available on FCA are given in **Table 3-3**. Injection delay, pre-combustion period, main combustion delay, main combustion period, end of main combustion, after burning period, end of combustion, and maximum pressure increase are defined on **Table 3-3**.

Table 3-3 Parameter types and definitions of pressure trace curve of FCA analysis

Parameters	Definitions
ID	Injection Delay. Period of time between the start of fuel injection and onset of combustion.
PCP	Pre Combustion Period. Difference in time between combustion delay and ignition delay (MCD-ID).
MCD	Main Combustion Delay. Period of time between the start of fuel injection and initiation of main combustion.
MCP	Main Combustion Period. Period of time between end of main combustion and main combustion delay.
EMC	End of Main Combustion. The period of time between the start of fuel injection and the point where most of the fuel has been combusted.
ABP	After Burning Period. The period of time between combustion completion and end of main combustion (EC-EMC).
EC	End of Combustion. Period of time between start of fuel injection and the point where the pressure increase as a result of combustion has reached its maximum and the derivative is back to zero.
MAX. PI	Maximum pressure increase

3.4 Thermo Gravimetric Analysis

Thermo Gravimetric Analysis (TGA) measures the change in sample weight with a variation in time and temperature. The principle of the analysis is based on fuel oil weight loss under heating, with the ratio of weight loss acting as one of the characteristics of fuel combustion. This study utilized the Q500 system manufactured by TA Instruments, with its detailed specifications given in **Table 3-4. Fig.3-7** show the image of Q500 which was the Thermo Gravimetric Analyzer to the study.

Table 3-4 Specification of thermo gravimetric analyzer

Temperature compensated Thermobalance	Included
Maximum sample weight	1g
Weighing precision	+/- 0.01%
Sensitivity	0.1㎍
Baseline dynamic drift	< 50㎍
Furnace heating	Resistance wound
Temperature range	Ambient to 1,000℃
Isothermal temp. accuracy	+/- 1℃
Controlled heating rate	0.01℃/min to 100℃/min
Furnace cooling [Forced air/N_2]	1,000℃ to 50℃ < 12 minutes
From 50 to 1,000℃ at 20℃/min using empty pans, no baseline/blank subtraction.	

Fig.3-7 Photo of Thermo Gravimetric Analyzer modelled Q500

Thermogravimetric analysis heats up the sample cells to 900℃ in an environment of air or nitrogen. The specific temperature at 10%, 50% and 90% weight loss can be measured, and the total weight loss ratio at 750℃ or 900℃ is used as the criteria for combustion characteristics in this analysis. During the process, combustion characteristics in different environments were not determined and hence, the test results with air alone are mentioned in this paper. The measuring conditions of reaction temperature and volume were placed at 900℃ and 40 ℃/min, respectively, with the rate of air purging set to 35 mL/min.

3.5 Engine and auxiliary system

3.5.1 Low engine load test setup

A trial for investigating vessel performance on board a ship was done by a study. However, field conditions are not reliable to be used as for performance comparison. Therefore, engine bed test had been carried out (Tadeusz B. et al., 2011). Arrangement of the experimental system is shown in **Fig.3-8.** Tanks of heavy fuel oil (HFO) were installed and were connected each other with a fuel-oil supply pipe; the supply pipe is equipped with a fuel oil shut-off valve for the maintenance of the experimental system. HFO supplying pump and mass flow meter were installed after installation of the heavy fuel oil tanks. Returned HFO was analyzed to calculate specific fuel oil consumption (SFOC) accurately with another fuel oil flow meter. Diesel oil (DO) tank is installed for flushing of the HFO line and for the starting of the engine. DO was supplied by individual DO pumps after closing the HFO shut-off valve. A three-way valve was installed to control the flow of different kinds of fuel oils. A fuel oil filter was installed at engine inlet, and was checked and cleaned before each sample test. MIP3000 indicator, a combustion pressure measurement system, was installed on the engine cylinder to analyze the engine performance and the combustion characteristic. Exhaust gas was analyzed with a Fourier-transform infrared (FTIR) spectrometer installed at the funnel of the engine. PM measurement system was also installed in line with the FTIR spectrometer. The engine was loaded by clutch and brake operations and the load was monitored by the MIP3000 indicator.

Fig.3-9 shows actual image of engine load test. The engine was installed on the bed and connected to a braking system to bring load to engine. The image was taken while the engine parameters are measuring during engine operation.

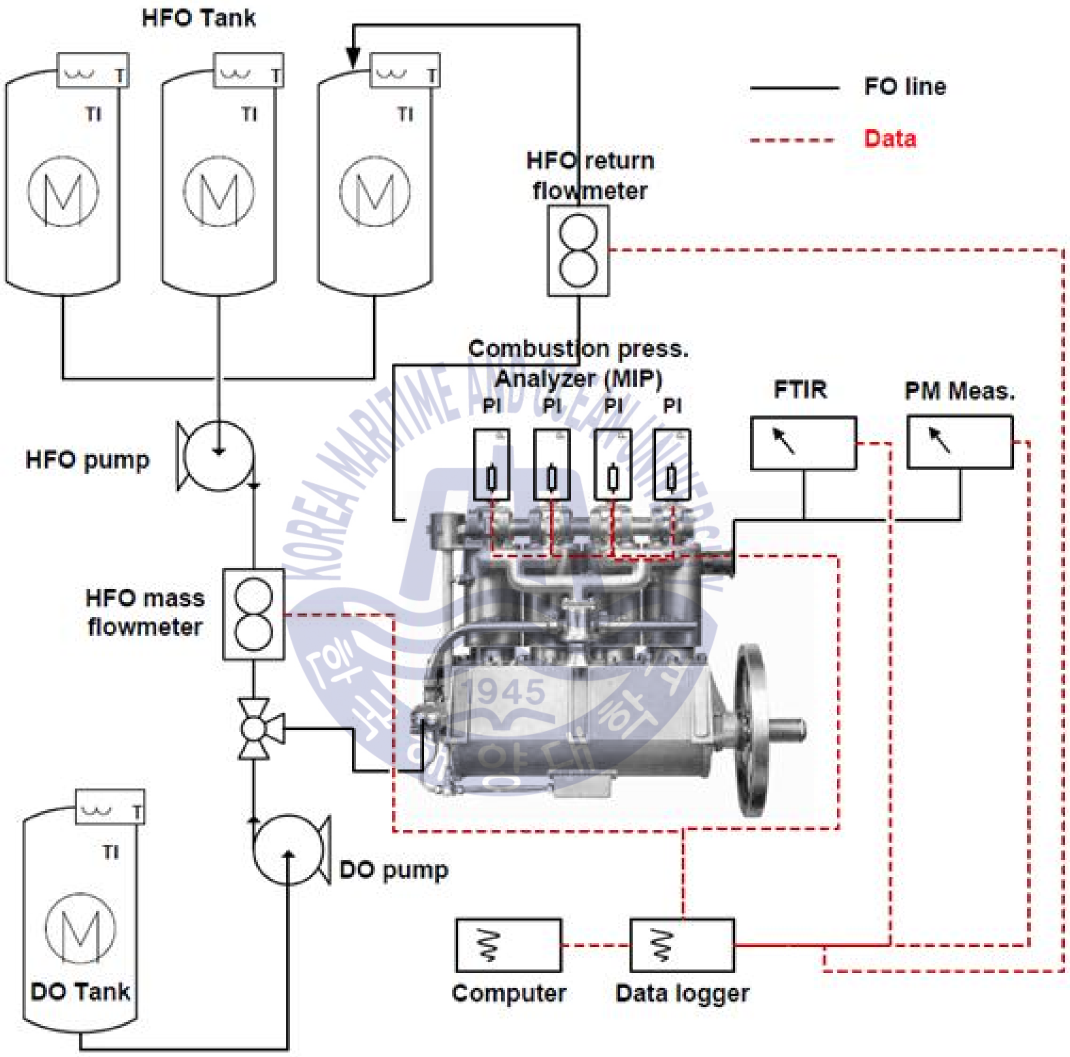


Fig.3-8 Schematic diagram of arrangements of engine test equipment

Fig.3-9 Picture of engine: Carrying out engine data measurement during engine operation

Table 3-5 shows the specifications of the engine test equipment. The test was performed with a heavy fuel oil consumable marine generator engine. The engine was manufactured by Ssangyong-Pielstick and its model number was 4PA5L (Operating manual, pp.2~4). A coriolis-type fuel mass flow meter was adopted to quantify the consumed fuel oil quantity. Detailed specification of the mass flow meter is shown in **Table 3-5** (Krohne.com) and the equipment has high level of precision and repeatability, as indicated by the table. MIP3000 indicator was employed to measure combustion pressure of each cylinder; the indicator can derive the indicated horsepower of the engine. The test adopted the indicated horsepower as a reference engine output (www.pentatech.com). PM was quantified by an analyzer following the standard announced by the Korea ministry of environment (ES01301). An FTIR spectrometer manufactured by Gasmet was adopted to measure NO_x, CO, CO_2, total hydrocarbon(THC), and O_2 (www.gasmet.com).

Table 3-5 Specifications of engine test equipment - Low load setup

Equipment	Items	Specification
Engine	Manufacturer	Ssangyong-Pielstick
	Model	4PA5L
	MCR	960 kW x 1,000 rpm
	Bore x Stroke (mm)	255 x 270
Flowmeter	Manufacturer	Krohne
	Model	Optimass 1300C
	Principle	Coriolis mass flow
	Accuracy	±0.15%
	Repeatability	0.05%
PMI	Manufacturer	Pentatech
	Model	MIP3000 Indicator
	Principle	Coriolis mass flow
	Accuracy	±1%
	Repeatability	0.05%
PM analyzer	Manufacturer	Astek
	Model	AST-MC
	Principle	Semi-Automatic
Gas analyzer	Manufacturer	Gasmet
	Model	DX4000
	Principle	FT-IR

The engine was warmed up before commencing the test for 30 minutes. Four different fuel oil samples were blended 48 hours before the test to ensure complete reaction of the fuel additive with heavy fuel oil. The fuel oil temperature was kept about 120℃ and was continuously varied within this range for the entire test. Flushing operation for 30 minutes was performed when the fuel oil changes to refresh the engine and related machineries for different fuel samples. Diesel oil pump and pipes were installed for the flushing of heavy fuel oil that can cause start failure after stopping the engine. The heavy fuel oil pipes were flushed with diesel oil before shutting off the engine.

3.5.2 Full load engine test set

After the initial engine test, test facilities were reinforced. During the test at the initial setup, dynamometer was absent. Therefore, exact engine power measurement and keeping engine load were not available.

The new facility was constructed at the other site and tests were additionally carried out. The specification of new set is given on **Table 3-6**.

Table 3-6 Specifications of engine test equipment - Full load setup

Equipment	Items	Specification
Engine	Manufacturer	STX Engine
	Model	5L23/30H
	MCR	650 kW x 720 rpm
	Bore x Stroke (mm)	225 x 300
Flowmeter	Manufacturer	Endress+Hauser
	Model	Promass 80F
	Principle	Coriolis mass flow
	Accuracy	±0.15%
	Repeatability	0.05%
PM analyzer	Manufacturer	Astek

	Model	AST-MC
	Principle	Semi-Automatic
Gas analyzer	Manufacturer	Gasmet
	Model	DX4000
	Principle	FT-IR
Engine dynamometer	Manufacturer	Go Systems
	Model	DT-3000
	Type	Water brake

Chapter 4 Results & Discussion

4.1 Dispersability

Ziman W. et al., (2016) investigated the dispersion characteristics of the nozzle tip spray-using image. Generally, this trial is regarded as very difficult study. The study found that high injection pressure leads to improved dispersion during the initial injection stage, which can lead to quicker formation of combustion air-fuel mixture. The study found that NOx increased and soot decreased with increased injection pressure. Generally, fuel atomization and fuel dispersion can be evaluated via an image of fuel injection. **Table 4-1** shows results of dispersability measured for each sample. The dispersability analysis was carried out immediately after the sample fuels were blended. Considering actual fuel oil storage environmental conditions, fuel oils might be stored for at least a week and up to several months. For this reason, a long-term dispersability analysis shall be the fundamental analysis for the evaluation of dispersability. Dispersability was analyzed on the first day and the third day. The analysis on the third day cannot be considered as the initial stage because it may also be commenced after sample fuels were agitated. However, for actual fuel oil applications, the ASTM D7061-12 of dispersability evaluated through the 3-day long-term dispersability analyses needs to be modified to reflect long-term dispersability. The study simulated long term dispersability using standard deviation based on individual dispersability analysis. The simulated result is given in **Table 4-1**.

Table 4-1 Comparison of fuel separability test results

	Blank	Sample A	Sample B	Sample C
Initial	6.2	4.7	0.1	0
3 days after	38.9	35.4	38.9	10.6

According to ASTM D7061-12, a dispersability number of 0–5 represents high dispersability and it prevents asphaltene coagulation. A dispersability number of 5–10 represents severely decreased dispersability and 10 or more represents easy coagulation of asphaltene or already coagulated state.

Therefore, samples A, B, and C can be distinguished to have good dispersabilty at the initial analysis. However, Sample A recorded a higher dispersability. In case of blank fuel oil, dispersability number was 6.2, which is over the limit of 5, and so it could be stated that the original residual fuel oil has poor dispersability.

Standard deviation was employed to simulate 3-day dispersability analysis. The ranks of dispersability number followed the order of blank fuel oil, sample A, and sample B in the descending order. In other words, sample C has high dispersability. A dispersability number of 35~39 represents easy coagulation of asphaltene, and poor dispersability of fuel oil might cause severe damage to the fuel oil system (MAN Diesel & Turbo). The analysis and simulation show that fuel dispersants are effective in the short term, but the effectiveness may vary with time. Therefore, special attention is required if the fuel is stored for a long time. According to the analysis, dispersant should be supplied considering that dispersability number may vary according to the type of fuel additive. The ASTM D7061-12, which is the standard of dispersabilty evaluation, must be modified to include considerations of long-term dispersability.

Dispersability pertains to a dispersant' s ability to suspend byproducts of combustion, such as soot, and lubricant degradation, such as resin, varnish, lacquer, and carbon deposits. The overall performance of a dispersant depends on all three of its structural features: the hydrocarbon chain, the connecting group, and the polar moiety. The molecular weight of the hydrocarbon group in a dispersant determines its ability to associate with undesirable polar species and suspend them in the bulk lubricant. For dispersants that have the same connecting group and the polar moiety, the lower the molecular weight, the higher the ability to associate with polar materials and the lower the ability to suspend them. Because of the tradeoff between the two properties, the hydrocarbon chain must have the correct size and branching.

The size affects a dispersant’s affinity toward polar materials, and branching affects its solubility, both before association and after association with the species a dispersant is designed to suspend in oil. Experience has demonstrated that hydrocarbon groups containing 70 to 200 carbon atoms and extensive branching, as in the case of polyisobutylenes, are extremely suitable to design dispersants with good dispersancy. The hydrocarbon chains of larger size, even if the branching is similar, lead to dispersants with low affinity toward polar materials.

That is why dispersant polymers possess lower dispersability than polymeric dispersants. However, since dispersant polymers have additional attributes, such as good thickening efficiency and in some cases good thermal and oxidative stability, their use is advantageous. They usually replace additives, called viscosity modifiers, in the package. Since they impart some dispersability because of their structure, the amount of polymeric dispersant in engine oil formulations is decreased somewhat.

Both the connecting group and the polar moiety are important to the dispersability of the dispersant molecule. They must be considered together since both contribute toward polarity. The polarity is a consequence of the electro negativity difference between carbon, oxygen, nitrogen, and phosphorus atoms. The greater the electro negativity difference, the stronger the polarity. This implies that groups that contain phosphorus-oxygen bonds are more polar than those containing carbon-oxygen bonds, carbon-nitrogen bonds, and carbon-phosphorus bonds.

An optimum ratio between the molecular weight of the hydrocarbon chain and that of the polar functionality (polar/nonpolar ratio) is a prerequisite for good dispersability.

4.2 Investigation of fuel dispersant mechanism

4.2.1 Basic properties

Suppressing creation of sludge on marine fuel oil and re-dispersing of created sludge are very important function of the fuel additives. These are treated by dispersant. The dispersant can also decrease viscosity to minimize fuel oil droplet (Renzhan Y. et al., 2016). At field environment, prevention of agglomeration of asphaltene and creation of sludge are very difficult task to the operators. Therefore, invention of alternative measure to prevent agglomeration, sludge creation and these measures will result in fuel oil saving and increase thermal efficiency. The dispersion force means the index of well dispersed particles including asphaltene and sludge which are constituents of heavy fuel oil. The dispersion stability can be translated into resistance to flocculation. The dispersant mechanism is consisting of 3 basic properties. The first one is wetting. The wetting is referred to a compound added to a liquid in small quantities in order to enhance the spreading of the liquid on a surface or the penetration of the liquid into the solid particles in the liquid or/and the solid substrate that gets in contact with the liquid. Thus an effective wetting agent should be a surfactant that has affinity groups to solid particles and able to replace air and moisture that traps in the solid particles in order to spread and penetrate to the surface of the solid particles.

The second character is dispersing. Dispersing is an act to move and separate an agglomerate particle to smaller particles. The ideal stage is to disperse the agglomerate particles to it primary particles size. However, for some oils, it is impossible to do so. Most of the time this action will mostly depends on the mechanical forces, which are applied to it such as stirring, grinding etc. A dispersing agent will only help to accelerate this process so that the time needed is shorter.

The last character is stabilization. Stabilization is the most complex process and a good wetting and dispersing agent should have these properties. Poor stabilization will lead to many defects that will be discussed later. Stabilization of solid particles in coating is defined as the ability to keep all solid particles separated in a certain distance and stop agglomerates, aggregates and flocculates after long period of storage. Solid particles in liquid will move around and collide with each other according to Brownian motion. If these particles are not well stabilized, due to the attraction forces between the particles, these forces will re-agglomerate and flocculation them together and this is not desired by all formulators. **Fig. 4-1** shows above three characteristics in order (Patrik L., 2009).

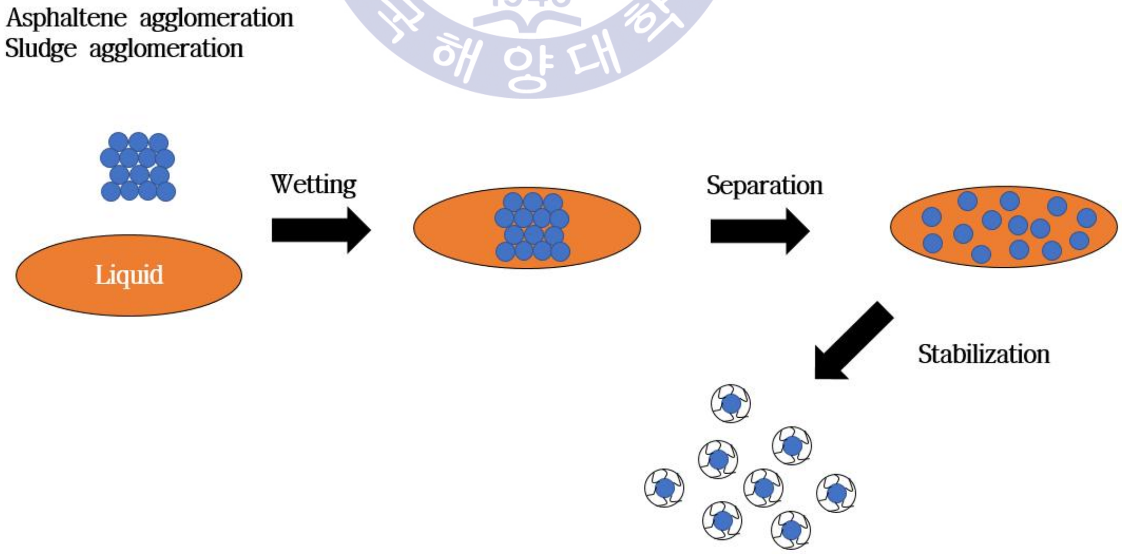


Fig.4-1 Dispersion process of asphaltene sludges contained in crude oil

Generally residual fuel oil has like to be aggregated. Thus, fuel molecules do collide with each other every second or even in shorter time. If there are forces enough to separate them after they collide, then this system is stable. However, due to the fact, that the size of fuel molecule are small, the attraction forces between these small particles are very strong and most of the time needs external forces to separate them, where re-grinding or applying substantial shear force is needed. Thus, the best way to prevent flocculation of fuel molecule is to prevent them come very close or near to each other. **Fig.4-2** shows the surface characteristic of solid particles such as fuel molecule, pigment, extender etc against flocculation tendency (www.afcona.com.my/DispersingTechnology.pdf). The smaller the particles, the stronger their flocculation tendency. Also, if a particle charges are too high, the stronger their flocculation tendency.

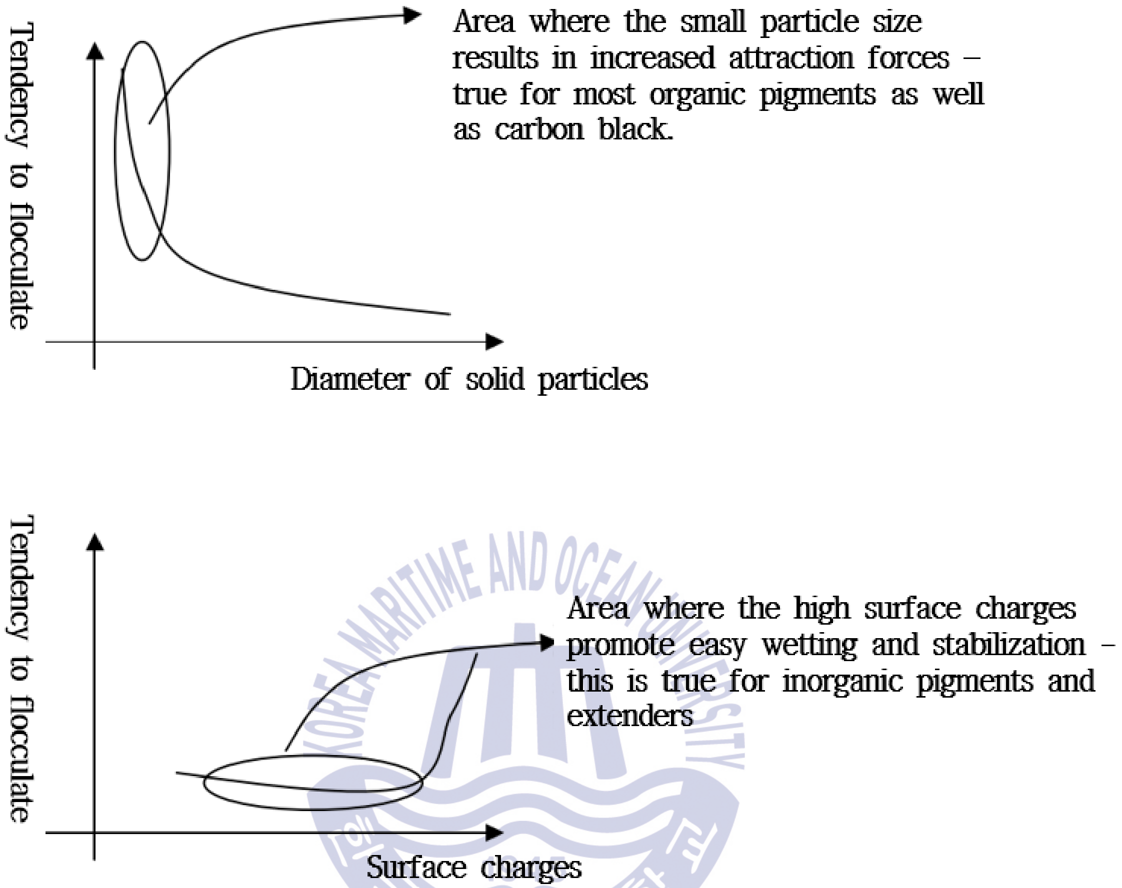


Fig.4-2 Surface characteristics of flocculation tendency

There are few types of flocculation. Agglomeration is referred to as where the fuel molecules are strongly attracted to each other and if we do fineness check of the system, it will show more coarse fineness. This is serious flocculation and needs re-grinding in order to separate the fuel molecules again.

As shown in **Fig.4-3**, the best separation distance between two particles is at best at the critical distance or even better at where combination of both forces is at zero (www.afcona.com.my/DispersingTechnology.pdf). In most cases, the D_{cd} distance is best at 200Å. However, for some small size organic molecules, this distance is greater than 200Å. Therefore, a higher molecular weight dispersant is needed in order to obtain the best.

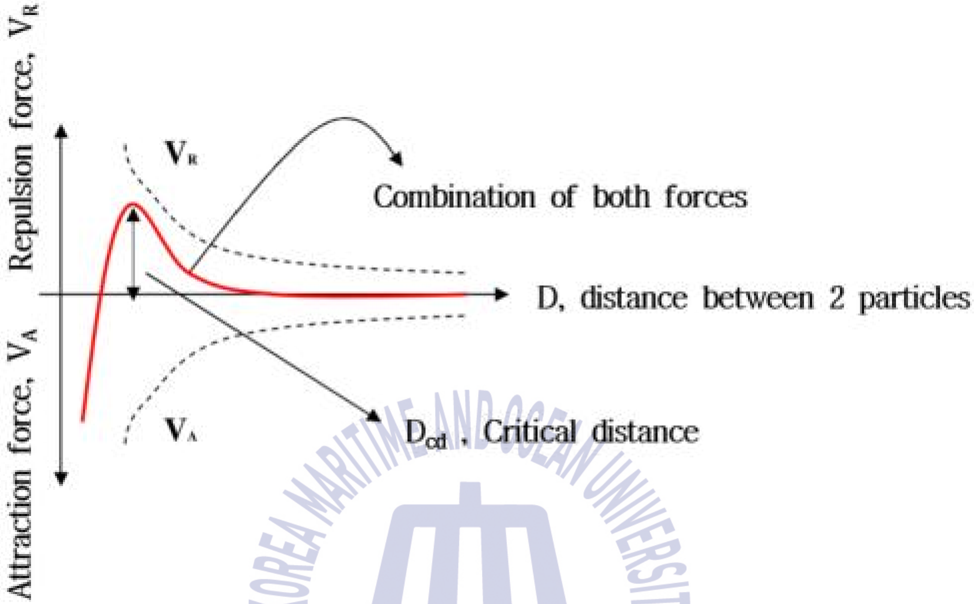


Fig.4-3 Combination of repulsion and attraction forces

Metallic fuel additives can only be effective if dissolved at the molecular level in the fuel or, at a minimum, dispersed at sub-micrometer size levels. The dispersant can be effective by reducing interfacial tension between particle surface and fuel oil droplet and it will result in effective wetting. The dispersant generally contains hydrophilic group which has polarity and hydrophobic group which has non-polarity at the same time in a molecule and it will be moved to between particle surface and boundary of fuel oil. **Fig.4-4** shows general structure and reaction of dispersant (www.afcona.com.my/DispersingTechnology.pdf).

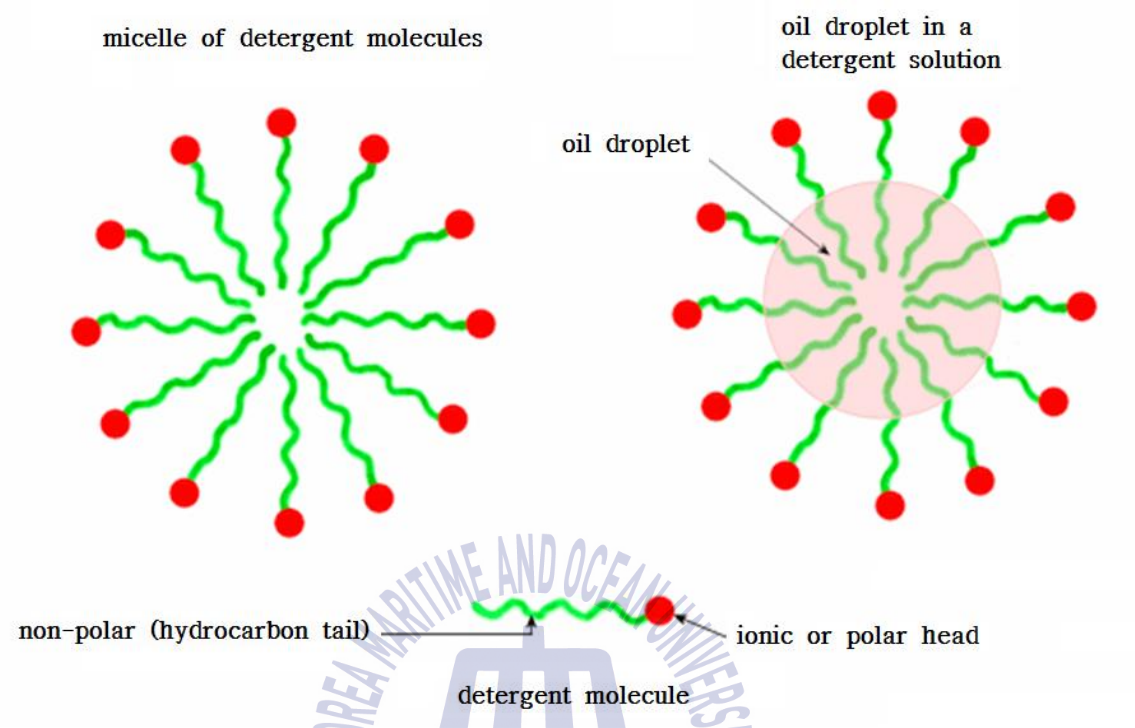


Fig.4-4 General structure of dispersing agents

The dispersant can be distinguished by referring polar structure and it is ionitropic and non-ionotropic. The non-ionotropic group is consisted with hydrocarbon chain. Therefore, it could be said that the dispersant is adsorbed onto particle surface and the reaction is resulted in stabilization due to static repulsive force or steric hindrance which will make constant distance among particles. Particles in liquid fuel contains charge and the dispersant can control intensity and it also is able to make all the particles contain charge. The charge can cooperate with ions and it can make bilayer. More thick bilayer can make more stabilized dispersing. **Fig.4-5** shows ionic or electronic model of dispersant (www.afcona.com.my/DispersingTechnology.pdf).

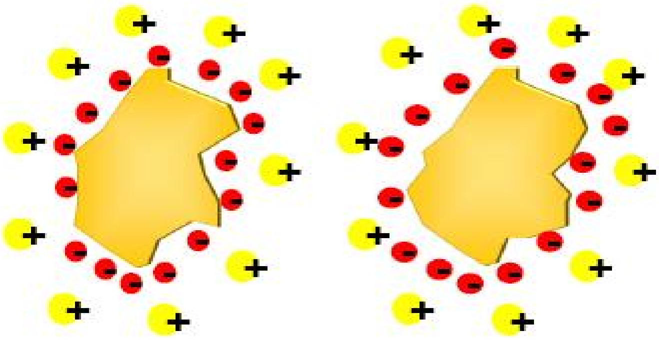


Fig.4-5 Electronic repulsion model of dispersing agent

Steric hindrance assists particles and familiar functional group to make strong adsorption on particle surface and prevent agglomeration among particles. Chain parts on dispersant adsorb on particle surface and make chains to be lengthened in residual fuel. Consequently, the dispersant isolate each particle and make residual fuel stabilize. **Fig.4-6** shows steric hindrance model in the dispersant (Schofield J.D., 2002).

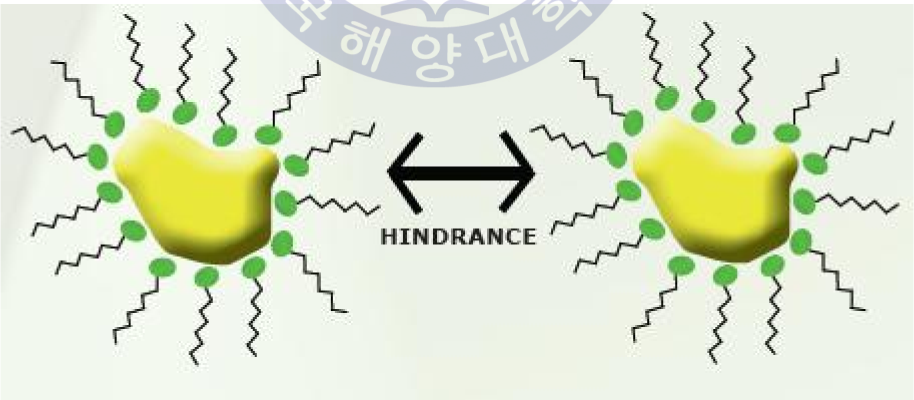


Fig.4-6 Steric hindrance model of dispersing agent

The dispersant of low molecular weight which is relatively small polymers stabilizes dispersion by adsorbing onto particle surface and it is resulted in prevention of agglomeration. One or many adsorbed point on particles which has polarity and chain which has non-polarity are majority of interfacial substance. **Fig.4-7** shows surface reaction of low molecular weight dispersant.

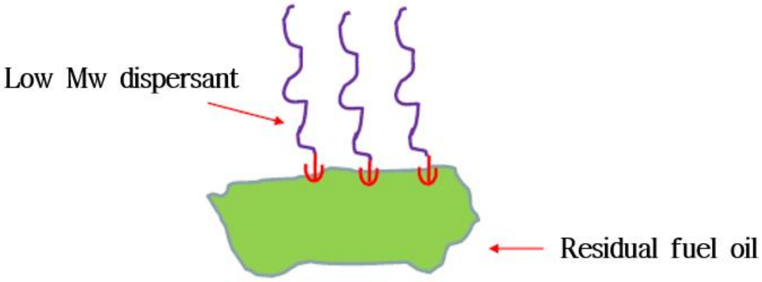


Fig.4-7 Fuel surface adsorption of dispersing agent with low molecular weight (Mw)

Low molecular weight dispersant can not be effectively react to steric hinderance with the range of 800~2,000 g/mol but, it is able to create synergy when cooperate with high molecular weight dispersant. High molecular weight dispersant has many adsorbability group in a chain. The chains can be adsorbed onto particle surface and it will result in dispersant stabilization by steric hindrance using chain of fuel oil. **Fig.4-8** shows surface adsorption characteristics on high molecular weight.

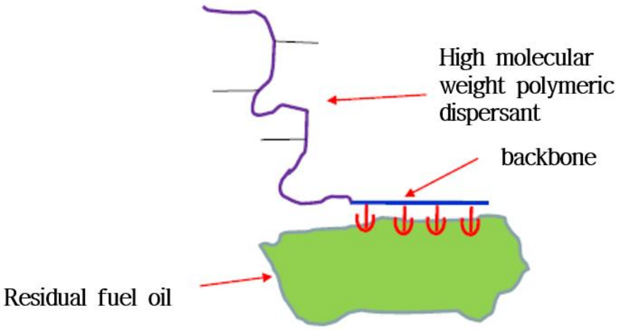


Fig.4-8 Fuel oil surface adsorption of dispersing agent with high Mw

4.2.2 Dispersants

Dispersants are metal-free, but detergents contain metals, such as magnesium, calcium and sometimes barium. This means that on combustion detergents will lead to ash formation and dispersants will not.

Dispersants have little or no acid-neutralizing ability, but detergents do. This is because dispersants have either no basicity, as is the case in ester dispersants, or low basicity, as is the case in imide/amide dispersants. The basicity of the imide/amide dispersants is due to the presence of the functionality. Amines are weak bases and therefore possess minimal acid-neutralizing ability. Conversely, detergents, especially basic detergents, contain reserve metal bases as metal hydroxides and metal carbonates. These are strong bases, with the ability to neutralize combustion and oxidation-derived inorganic acids, such as sulfuric acid and nitric acid, and oxidation-derived organic acids.

Dispersants are much higher in molecular weight, approximately 4~15 times higher, than the organic portion (soap) of the detergent. Because of this, dispersants are more effective in fulfilling the suspending and cleaning functions than detergents. Dispersants and oxidation inhibitors make up the general class of additives called stabilizers and deposit control agents. The goal of oxidation inhibitors is to minimize the formation of deposit precursors, such as hydroperoxides and radicals. This is because these species are reactive and they attack the hydrocarbon base oil and additives, which make up the residual fuel oil, to form sludge, resin, varnish, and hard deposits. The goal of the dispersants and the soap portion of the detergent is to keep these entities suspended in the bulk residual fuel oil. This not only result in deposit control, but also minimizes particulate-related abrasive wear and viscosity increase. The dispersants suspend deposit precursors in oil in a variety of ways. These comprise:

- Including the undesirable polar species into micelles

- Associating with colloidal particles, thereby preventing them from agglomerating and falling out of solution.

- Suspending aggregates in the bulk lubricant, if they form.

- Modifying soot particles so as to prevent their aggregation. The aggregation will lead to oil thickening, a typical problem in heavy-duty diesel engine oils.

- Lowering the surface/interfacial energy of the polar species in order to prevent their adherence to metal surfaces.

4.2.3 Deposit control by dispersants

Fuel oxidation and degradation products, such as soot, resin, varnish, lacquer, and carbon, are of low hydrocarbon solubility, with a propensity to separate on surfaces (Norhasyimi R. et al., 2010). The separation tendency of these materials is a consequence of their particle size. Small particles are more likely to stay in oil than large particles. Therefore, resin and soot particles, which are the two essential components of all deposit-forming species, must grow in size via agglomeration prior to separation. Growth occurs either because of dipolar interactions, as is the case in resin molecules, or due to adsorbed polar impurities such as water and oxygen, as is the case in soot particles (Rebola A. et al., 2002). Alternatively, soot particles are caught in the sticky resin, which is shown in upper parts of the **Fig.4-9.** Dispersants interfere in agglomeration by associating with individual resin and soot particles. The particles with associated dispersant molecules are unable to coalesce because of either steric factors or electrostatic factors. Dispersants consist of a polar group, usually oxygen or nitrogen based, and a large nonpolar group. The polar group associates with the polar particles and the nonpolar group keeps such particles suspended in the bulk lubricant. This is shown in lower parts of the **Fig.4-9**. Neutral detergents, or soaps, operate by an analogous mechanism.

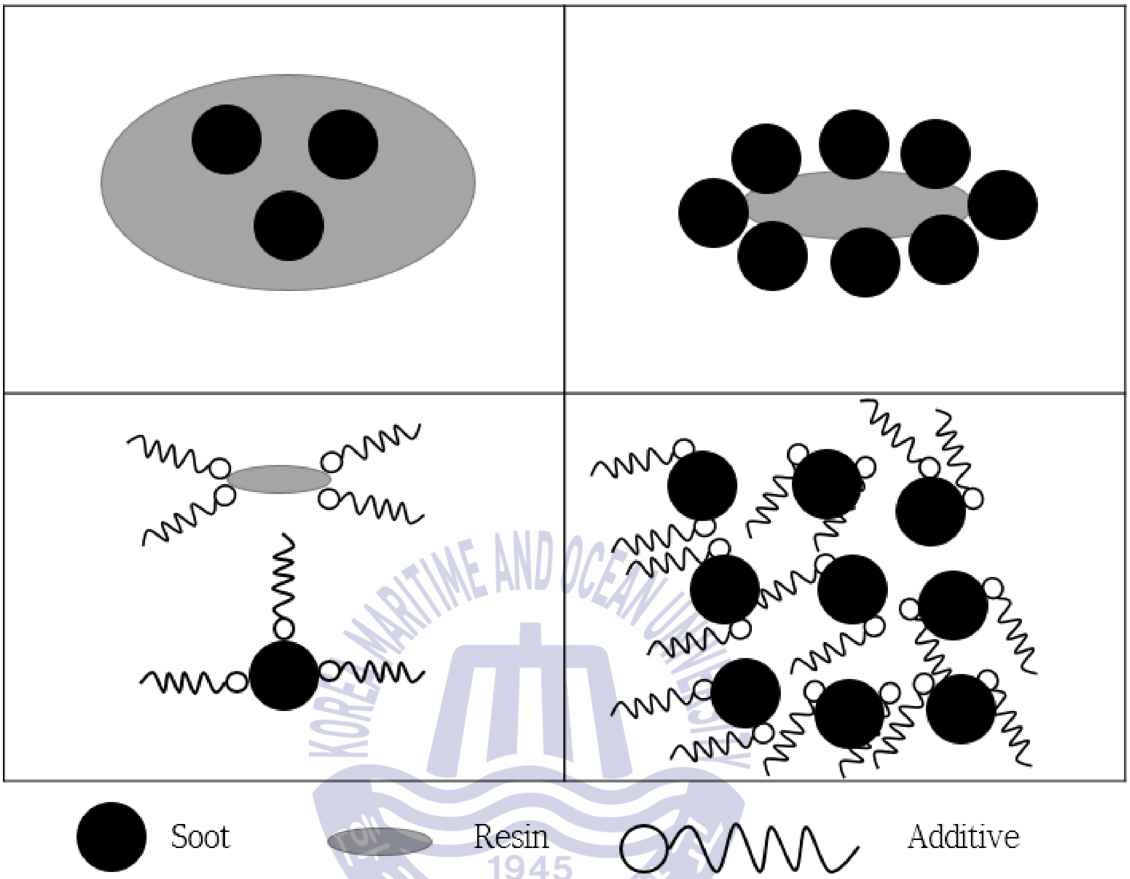


Fig.4-9 Residual fuel agglomeration and prevention by the dispersants

4.2.4 Dispersant structure

A dispersant molecule consists of three distinct structural features: a hydrocarbon group, a polar group, and a connecting group or a link as shown of see below **Fig.4-10**.

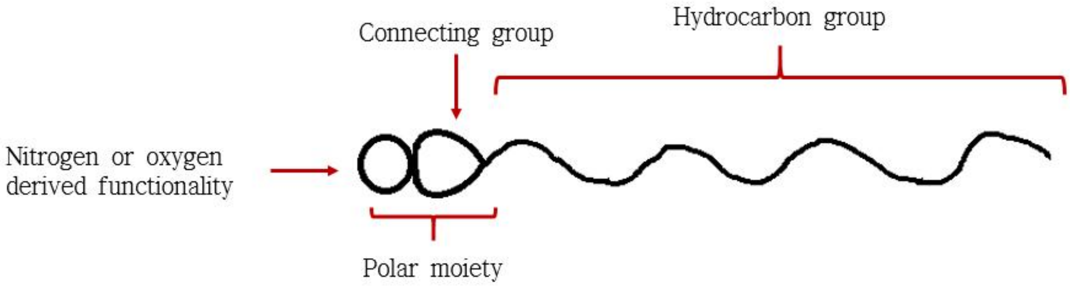


Fig.4-10 Graphic representation of a dispersant molecule

The hydrocarbon group is polymeric in nature and, depending on its molecular weight, dispersants can be classified into polymeric dispersants and dispersant polymers. Polymeric dispersants are of lower molecular weight than dispersant polymers. The molecular weight of polymeric dispersants ranges between 3,000 and 7,000 as compared to dispersant polymers, which have a molecular weight of 25,000 and higher. While a variety of olefins, such as polyisobutylene, polypropylene, polyalphaolefins, and mixtures thereof, can be used to make polymeric dispersants, the polyisobutylene derived dispersants are the most common. The number average molecular weight being typical. In addition to Mn, other polyisobutylene parameters, such as molecular-weight distribution and the length and degree of branching, are also important in determining the overall effectiveness of a dispersant.

Substances obtained via a polymerization reaction, especially those made by using an acid catalyst or a free radical initiator, often contain molecules of different sizes. Molecular-weight distribution, or polydispersity indexes the ratio of weight average molecular weight (Mw) and number average molecular weight (Mn), or Mw/Mn. These molecular weights are determined by subjecting the polymer to gel permeation chromatography (GPC). The method separates molecules based on size. The larger molecules come out first, followed by the next size. When the molecules are of the same size, Mw/Mn equals 1 and the polymer is called a monodisperse polymer. The polymers with an index greater than 1 are called polydisperse polymers. For most applications, a monodispersity is desired. Derived from acid-catalyzed polymerization reaction, polyisobutylene typically has a polydispersity index between 2 and 3. This will impact many of the dispersant properties described below.

Dispersant polymers, also called dispersant viscosity modifiers and dispersant viscosity index improves are derived from hydrocarbon polymers of molecular weights between 25,000 and 500,000.

The polar group is usually nitrogen or oxygen derived. Nitrogen based groups are derived from amines and are usually basic in character. Oxygen based groups are alcohol derived and are neutral.

4.3 Fuel oil combustion characteristics by FIA/FCA

Table 4-2 shows numerical data derived from the pressure trace curve and **Fig. 4-11** shows the results of FIA/FCA result with graph. **Table 4-2** shows also relative comparison of combustion characteristics to each additive.

Table 4-2 Results of pressure trace from FCA analysis

Parameter	Unit	Blank	Sample A	Sample B	Sample C
ID	ms	5.97	6.11	6.04	5.91
MCD	ms	7.22	7.48	7.21	7.18
PCD	ms	1.26	1.36	1.17	1.27
EMC	ms	13.37	13.67	13.46	12.91
EC	ms	20.84	21.51	21.83	19.1
MCP	ms	6.15	6.19	6.25	5.74
ABP	ms	7.46	7.84	8.37	6.19

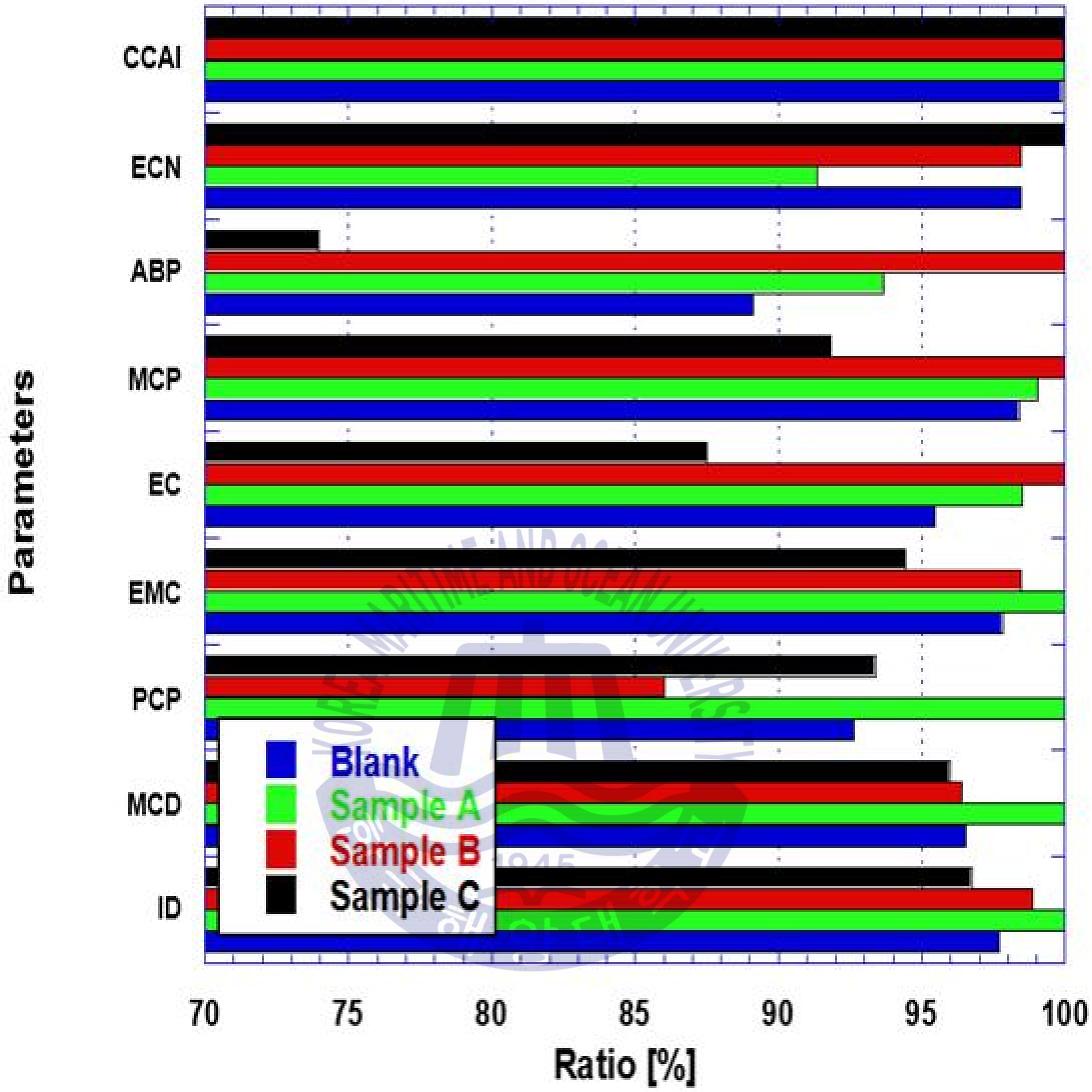


Fig.4-11 Comparison of pressure trace analysis parameters obtained via FIA/FCA

Different combustion characteristics were found from the FCA. The correlation between combustion characteristics and real engine performance has not yet been verified according to IP541/06. Therefore, the data analyzed in this study involves fuel oil combustion and ignition characteristics only considering the constant volume combustion chamber.

Sample B shows a superior pre-combustion delay, while sample C shows superiority in the parameters of ignition delay, main combustion delay, end of main combustion, end of combustion, main combustion period, and after burning period. Based on the IP541/06 analysis, sample C shows superior characteristics for improving combustion.

Monique V. et al. (2007) studied the combustion characteristics using simple analyzers. It was reported that ignition delay (ID), end of combustion (EC) and after burning period (ABP) are the major criteria of combustion characteristics. EC-ID refers to the duration for which the complete flame lasts when the fuel burns. Therefore, this period can be regarded as an important criteria for combustion properties. The difference in time between the end of main combustion and the end of combustion is specified as ABP. The period is related to the creation of carbon deposit, soot and PM after burning. While that study is acknowledged to be correct, the change in energy magnitude according to the time frame is an important parameter, which can also be regarded as a fuel combustion characteristic. It also means that only the combustion characteristics verified by FIA/FCA can be generated under CVCC conditions. Internal heat flow and environmental conditions inside an actual engine are noticeably different from CVCC and quite complex conditions. Hence, the data given by FCA/FIA analysis shall only be limited to understanding simple combustion in steady state.

ID is 5.97 ms for the blank and 6.11/6.04/5.91 for samples A/B/C respectively. ID for samples A and B has been extended compared to the blank. Sample C recorded a shortened ID compared to blank.

CCAI (calculated carbon aromaticity index), which is derived from the density and viscosity of fuel oil, has widely been used since the 1970s as a fuel combustion quality index of heavy fuel oil. CCAI was also adopted by the ISO as the quality criteria of heavy fuel oil. Although fuel oils have similar CCAIs, their combustion characteristics differ significantly in some cases. This study assumes that these differences occur because of the limitation of CCAI, and therefore, fuel quality indices with ECN (estimated cetane number) are alternatively increasing. ECN can be derived from the equation using main combustion delay.

$$ECN = 153.15e^{-0.2861 \cdot \ MCD} \tag{4-1}$$

where ECN: Estimated Cetane Number

MCD: Main Combustion Delay

$$CCAI = \rho_{15} - 81 - 141 \cdot \ \log_{10}[\log_{10}(\theta + 0.85)] - 483 \cdot \ \log_{10}\left(\frac{T+273}{323}\right) \tag{4-2}$$

where ρ_{15}: Fuel density at 15℃ (kg/m^3)

υ : Fuel viscosity (cSt)

T: Fuel temperature (℃)

This study compares ECN and CCAI, which are calculated with data from the FCA analysis presented in **Table 4-3**. Sample C shows the highest ECN and CCAI values, which are compatible with other ignition and combustion parameters described in **Table 4-4**. ECN is a function related to MCD, and ECN of blank fuel oil and sample B were identical. For this reason, both sample B and blank fuel showed similar ECN values. Sample B had a lower CCAI value than sample A. Result of CCAI for this study is 851.08, 851.91, 851.78, 852.14 respectively in the order of Blank, sample A, sample B and sample C. Although the CCAI is widely used, the deviated order cannot be easily compared with each sample, and the FIA/FCA analysis gives more coherent information to evaluate fuel ignition quality for the purpose of this study. According to the FCA analysis, sample B exhibited more superior combustion characteristics than sample A.

The ignition characteristics of a compression ignition engine are indicated by its cetane number. The FIA/FCA analysis can expressed via a similar index known as the Estimated Cetane Number [ECN] (CIMAC, 2011). Hence, the present study compare ignition characteristics by using both ID and ECN. The value of ECN is 19.4/18/19.4/19.74 as per the order on the **Fig. 4-11**. Sample C recorded the shortest ID followed by blank. Both samples recorded highest ECN.

Table 4-3 Results of ECN and CCAI calculation for each fuel sample

	Blank	Sample A	Sample B	Sample C
ECN	19.4	18	19.4	19.7
CCAI	851.08	851.91	851.78	852.14

Fig.4-12 and **Table 4-4** show the rate of heat release for the fuel samples. **Fig. 4-12** shows the result of analysis of the ROHR. The maximum heat release rate, position of maximum heat release rate, and accumulated heat release rate are presented in **Table 4-4**.

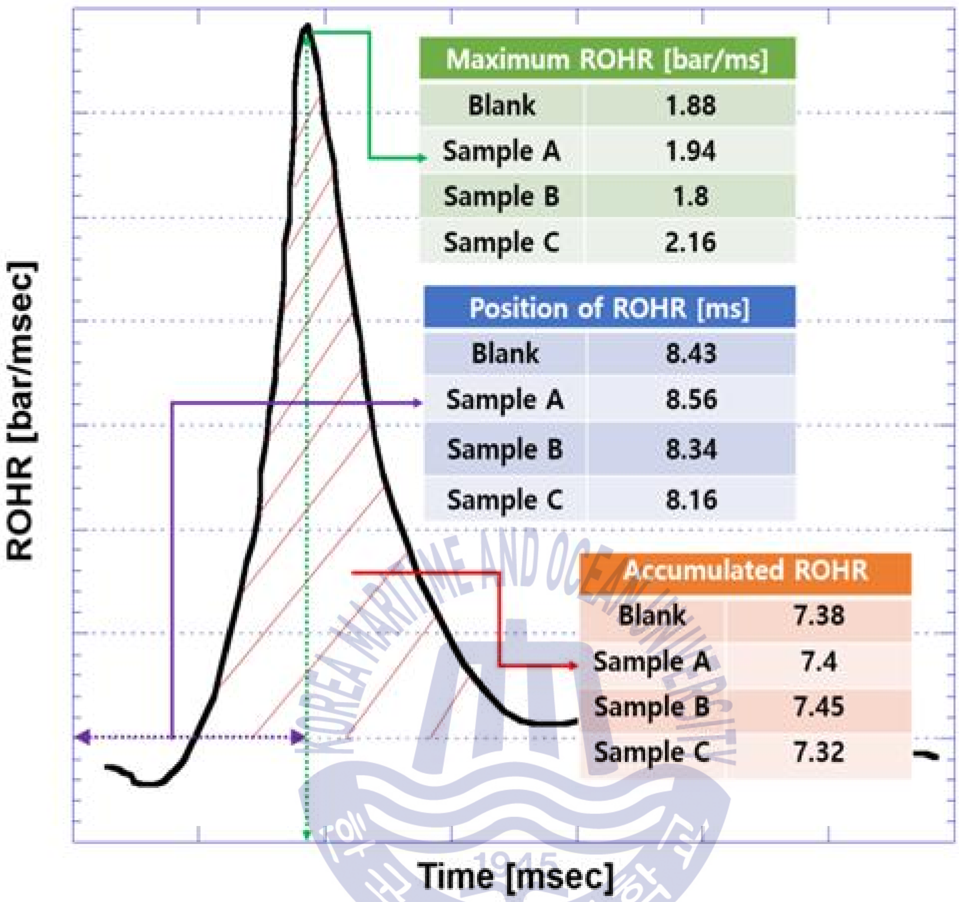


Fig.4-12 Analysis result of the rate of heat release

Table 4-4 Numerical data of rate of heat release

Parameter	Unit	Blank	Sample A	Sample B	Sample C
M.ROHR	bar/ms	1.88	1.94	1.8	2.16
P.ROHR	ms	8.43	8.56	8.34	8.16
AR		7.38	7.4	7.45	7.32

The maximum heat release rate was 0.216 MPa/ms in sample C and the position of maximum heat release rate was 8.16ms which is the fastest position among samples. The maximum heat release for sample A was the second highest value. However, the position of maximum heat release for sample A was delayed later than blank fuel oil. These cases explain that combustion occurred most vigorously in sample C with high combustion efficiency.

From the results of the analysis presented in **Table 4-2**, some fuel additives affect combustion characteristics in such a manner where these characteristics are not accounted by the ECN and CCAI. Sample C was the most effective at improving ignition and combustion characteristics of the fuel oil. Sample B also improved the performance up to some extent compared with blank fuel oil; however, sample C was more superior then sample B. The reliability of CCAI and/or ECN regarding fuel combustion and ignition is under extensive discussion.

The improvement in combustion characteristics has been explained in other studies as the effect of increased radical pool due to the fuel additive at the initial stage of auto ignition (Higgins B. et al., 1998).

Based on data derived from the FCA analysis, the study can conclude that ECN is more reliable than CCAI. However, this conclusion is based only on available laboratory tests. The effect of increased ECN on actual engine performance has not been verified.

Combustion characteristics were evaluated by calculating the value of (EC-ID). This value refers to the entire flame propagating period of the analysis and the result is 14.87/15.4/15.79/13.19. Hence, as far as only time frame is concerned, Sample C finalize the combustion at the earliest, implying that combustion happens the fastest in Sample C. But the time frame alone cannot be a criteria for fuel combustion characteristics. Hence, the rate of heat release, which will be explained in the next chapter, is also considered at the same time to understand the amount of work done by combustion of fuel.

The end of main combustion (EMC) is defined as the period between fuel injection and the time taken to reach 90% of maximum combustion pressure. End of combustion is defined as period between fuel injection and time to reach maximum combustion pressure. After burning period is defined by (EC-EMC) and the analyzer manufacturer has specified that, this value may be proportional to the emission of black smoke from residual fuel oil. This implies that if the ABP is comparatively longer, the fuel oil will have a greater tendency to emit black smoke in actual combustion. The present study anticipated above relation. ABP of Sample C is the shortest as 6.19ms followed by blank and sample A. Sample B recorded the longest ABP. Hence, the tendency to emit black smoke can be given by Sample B > Sample A > Blank > Sample C. But this expectation is purely based on the test at CVCC and the result could be different if the fuel combustion take place inside a real reciprocating engine. This is because the piston is continuously in motion inside the engine, keeping the temperature high and creating various orders of vibrations. These factors will affect the emission of black smoke, possibly causing the actual result to deviated from expectations.

According to given **Fig.4-12**, M.ROHR is the highest for Sample C at 2.16 bar/ms and the values for the other samples can be given by: Sample A > Blank > Sample B. However, the position of M.ROHR displays the time at which maximum ROHR was reached, indicating that the shortest position with a value of 8.16ms is found in Sample C. The order for the remaining samples is once again given by: Sample B > Blank > Sample A. The tendency of these values implies that the M.ROHR can be varied with different fuel oils and the P.ROHR, which is the index of combustion speed, can also be varied accordingly.

According to IP 541/06, accumulated ROHR [AR] is the area under the ROHR plot and can be an indicator of energy conversion by fuel oil combustion. Based on IP 541/06, the AR of Sample B is the highest at 7.45 and the order for the remaining sample is given as Sample A > Blank > Sample C with the values being

7.4, 7.38 and 7.32 respectively. These values are related to the energy conversion of fuel oil and Sample C shows the least amount of fuel-to-energy conversion. When it comes to other parameters, Sample C shows better results than the others but in the case of AR, the tendency is different.

For this reason, the study assumes that the ROHR analysis does not consider the combustion efficiency. The analysis is focused solely on time and the amount of energy produced. The IP 541/06 standard and references only focus on the time up to P.ROHR. The actual combustion continues after P.ROHR and until EC. Hence, combustion characteristics after P.ROHR should also be considered to determine the combustion efficiency.

This study investigates a simple method to evaluate combustion characteristics during the entire combustion period center around P.ROHR. Pre-P.ROHR characteristics and Post-P.ROHR characteristics could be evaluated individually and their average value calculated. This simple consideration can be attained from **Fig.4-13**. **Table 4-5** represents the example of simplified calculation of relative combustion characteristics.

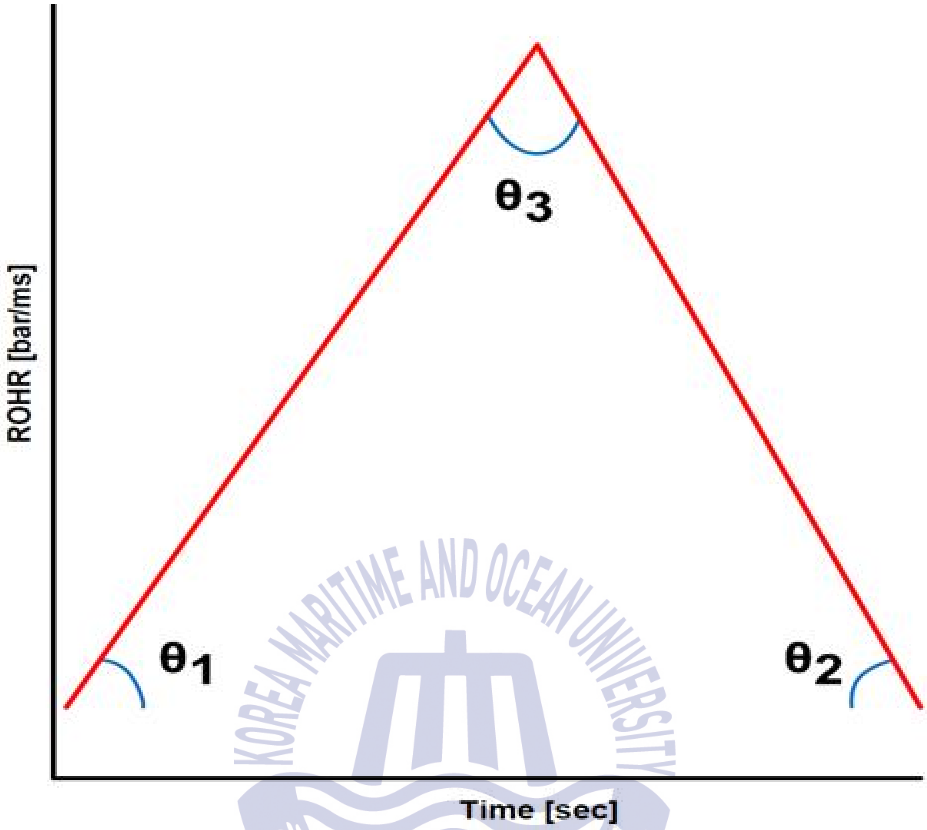


Fig.4-13 Simplified ROHR curve and suggestion of new parameters for consideration

Table 4-5 Example of simplified calculation of relative combustion characteristics

	Unit	Blank	Sample A	Sample B	Sample C
Time after P.ROHR (TPR)	ms	12.41	12.95	13.49	10.94
Angle of M.ROHR (θ_1,AMR)	°	87.43	87.47	87.35	87.84
Angle of time After ROHR (θ_2,ATR)	°	86.22	86.18	85.71	87.1
Sum of angles ($\theta_1+\theta_2$)	°	173.65	173.65	173.06	174.94
Simple indication		6.35	6.35	6.94	5.06

The simple method involves the simplification of ROHR curve. Simplify the ROHR curve as shown in **Fig.4-13**. The angle θ_1 can be obtained by using the information of P.ROHR, M.ROHR and a trigonometrical function. Time after P.ROHR[TPR] can be calculated from EC-P.ROHR, and the result displayed in **Table 4-5** as the parameter TPR. The angle θ_2 can be attained by using TPR, M.ROHR and trigonometric function repeatedly. The sum up of the value of ($\theta_1+\theta_2$) can be evaluated by its proximity to 180° . Calculating the angle θ_3 can be an alternative measure because of the simplified ROHR curved-shaped triangle.

This simple method is derived from the concept that the ROHR and the Position of ROHR shall simultaneously be considered. Therefore, it could be theorized that stronger combustion occurs at larger angles of θ_1 and θ_2 than at smaller angles of θ_1 and θ_2. In case of θ_3, a smaller angle can be indicative of more active combustion.

However, it is important to note that vigorous combustion is not always good for the internal combustion engine. This is because vigorous combustion will lead to high combustion temperature and subsequently higher emission of NOx.

The result of calculation, performed by utilizing the method described above, is that Sample C is the closest to 180 ° with only 5.06 ° remaining, blank and Sample A record a value of 6.35 ° and Sample B has recorded the lowest level at 6.94 °. Such a trend was similar to the analysis trend of (EC-ID) value obtained from the Pressure trace curve.

4.4 Thermogravimetric Analysis

Fig.4-14 displays the result of TGA analysis on the fuel oil, with mass reduction (mg) on the Y-axis. To perform this analysis, each fuel oil sample was transferred into a sampler. The mass of the injected fuel oil was differentiated for each sample due to a measurement error, but the error itself is not significant since the data can be analyzed using the mass conservation ratio. The process commenced with different masses of samples: 39.355mg of blank, 29.547mg of sample A, 17.112mg of sample B and 21.036mg of sample C.

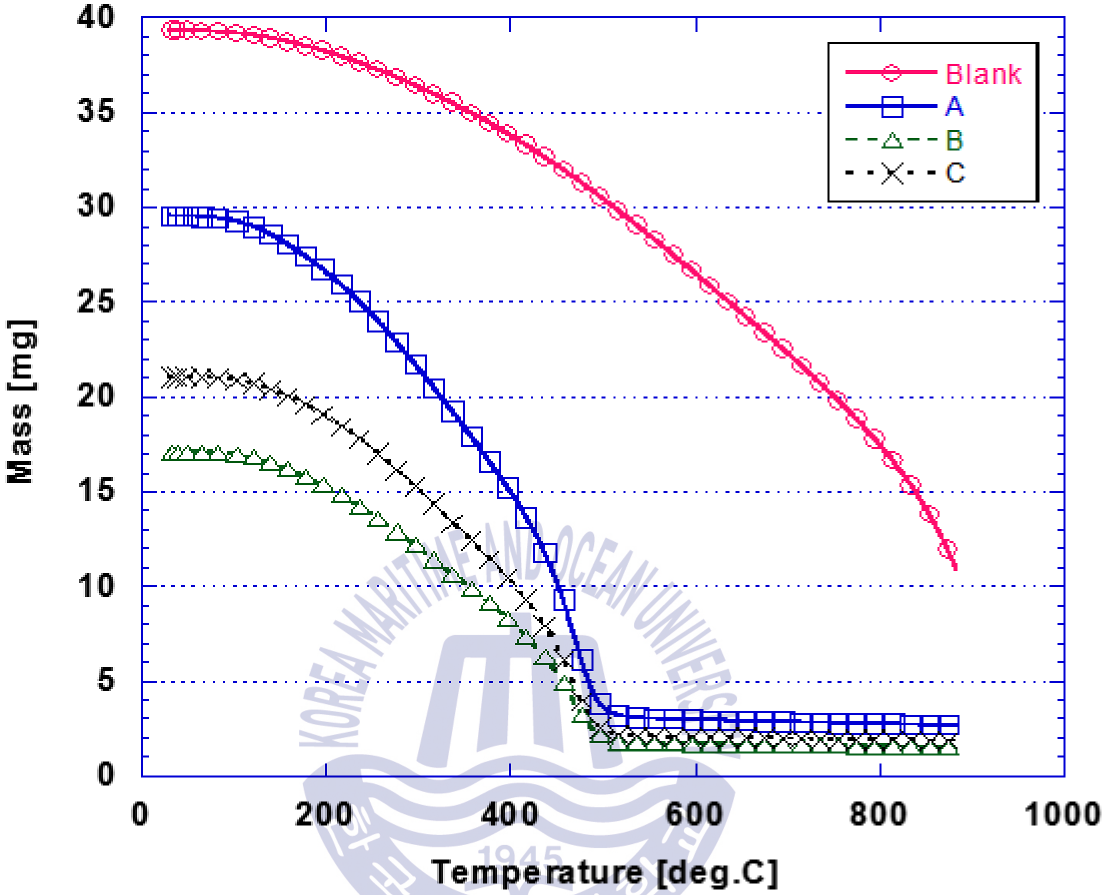


Fig.4-14 TGA analysis of fuel mass reduction with respect to temperature

Fig.4-14 indicates arch-shaped loss in mass from the beginning to up to 500℃ for samples A, B and C. A remarkable mass loss in mass cannot be seen from 500℃ to 900℃. On the other hand, Blank maintains an arch-shaped mass loss from the beginning to the end of the analysis, i.e., up to 900℃.

Fig.4-15 represents mass conservation ratio of **Fig.4-14** at the same temperature scale.

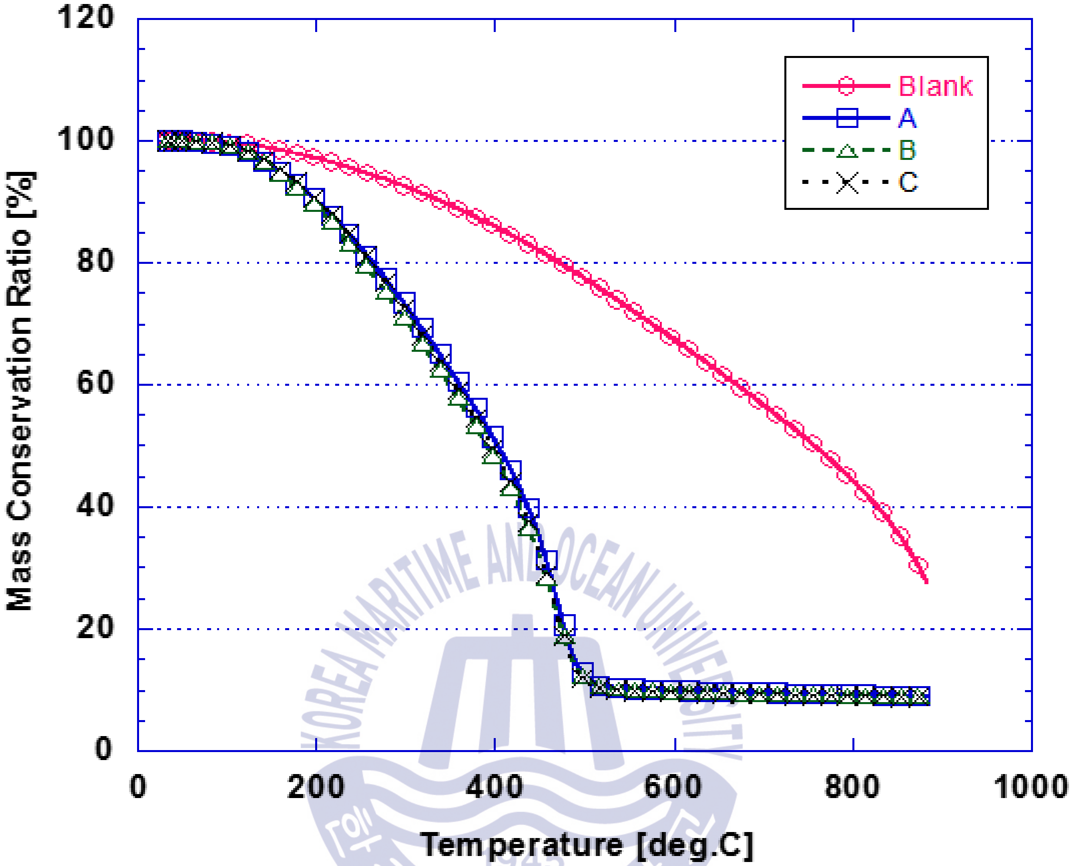


Fig.4-15 TGA analysis of fuel mass conservation ratio with respect to temperature

Similarly, as observed on **Fig.4-14**, the mass conservation ration of samples A, B, C drop to 10% up to 500℃ with an arched shape. Even after 500℃, the mass conservation ratio has not decreased noticeably. On the other hand, the mass conservation ratio of Blank steadily arched down from the initial value until the final value at 900℃. Finally, mass conservation ratio at 900℃ is about 25%.

In **Fig.4-14** and **Fig.4-15**, the effects of additive can be clearly seen. These phenomena can be explained by the fact that a common effect of the constituents of the additive is to reduce the surface tension of the fuel oil. These phenomena can be caused by the fuel additive, which acts as a dispersant and combustion improver, because the ultimate purpose of both is to enhance the availability of residual fuel. They are also specifically designed to make the fuel droplets smaller, and in order to achieve this, reduction of surface tension takes priority.

However, if the additive manufacturer only concentrates on the result of TGA, its actual effect on real engine combustion can be in questioned. Therefore, other reliable analysis method shall be referred to along with TGA for development.

If the effects of the iron-based fuel additives were to be discussed based on the result of **Fig.4-14** and **Fig.4-15**, it could be said that, regardless of the various kinds of additives, there is still a positive and clear effect on the more rapid reduction of fuel mass compared to the blank fuel oil.

Based on components, iron-based fuel additives have a greater effect on reducing thermo gravimetric characteristics. However, it is interesting to note that the concentration of iron itself was not a criteria for the additive’s performance. Although the additive does not contain iron, the dispersant alone has also shown a similarly good thermo gravimetric performance.

However, it should be noted that the study involved two kind of analyses to evaluate combustion characteristics of fuel additive, and the results were not similar from both processes. In case of FIA/FCA analysis, the pressure trace and ROHR tendency were not very clear except in Sample C. Otherwise, the distinguished result of additive effects can be found in the TGA analysis. This paper cannot currently decide which process is more reliable due to lack of references and data. Hence, the reliability of the processes need to be studied further.

The above mentioned analyses was conducted on a stable and steady laboratory-scale, and it is definitely different from heat flow and combustion conditions in a real engine. Therefore, data obtained by laboratory-scale analysis can only be used as a reference for simulation of real engine combustion. This must be followed by a test on a real engine to objectively evaluate fuel additive performance. In case of the tests on a real engine, the combustion characteristics of four stroke cycle engine and a two stroke cycle engine will provide different results.

4.5 Fuel oil consumption

4.5.1 Fuel oil consumption at low engine load

Fuel consumption rate was measured in this study. The engine was equipped with a physical braking system on the shaft and the brake force applies load on the engine. Brake power was determined by measuring the indicated pressure using MIP3000 Indicator. The study calculated specific fuel oil consumption (SFOC) for each fuel oil sample.

Fig.4-16 represents distinguished SFOCs of each fuel sample for engine speed (rpm) at low load engine operation after performing the engine test with different fuel samples.

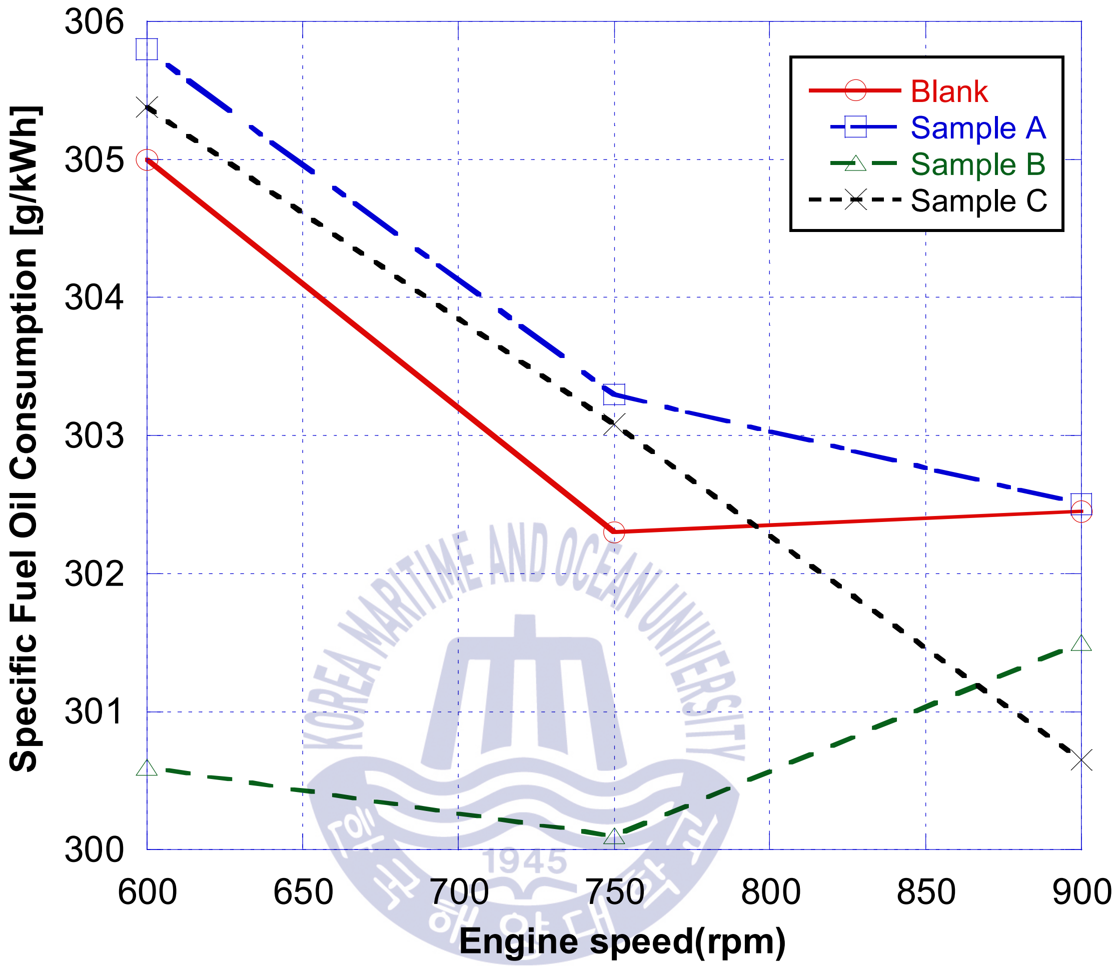


Fig.4-16 Comparison of specific fuel oil consumption at low engine load with different fuel oil additives

Sample A consumed the highest fuel oil, surpassing that of blank fuel oil. Sample C showed a contrasting tendency. Samples C and A had a break point on 750rpm, above which more or less fuel was consumed. In case of sample C, the SFOC curve directly goes down as engine rpm increases. Sample C consumed a high quantity of fuel oil followed by Sample A at 600rpm and 750rpm. At 900rpm, Sample C recorded the lowest fuel oil consumption. Sample B recorded the lowest fuel oil consumption at every engine rpm except at 900rpm.

The reason behind this large difference is that the engine test was performed at low load and engine operation of 30 minutes was not fully stabilized. Therefore, the analysis cannot insist that Sample B is quantitively verified but the test verified that fuel additive of Sample B and Sample C has somewhat positive effects on fuel consumption compared to Sample A.

4.5.2 Fuel oil consumption at full engine load

Fig.4-17 shows the SFOC result of full load engine test data. Reference fuel oil is non-additive fuel oil and it recorded the highest fuel consumption. Sample C recorded highest SFOC among fuel additives at every engine load. Samples B and A recorded the lowest SFOC but sample B recorded more higher SFOC at 25% engine load. 3.87%~16.09% SFOC saving recorded every fuel additive comparing with non-fuel additive case.

The SFOC data were verified via exhaust gas amount and some other emission constituents such as CO, water and SO_2. **Fig.4-18** shows calculated exhaust gas amount. The exhaust gas amount calculation is based on the engine maker' s calculation recommendation. As the figure demonstrating, exhaust gas amount for blank is more higher than other samples and the increased ratio was 6~14%. The increased exhaust gas amount range was generally proportional to the ratio of increased SFOC with blank.

CO and HC are well known indication of incomplete combustion and lubrication oil combustion. The CO concentrations had been measured however, HC had not been measured. Therefore, the study evaluates engine combustion status by the concentration of CO. **Fig.4-19** shows concentration of CO. At every engine load, blank fuel emitted higher concentration of CO than other fuel additives. It means combustion characteristics had been improved by applying fuel additives. Deviation of CO emission was high at low load and the deviation had been reduced as engine load increased.

Fig.4-20 represents water concentration in the exhaust. Water can be created during combustion processes. **Fig.4-20** shows that water can be increased at higher engine load and it shall also be stressed that the blank created higher water than other additives. If the engine operates under stoichiometric the water concentration can be regarded as combustion efficiency but, the test engine is turbocharged diesel engine which means the engine is operating normally under excessive oxygen condition and it will lead to water creation. Water in the exhaust can assist the creation of PM. The PM initially created with fine particle of soot during nuclei mode and it grows up by adsorption of hydrocarbon, water, sulfur, ash and metals in the exhaust.

Based on the possibilities of PM creation, the study investigated SO_2 concentration. **Fig.4-21** shows SO_2 concentration at every engine load with various fuels. Blank shows the highest SO_2 emission at entire engine loads and sample C, B and A are order for remainders.

The study could not measure HC and PM concentration therefore, exact evaluation for the combustion status was not available but, the combustion condition was able to be estimated by using concentration of CO, SO_2 and water. According to the investigations on the previous chapters, blank sample consumed much higher fuel oil and it could be emitted as increased portion of PM at the exhaust with the assistance of SO_2, water and unburnt hydrocarbon. It is well corresponding with other studies that the fuel additives can reduce PM emissions.

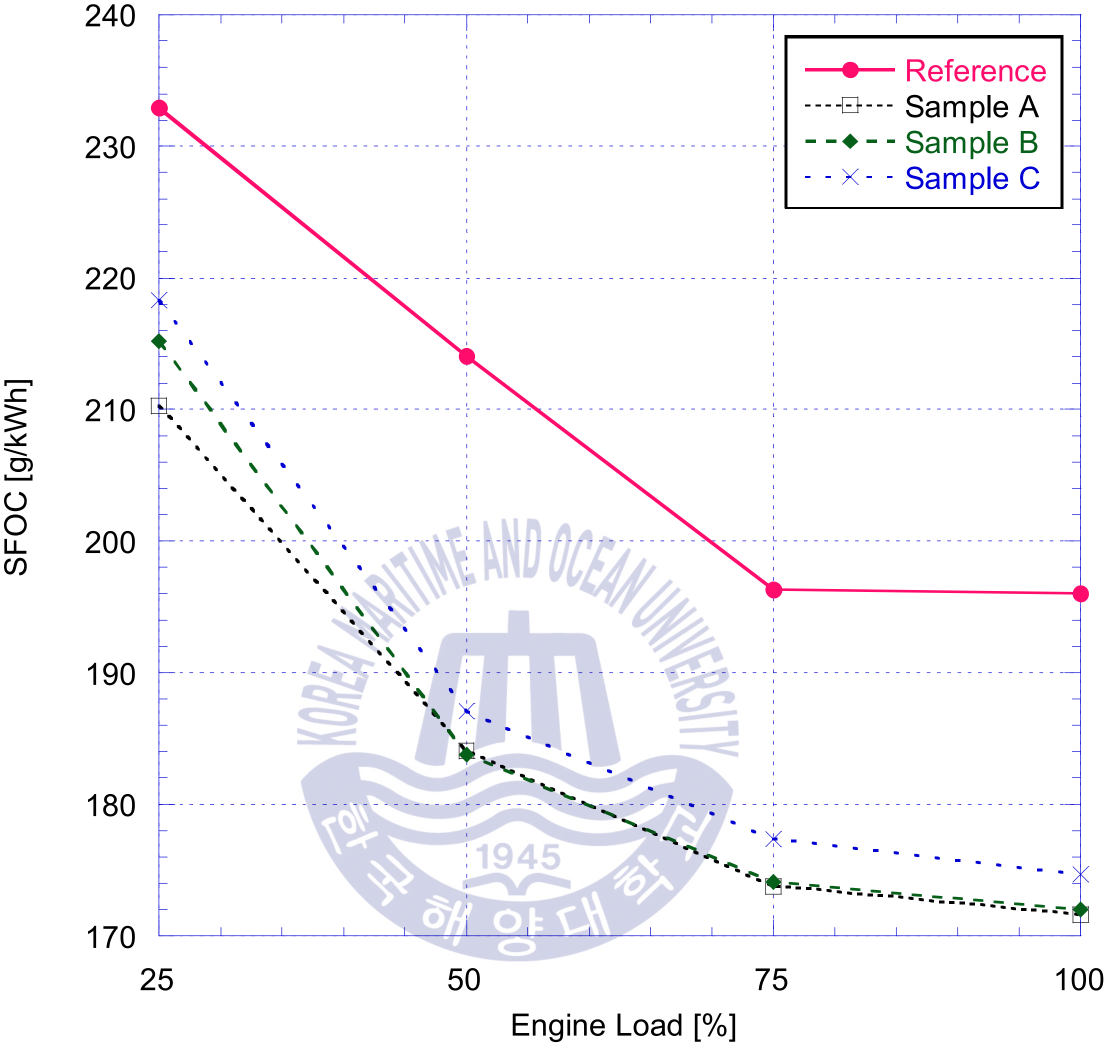


Fig.4-17 Comparison of specific fuel oil consumption at full engine load with different fuel oil additives

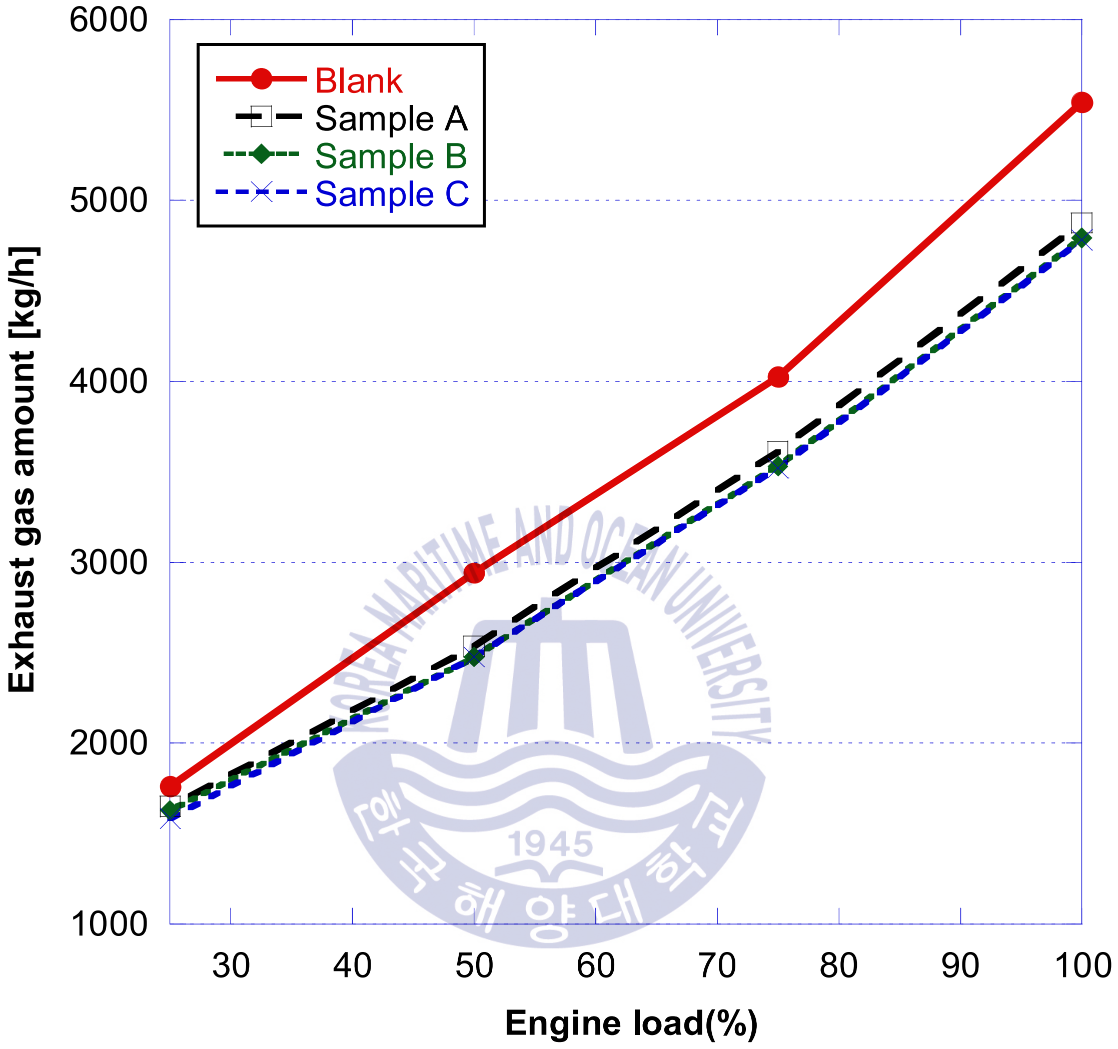


Fig.4-18 Comparison of exhaust gas amount created by different fuel oil

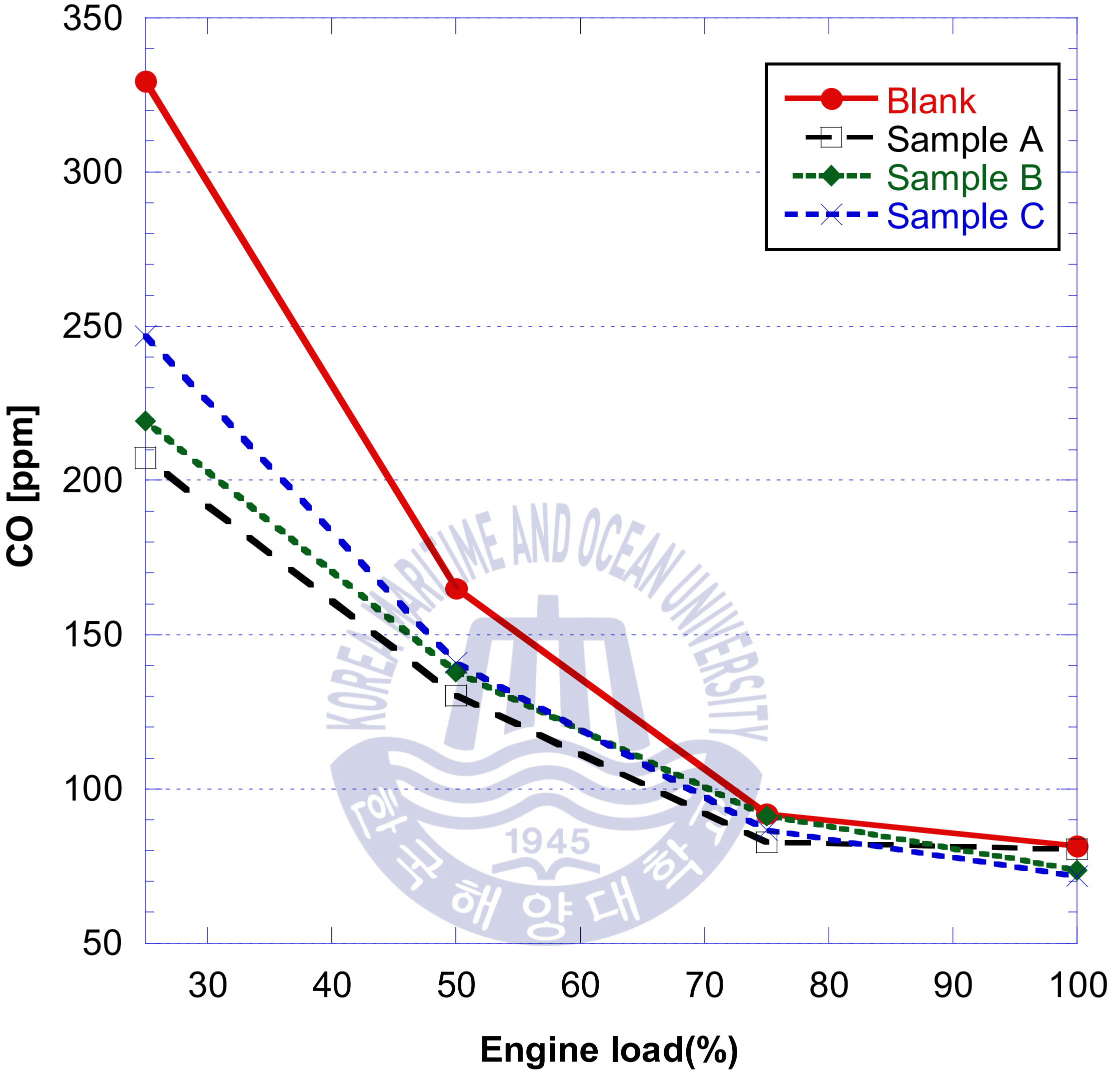


Fig.4-19 Comparison of CO emission

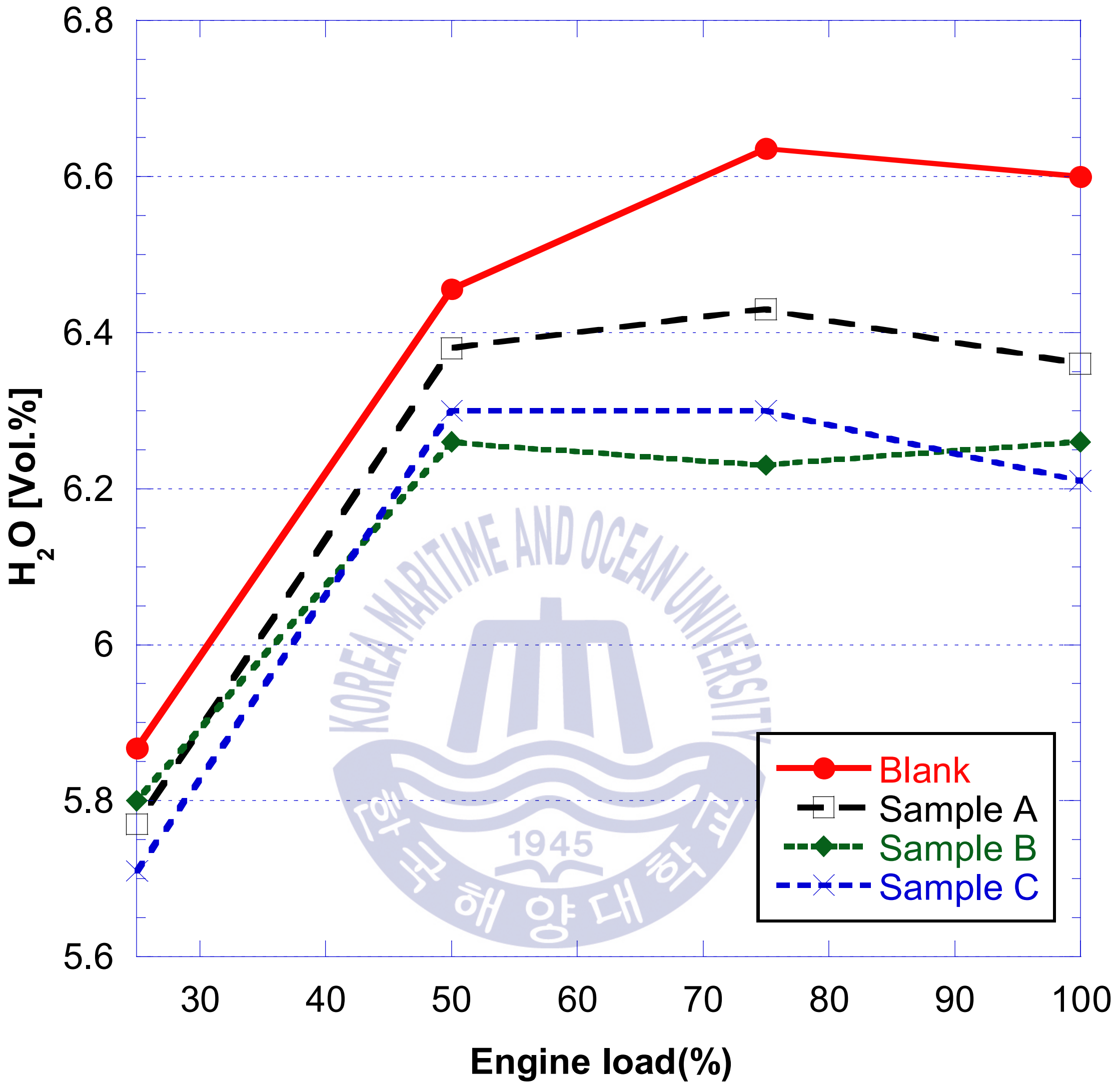


Fig.4-20 Comparison of water concentration

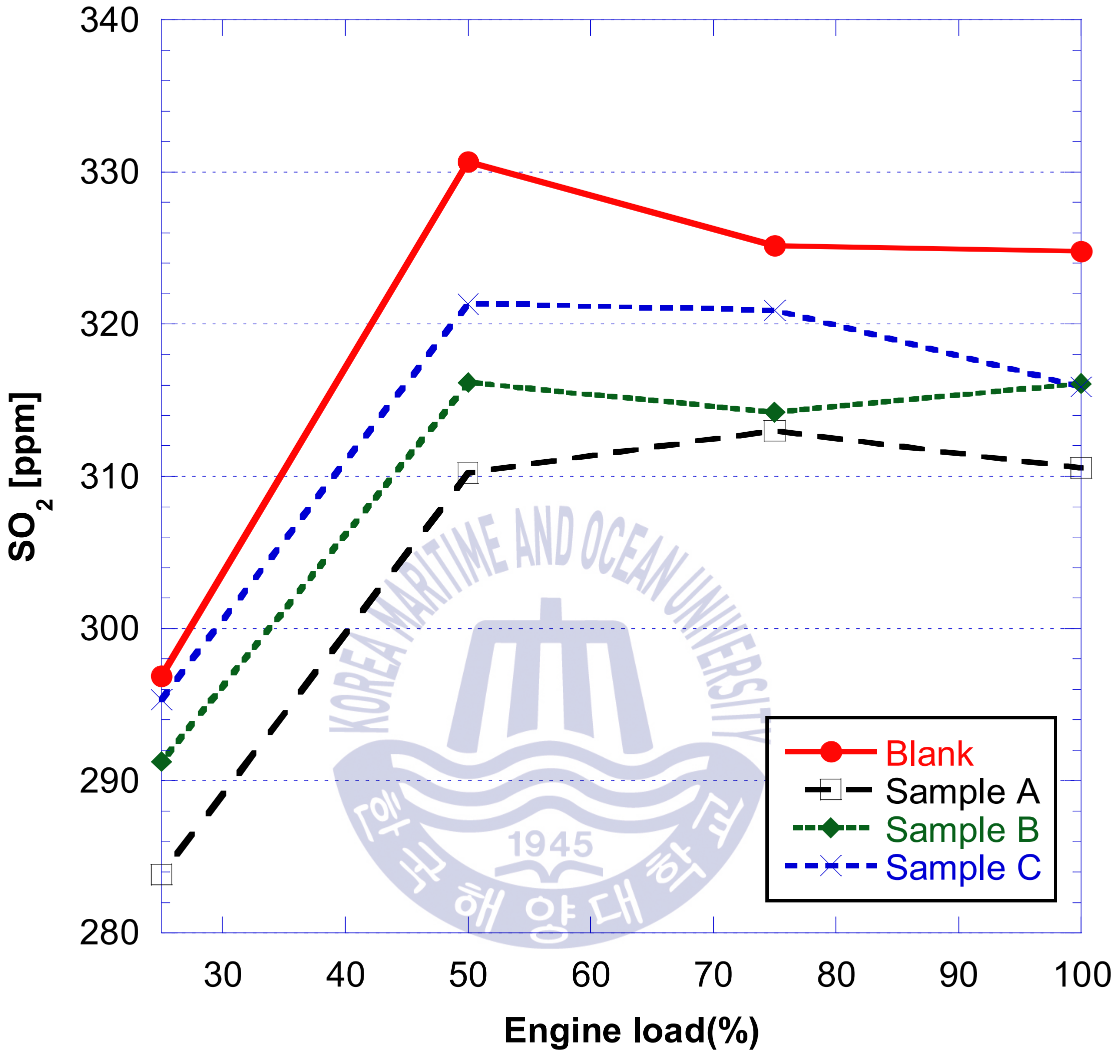


Fig.4-21 Comparison of SO_2 concentration

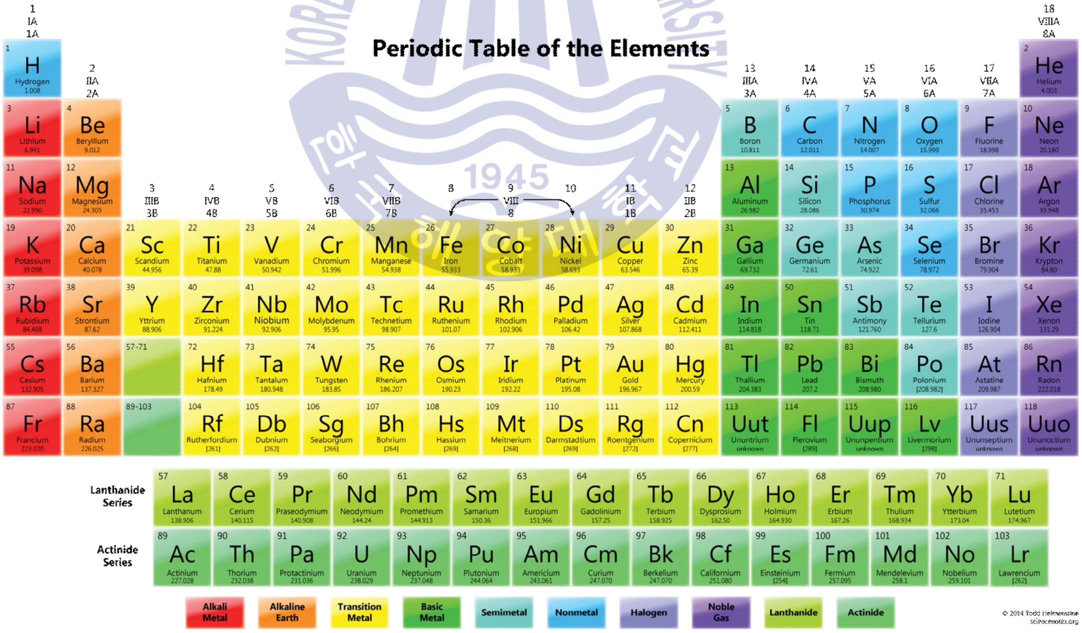
4.6 Investigation of fuel combustion improver effect to engine combustion

Combustion improver generally employ elements of organometallic, such as Fe, Mn and Cu of transition metal, and alkali earth metals of Ba and Ca. Various approaches have been tried to enhance concentration of elements.

Ferrocene is representative iron compound and various approaches have been made to make more higher concentration to 20ppm or 300ppm. The high concentration of iron can be effective to remove carbon deposit and enable to improve combustion.

U.S. Environmental Protection Agency already announced that fuel additives are effective to reduce particulate matter. However, the announcement did not constrain the type or element (EPA, 1997).

The study try to find out reaction mechanism of iron compounds which are contained in widely using fuel combustion catalysts. As the first step of the study, concentrated on the periodic table as given below. **Fig.4-22** represents the periodic table of the elements.



Periodic Table of the Elements

1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 84.80
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.29
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown
	Lanthanide Series	57 La Lanthanum 138.906	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.966	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967	
	Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]	

Fig. 4-22 Periodic table of the elements

As stated on the periodic table, 1A series means alkali metal. 2A series is alkali earth metal. Understanding the characteristics of 1A alkali metal is necessary to know about the 2A series which is the topic of the study. Following is the characteristics of alkali metal.

The alkali metal has low density and melting point and these tendency become regularly as atomic number increases. Atomic radius increase and decrease ionic energy as periods increased. Therefore, alkali metal has the lowest ionic energy in a same period. These characteristics mean that alkali metal has good reactivity and easily lose an electron and become an ion which contains 1+ charge. Alkali metal easily react with water and produce hydrogen gas and alkali metal hydroxide solution.

$$2M(s) + 2H_2O(l) \rightarrow 2MOH(aq) + H_2(g) \qquad (4\text{-}1)$$

The above reaction exothermic with very high heat. In some case, hydrogen ignitable heat created and flame or explosion can be made. The reaction is more vigorous when period increased.

2A series is named alkali earth metal and it has more harder, higher density and higher melting point than alkali metal. It has less reaction than neighbored alkali metal. Reaction can be increased when periodic and series increased therefore Be and Mg are the least reactive element among the alkali earth metal.

Table 4-6 summarizes simple properties of alkali metal and **Table 4-7** shows properties of alkali earth metal.

Table 4-6 Simple properties of alkali metal

Element	Electronic configuration	Melting point (℃)	Density (g/㎤)	Atomic radius (Å)	Ionic energy (I_1, kJ/mol)
Li	[He] $2S^1$	181	0.53	1.34	520
Na	[Ne] $3S^1$	98	0.97	1.54	496
K	[Ar] $4S^1$	63	0.86	1.96	419
Rb	[Kr] $5S^1$	39	1.53	2.11	403
Cs	[Xe] $6S^1$	28	1.88	2.25	376

Table 4-7 Simple properties of alkali earth metal

Element	Electronic configuration	Melting point (℃)	Density (g/㎤)	Atomic radius (Å)	Ionic energy (I_1, kJ/mol)
Be	[He] $2S^2$	1,287	1.85	0.90	899
Mg	[Ne] $3S^2$	650	1.74	1.30	738
Ca	[Ar] $4S^2$	842	1.55	1.74	590
Sr	[Kr] $5S^2$	777	2.63	1.92	549
Ba	[Xe] $6S^2$	727	3.51	1.98	503

From above fundamental characteristics of 1A and 2A series, metal, metalloid, and nonmetal characteristics shall be reviewed, because combustion catalysts are normally iron which is known as metalloid and Cs which is known as metal. Additionally, other metal and metalloid are continuously investigating as a combustion catalyst.

Metal has gloss on the surface, malleability, ductility, good conductor of electronic and heat, and tend to create a cation at aqueous solution. Non-metal has normally opposite characteristics with metal. The metalloid has intermediate characteristics among metal and nonmetal. From above summary of periodic table, stable, easily maintainable and high reactivity metal can be in transition metal. It is precious metal when the period increases therefore, Mn, Fe, Co, Ni and Cu can be candidate group. Toxicity of the element to the human being, engine and environment is considered and economic feasibility also will be in mind.

The fuel borne catalysts are generally, fuel soluble organometallic forms of iron, colloidal suspensions of cerium or iron oxide, or a combination. Other chemistries involving copper, manganese, platinum and combinations of metals are also known. Actually, the term fuel borne catalyst is aimed to be used on the after-treatment of the vehicle such as regenerative diesel particulate filter (DPF). When back pressure increases at the DPF, system will burn out accumulated diesel particulate and the combustion can be accelerated by the catalyst contained in the fuel. Without some form of catalyst, regeneration requires a high energy input over significant periods of time, which creates a potential fuel consumption penalty estimated to be about 5% of vehicle consumption. Fuel borne catalysts significantly reduce the energy input required to achieve regeneration, and generally facilitate the operation of diesel vehicles fitted with DPFs (Stefano C. et al., 2016).

The metallic portion of the fuel borne catalyst added to the diesel fuel survives during the combustion process, usually in the form of finely divided oxides. These particles are bound up with agglomerations of tiny soot particles leaving the combustion chamber and pass into the filter. This well distributed catalyst in the soot assists the process of filter regeneration. A trigger for regeneration of the catalysed soot is typically an energy input in the form of increased exhaust gas temperature, which takes some of the catalysed soot above a threshold ignition temperature. Once combustion is initiated, the accumulated pre-catalysed soot rapidly burns to leave a clean filter and reduced back pressure. Typical active metal treat levels for fuel borne catalysts lie in the range 5~30mg/kg.

Combustion improver chemistry employed in heating fuels includes both ashless and metal containing additives. Ashless combustion improver additives typically employ nitrogen functionality on fuel soluble hydrocarbon molecules, while metal containing additives are normally fully fuel soluble organometallic molecules.

Incomplete combustion can lead to soot deposits in the combustion chambers, on heat transfer surfaces and in flues of boilers and stoves, which can impair heat transfer and may result in unwanted fires. Combustion improver additives have demonstrated improved efficiency through reduced soot deposition, and have reduced the frequency of flue and chimney fires.

Ashless combustion improver additives function by decomposing early in the combustion process to provide a source of free radicals, which increase the rate of decomposition of the fuel to ensure more complete combustion with reduced formation of sooty particulates. Surface active deposit control chemistry employed for burner nozzle cleanliness can also reduce droplet size during atomisation, with resulting benefits in smoke and soot reduction during combustion. Metal-containing combustion improver additives function by catalysing the burn-out of soot particles formed during combustion, thus reducing the extent and weight of soot deposited on heat transfer and flue surfaces. Typical treat rates are in the range 5~50 mg/kg and 150~500 mg/kg for metallic and ashless additives respectively.

The term Heavy Fuel Oil or Residual Fuel is applied to the refinery product produced from the higher boiling fractions of crude oil which remain after automotive and jet fuels, and lubricant base-stock fractions have been removed. This type of fuel is used where large amounts of energy or power are required from industrial-scale plant, such as refineries, large marine diesel engines, power stations and large-scale industrial heating. Residual fuel properties vary more widely than lighter fuels for automotive or aviation applications, and are more likely to require some type of chemical treatment prior to use. Frequently it is the end-user who decides on the nature and scope of the chemical treatment employed, usually based on an assessment of fuel properties carried out prior to combustion. Although precise additive treatments may vary with the different applications, the fuel characteristics requiring treatment are broadly common to all the uses of heavy fuel oil. To avoid undue repetition, additive treatments will be considered as applying to all the end uses of this fuel.

The study can assume the combustion catalyst mechanism based on the above fundamental chemical consideration for iron and ferrocene. Both mechanisms suggested hereinafter are similar but different in detail.

Oil soluble metal compounds basically contains high reactivity metal and good heavy fuel soluble characteristics. Combustion improving metals are Ba, Ca, Mg for alkali earth metal, and Ni, Co, Mn, and Fe for transition metal. Alkali earth metals of Ba, Ca, and Mg decompose water in heavy fuel oil and it will lead to decrease unburnt carbon concentration. Transition metals of Mn, Ni, Co and Fe enhance reaction with oxygen on the air and it will result in improving combustion. Among various metals Fe is widely known due to economic reason. The weak point of Fe is solubility in heavy fuel oil therefore, organic ligand are combined to improve oil solubility of Fe. Acetylacetonate, naphthenate, and oxlate are well known organic ligand (Ali K. et al., 2015).

Concentrations of organometallic compounds and combustion characteristics are proportional. Therefore, making more higher concentration of metal solution and solubility are regarded as a key technologies. Ferrocene and iron derivatives are widely used as a combustion improver but solubility of ferrocene in solvent is very low. Ferrocene can be used in combustion catalyst or fuel additive formulations when dissolved in a solvent so that it will disperse thoroughly into the fuel. Performance of a combustion catalyst containing iron (or iron plus magnesium) requires sufficient dosage. Optimum dosage levels are 10 ppm iron in compression-ignited reciprocating engines and 50 ppm iron in continuous firing equipment such as combustion turbines, boilers and process heaters. Lower dosage rates based on economic considerations are ill advised and will not produce desired results. **Table 4-8** describes solubility in organic solvent for various iron compounds. The key to succeed in combustion improver is improving solvent solubility. Fuel combustion improver can decrease pollutants by directly reacting with fuel oil and it helps to lead complete combustion.

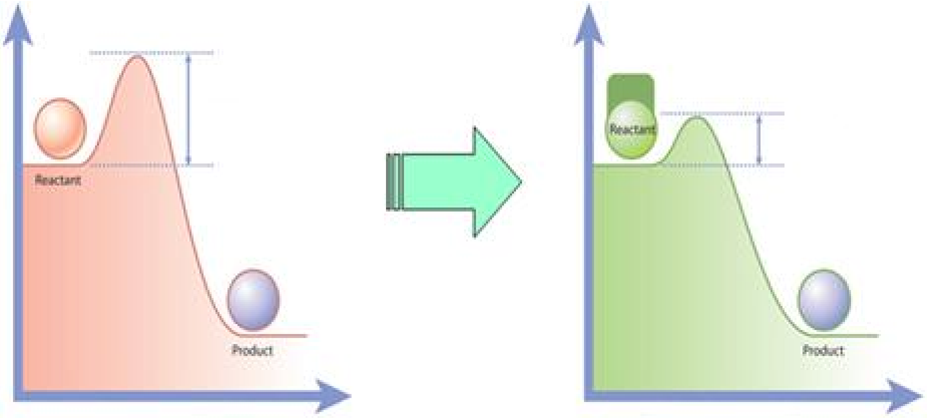
Table 4-8 Solubility of ferrocene in organic solvents

Solvent	Solvent Mol. Wt.	Mole Fraction Solubility	% Sol.	% Fe
n-Hexane	86.178	0.0226	4.75%	1.43%
n-Heptane	100.205	0.02489	4.52%	1.36%
2,2,4-Trimethylpentane	114.232	0.02179	3.50%	1.05%
Benzene	78.114	0.087586	18.61%	5.59%
Toluene	92.141	0.08321	15.49%	4.65%
Ethylbenzene	106.168	0.07703	12.76%	3.83%
o-Xylene	106.168	0.08014	13.24%	3.98%
m-Xylene	106.168	0.07436	12.34%	3.70%
p-Xylene	106.168	0.07785	12.89%	3.87%
Dibutyl ether	130.232	0.05107	7.14%	2.14%
1,4-Dioxane	88.108	0.0683	13.40%	4.02%
Methanol	32.043	0.003298	1.88%	0.57%
Ethanol	46.07	0.005976	2.37%	0.71%
2-Propanol	60.097	0.007078	2.16%	0.65%
1-Butanol	74.124	0.001181	0.30%	0.09%
2-Methyl-1-propanol	74.124	0.009621	2.38%	0.71%
Butyl acetate	116.162	0.0558	8.65%	2.60%
Ethyl acetate	88.108	0.043	8.67%	2.60%
Acetonitrile	41.05	0.00756	3.34%	1.00%
Dimethyl sulfoxide	78.13	0.0141	3.29%	0.99%

Based on the concept of ‘Arrhenius equation’ given on equation (4-2), reaction speed is governed by (1) Ea or more higher molecule portion, (2) number of collision in each second, (3) molecule portion which has directional nature.

$$k = Ae^{\frac{-E_a}{RT}} \tag{4-2}$$

Where k means speed constant, E_a means activation energy, R means gas constant (= 8.314 J/mol K), T means absolute temperature. ‘A’ becomes almost constant whenever temperature changes. ‘A is related with number of collision. When Ea increases k decrease. Therefore, important parameter in chemical reaction is decreasing activation energy and it is well described on **Fig.4-19** describes concept of fuel combustion catalyst.



General combustion ->
Hard to attain combustion

Combustion catalyst ->
Easy combustion because
of low activation energy

Fig.4-23 Effect of combustion catalyst.

From the **Fig.4-23** and equation (4-2), importance of activation energy is well described. By using simple mathematical treatment, and information gas properties the activation energy can be calculated by following equation (4-3)~(4-7). The equation (4-3)~(4-7) describes activation energy on unknown status.

$$\ln k = -\frac{E_a}{RT} + \ln A \tag{4-3}$$

$$\ln k_1 = -\frac{Ea}{RT_1} + \ln A \tag{4-4}$$

$$\ln k_2 = -\frac{Ea}{RT_2} + \ln A \tag{4-5}$$

$$\ln k_1 - \ln k_2 = \left(-\frac{Ea}{RT_1} + \ln A\right) - \left(-\frac{Ea}{RT_2} + \ln A\right) \tag{4-6}$$

$$\ln \frac{k_1}{k_2} = \frac{Ea}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{4-7}$$

The equation can give a result when knows temperature (T_2) and gas constant (k_2). However, these are chemical engineers basic sector. Currently, effort to know these fundamental calculation of residual fuel and additive sector are not officially announced.

The study results in action of combustion catalyst as following image. The mechanism is anticipated to be consisted with two stages. The one is pre-combustion stage and the next one is post-combustion stage. The pre-combustion stage can be described as following figure. **Fig.4-24** shows anticipated fuel catalyst mechanism on pre-combustion stage.

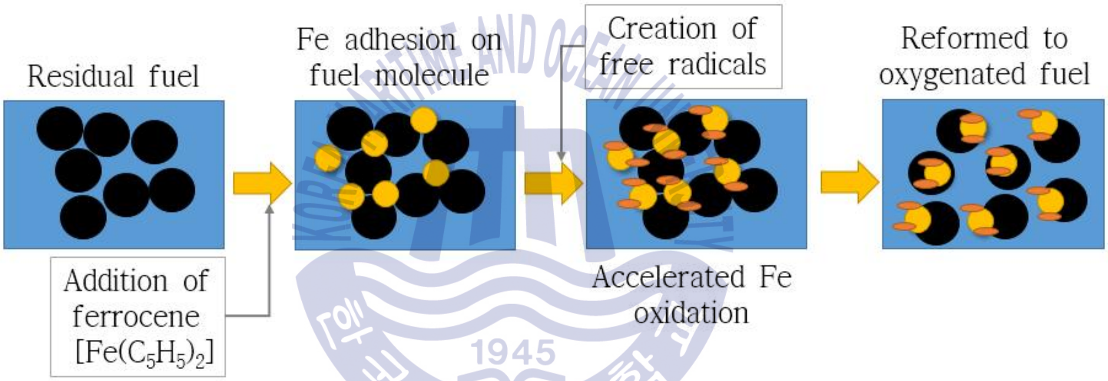


Fig.4-24 Expected fuel catalyst mechanism on pre-combustion stage

Ferrocene or iron catalysts add on residual fuel. Fine particle of Fe is able to adhesive to fuel molecule. The Fe atom has high oxidation characteristics and the oxidation will be resulted in after Fe atom attached to fuel molecule. Oxidation of Fe can result in fuel with oxygen content which is capable of leading to fuel lean combustion and it will also help to become closer to complete combustion. The study results in another action of combustion catalyst for post-combustion. **Fig.4-25** shows mechanism of fuel combustion catalyst on post-combustion.

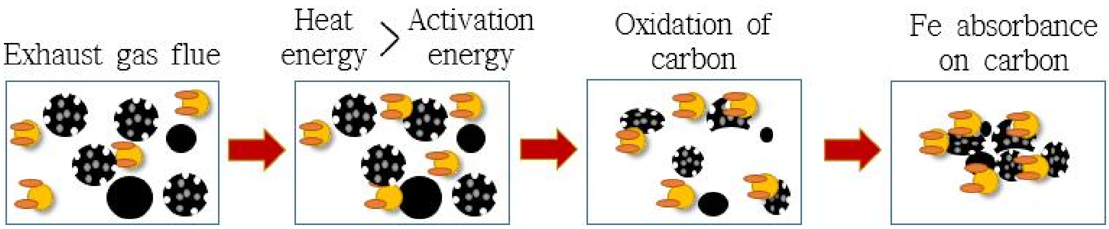


Fig.4-25 Expected fuel catalyst mechanism on post-combustion stage

Ash, unburned metal and carbon is contained in the exhaust gas flue. When the exhaust gas flue has sufficient heat energy to overcome activation energy, the remained metal can do additional catalyst reaction. Therefore, it can make more lighter carbon, and ash by oxidation. However, after exhaust gas lose heat energy the metal can be adhered on the surface of carbon or ash and water. It will make agglomerated particulate matters.

Wouters et al., (2004) explained combustion catalyst mechanism which can describe into three steps. The first step is 'Combustion of ferrocene and fuel oil'. The combustion of fuel oil leads to carbon dioxide, carbon monoxide and soot.

$$C_mH_n + zO_2 \rightarrow CO, CO_2, C_{Solid} \qquad (4\text{-}8)$$

The combustion products of ferrocene are iron oxide of Fe_2O_3, slights amounts of FeO, and carbon dioxide.

$$Fe(C_5H_5)_2 + O_2 \rightarrow Fe_xO_y + CO_2 \cdots \qquad (4\text{-}9)$$

The second step is 'Soot reduction activity of ferrocene'. In this step, the iron oxides and soot react to carbon monoxide or carbon dioxide and iron.

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2 \qquad (4\text{-}10)$$

$$FeO + C \rightarrow CO + Fe \qquad (4\text{-}11)$$

The third step is 'reactivation of the catalytic activity'. Iron and oxygen react to iron oxide and the catalytic cycle can start again.

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3 \qquad (4-12)$$

The mechanism described above indicates that the active compound is Fe_2O_3 that is the base of the catalytic cycle. This study basically agree with above chemical reaction. However, the above mentioned mechanism does not keep the important concept of free radical creation. Reaction 4-12 governs basic of fuel catalyst reactivation process. Therefore, mechanism on this study and three step mechanisms are necessary to be merged in future investigation.

4.7 Emission Characteristics

4.7.1 Emission characteristics at low engine load

Fig.4-26 shows nitrogen oxide emission values according to each fuel oil sample against engine speed (rpm). The highest concentration of NOx emitted at every engine rpm while operating with blank fuel oil. Sample A recorded the lowest NOx concentration at 600rpm and 900rpm. NOx concentration with sample B was almost constant. Sample C recorded the lowest NOx emission at 750 rpm. At 900rpm, NOx emission was about 500ppm except for sample A.

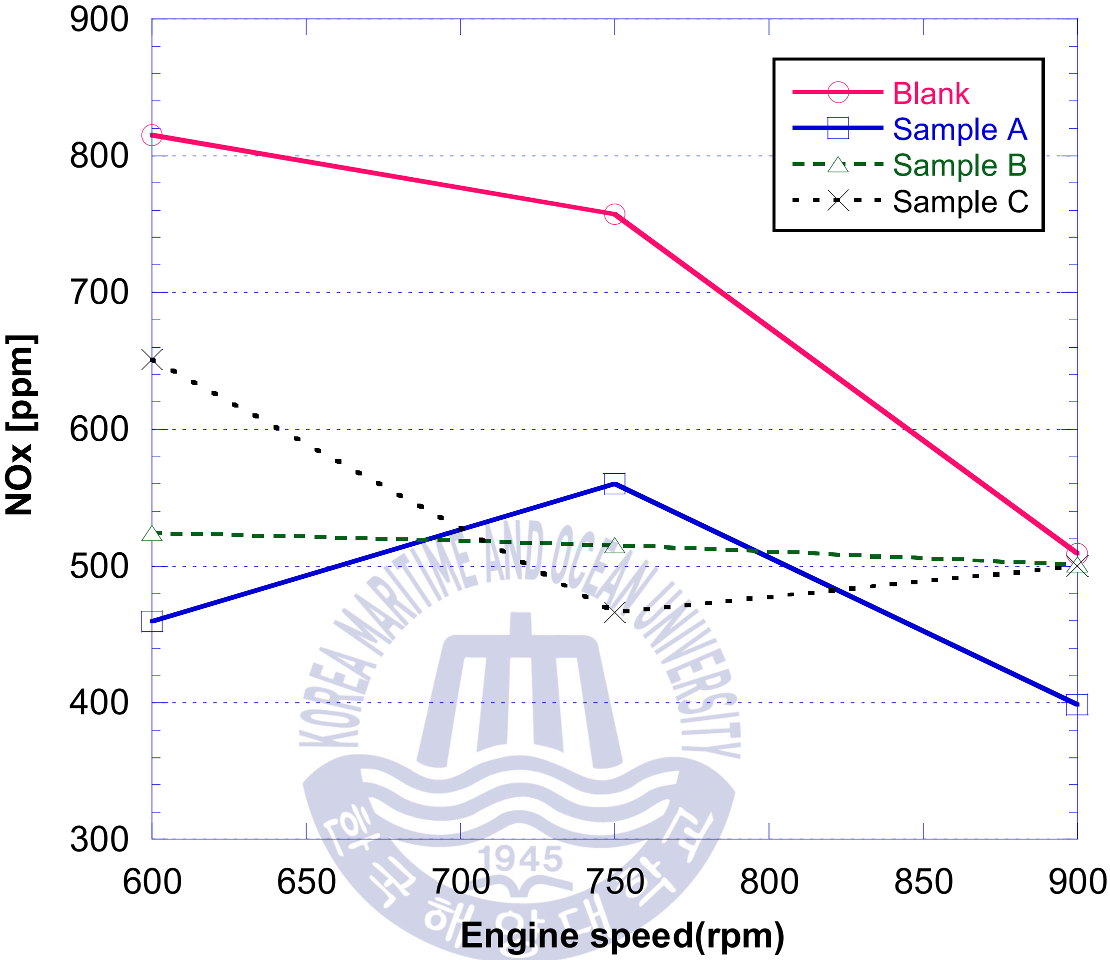


Fig.4-26 Comparison of measured NOx emission with different fuel additives at low engine load

NOx emission and SFOC have a trade-off relationship (Larsen et al., 2015). If the trade-off relationship was reflected in this study, NOx emission should be higher for sample B and sample C. However, no trade-off relationship was found. NOx emission followed the order Blank > Sample C > Sample B > Sample A. Nitrogen oxide created in the diesel engine is governed by the thermal NOx mechanism, which depends on the temperature during combustion (Choi B.C., 2001). According to the SFOC tendency, NOx emission should be Sample B >

Sample C > Blank > Sample A. The reason for the absence of the trade-off relationship between SFOC and NOx is that based on the chemistry of the fuel additive. The combustion and emission characteristics of the engine has been modified and general NOx mechanism was affected.

This phenomenon could be supportive from the study explaining that by the effect of fuel additives in the pre-mixing period of the fuel-air mixture, vigorous combustion was reduced (Nicolas L. et al., 1996) leading to NOx reduction.

Fig.4-27 shows the emission characteristics of PM, which normally decreased as engine rpm increased except in the blank sample during the test. The blank sample showed increased PM emission as engine rpm increased. The blank sample emitted the lowest PM at 600rpm and emitted the highest PM at 900rpm. Sample A emitted the highest PM at 600rpm and PM emission decreased as engine rpm increased and it emitted the second highest PM at 900rpm. Sample B showed the lowest PM emission throughout the PM measurement and the load point was 900rpm.

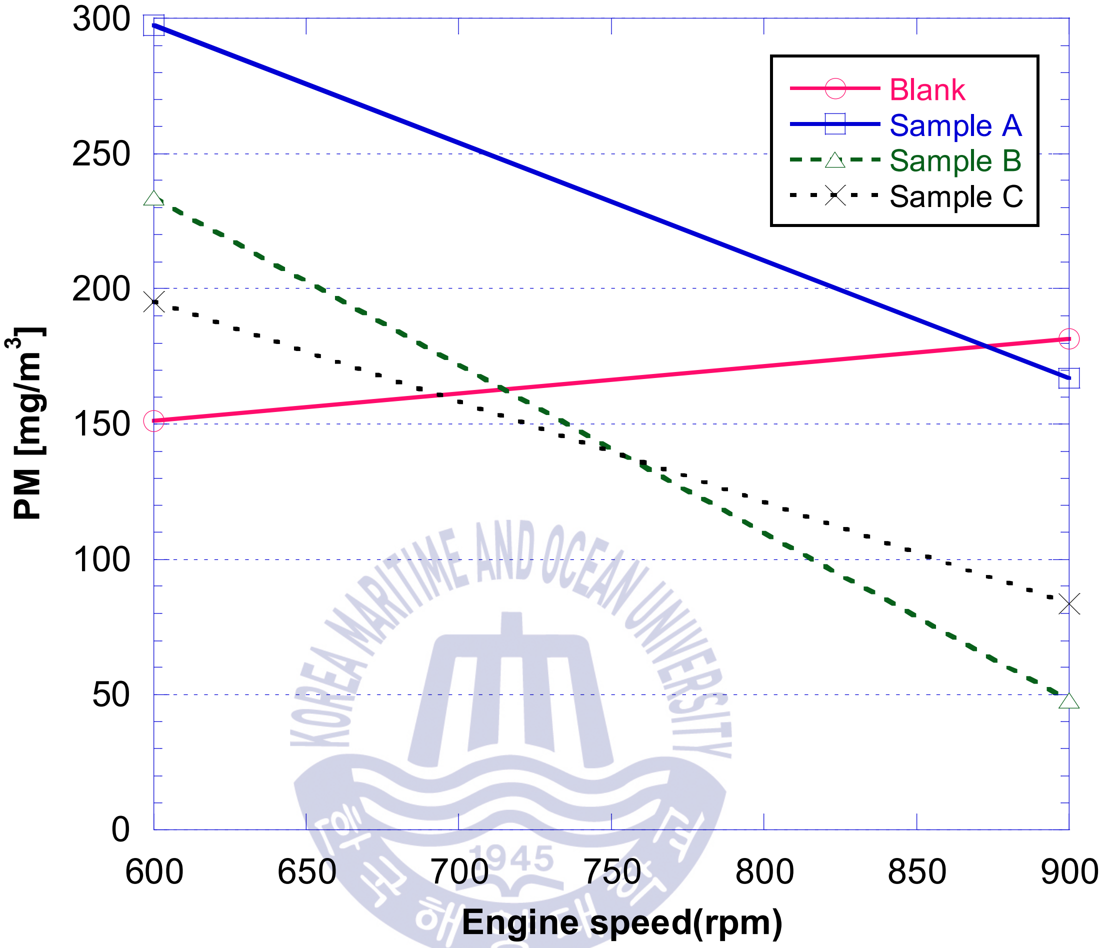


Fig.4-27 Comparison of measured PM emission with different fuel additives at low engine load

For heavy fuel oils, PM emission was affected by various parameters, mainly by specific gravity, viscocity, asphaltene concentration, carbon fraction, engine operating load, and oxygen concentration in the fuel (Lee Y.I. et al., 2006). PM structure could also be affected by metal content in the fuel. According to the PM measurement, the study found a tendency that PM emission was decreased for every fuel additive added sample as engine rpm was increased. In other cases, PM emission for the blank fuel oil was increased as engine rpm increased. This tendency indicates that fuel additive could modify physical or chemical characteristics of the fuel and this is reflected in the results of the test. For a clearer verification of PM generation and emission tendency, PM content and structure analysis will be necessary.

As witnessed on the emission tendency, iron contained hybrid type fuel additives were effective to enhance combustion at low engine load. However, dispersant only which contains fatty acid was not effectively react with residual fuel oil.

4.7.2 Emission characteristics at full engine load

CO_2, NOx, and O_2 are measured under given test condition. **Fig.4-28** shows NOx emission record at entire engine load condition. Blank fuel emitted the minimum NOx among sample fuels and the NOx emission increases as engine load increases. It could be explained that the engine combustion temperature rises as engine load increase. Generally, NOx creation during combustion can explain more active flame took place in the process. Therefore, additive dosed fuels show more active combustion than blank fuel oil.

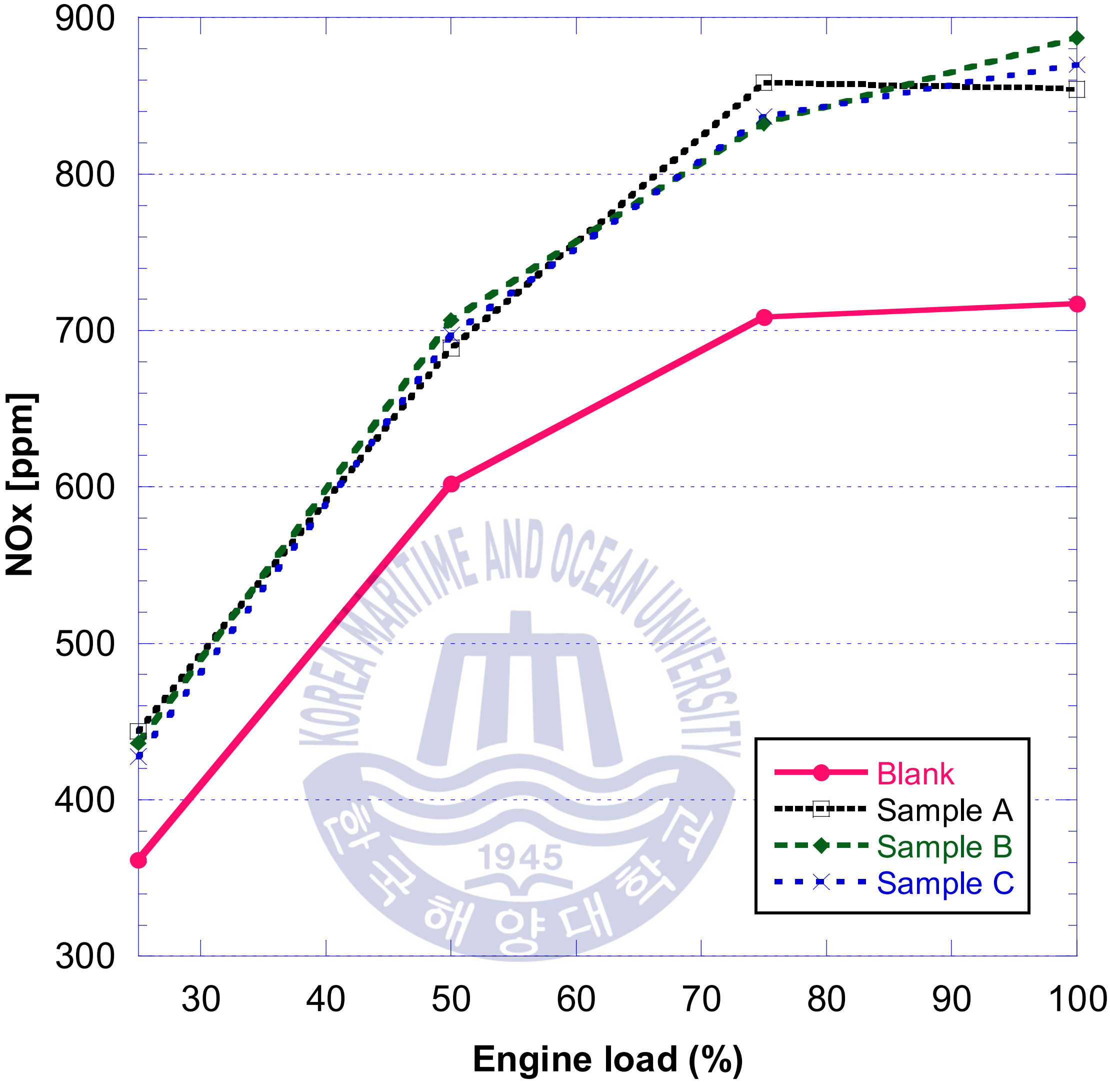


Fig.4-28 Comparison of measured NOx emission with different fuel additives

Fig.4-29 represents CO_2 emission. Blank recorded lowest CO_2 concentration and the minimum was 5.1%. CO_2 is representative combustion product with water. When evaluating CO_2 emission, O_2 concentration shall consider simultaneously. **Fig.4-30** shows O_2 tendency and blank had the highest O_2 concentration. High O_2 and low CO_2 concentration can be explained that the fuel was not effectively reacted during the combustion with O_2. Therefore, the O_2 emission which was not reacted with fuel oil increased. On the other hand, fuel additive samples show commonly low O_2 and high CO_2 concentration. It means O_2 had well reacted with fuel during combustion (Lee M.H. et al., 2009).

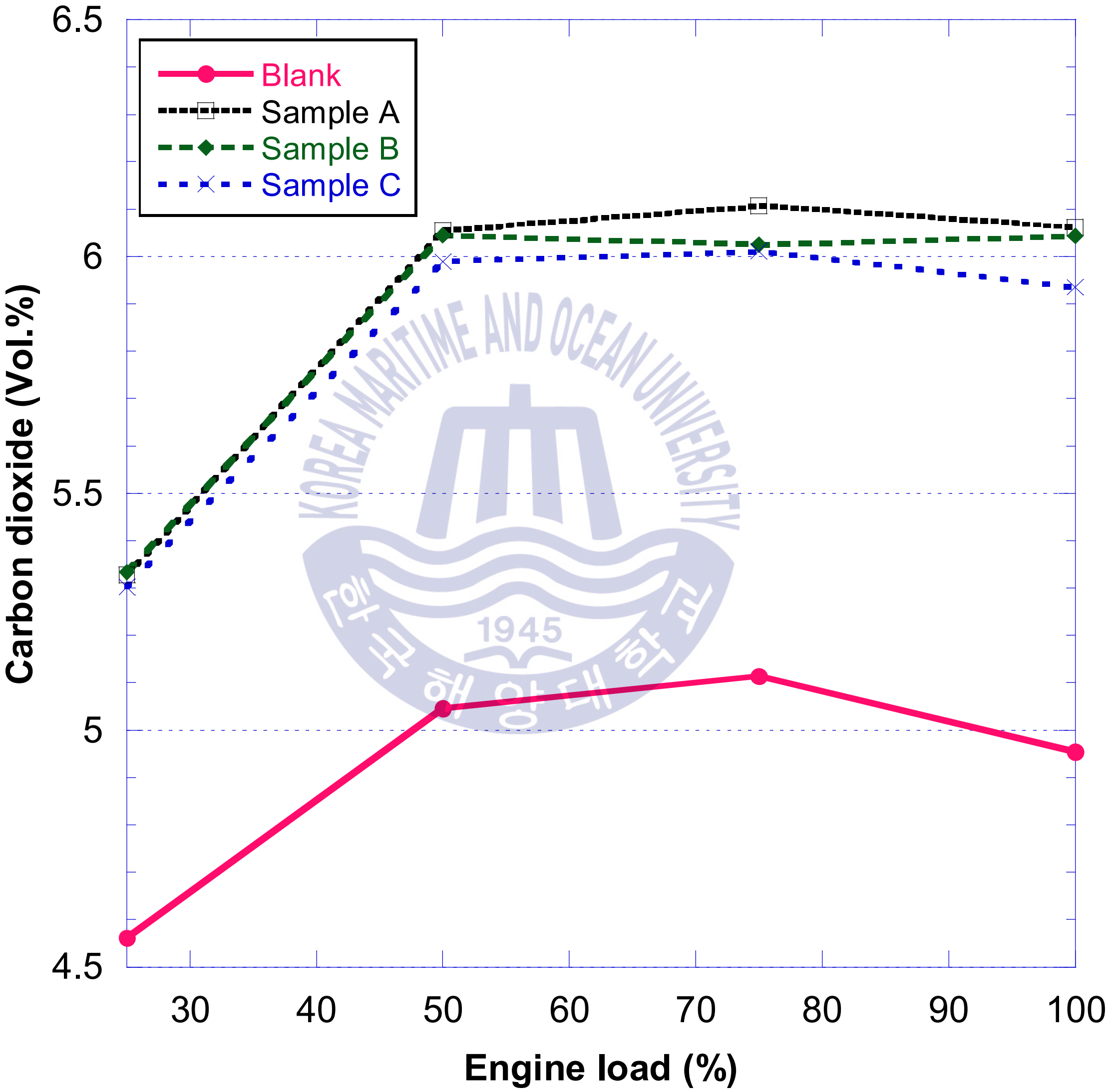


Fig.4-29 Comparison of measured CO_2 emission with different fuel additives

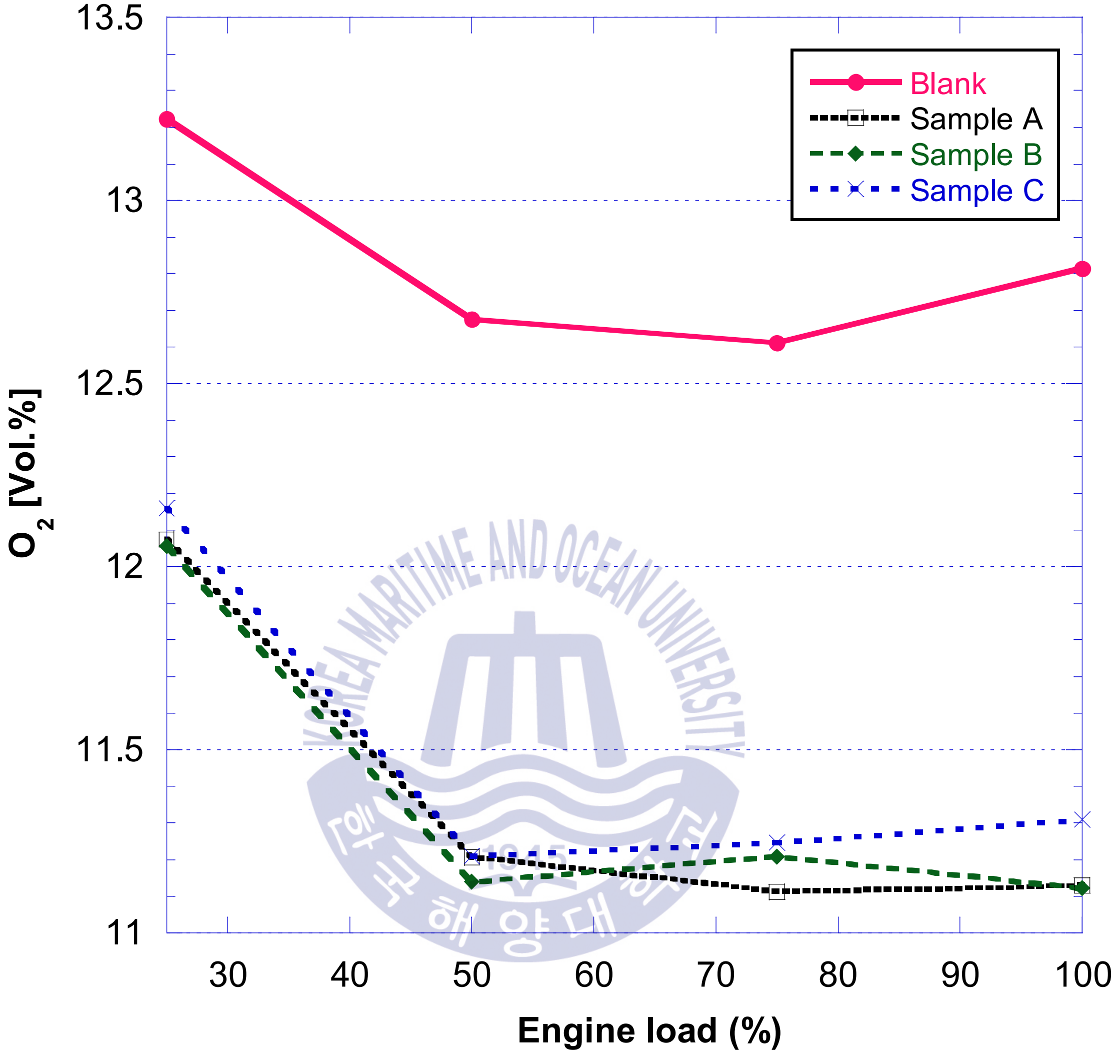


Fig.4-30 Comparison of measured O_2 emission with different fuel additives

4.8 Optical analysis

This study was assisted by Korea Institute of Science and Technology (KIST) and the optical analysis of Raman spectroscopy and Transmission Electron Microscope(TEM) were carried out by KIST.

4.8.1 Raman spectroscopy

Raman spectroscopy is used in the field to distinguish amorphous and crystalline investigation. Because, Raman scatters are not only symmetrical but also sensitive to silicon bonds. Different peak locations and peak shapes of raman spectroscopy can help finding small change in material. In this study, particulate matters were sampled at the end of tail pipe and these were analyzed with raman spectroscopy. **Fig.4-31** shows the results of raman spectroscopy. One important parameter on raman analysis is G/D ratio. It is the ratio between scattering intensity of D peak and G peak (Ryu S.M., 2012). **Table 4-9** shows specific data of scattering intensity for every sample. According to the G/D ratio, sample B can be told that it had most efficient combustion. On the other word, sample A showed the least efficient combustion. **Fig.4-32** shows image of Raman at 30,000 magnification. Sample B shows well dispersed components. Sample A shows agglomerated condition of particles which is comparatively large. Sample C shows agglomerated condition of particles. The agglomeration is consisting of fine particles with each other. **Fig.4-33** shows image of Raman at 50,000 magnification. As same with **Fig.4-32**, sample B has fine particles which are well dispersed on the surface. Sample A and C shows agglomeration of particles and sample A is normally with bigger particles than sample C. However, although it is raman scattering spectroscopy, it can not absolutely be spoken that the above mentioned tendency is exact analysis. Because, due to the small intensity gap, the analysis result is within the tolerance range. Therefore, further investigation was necessary.

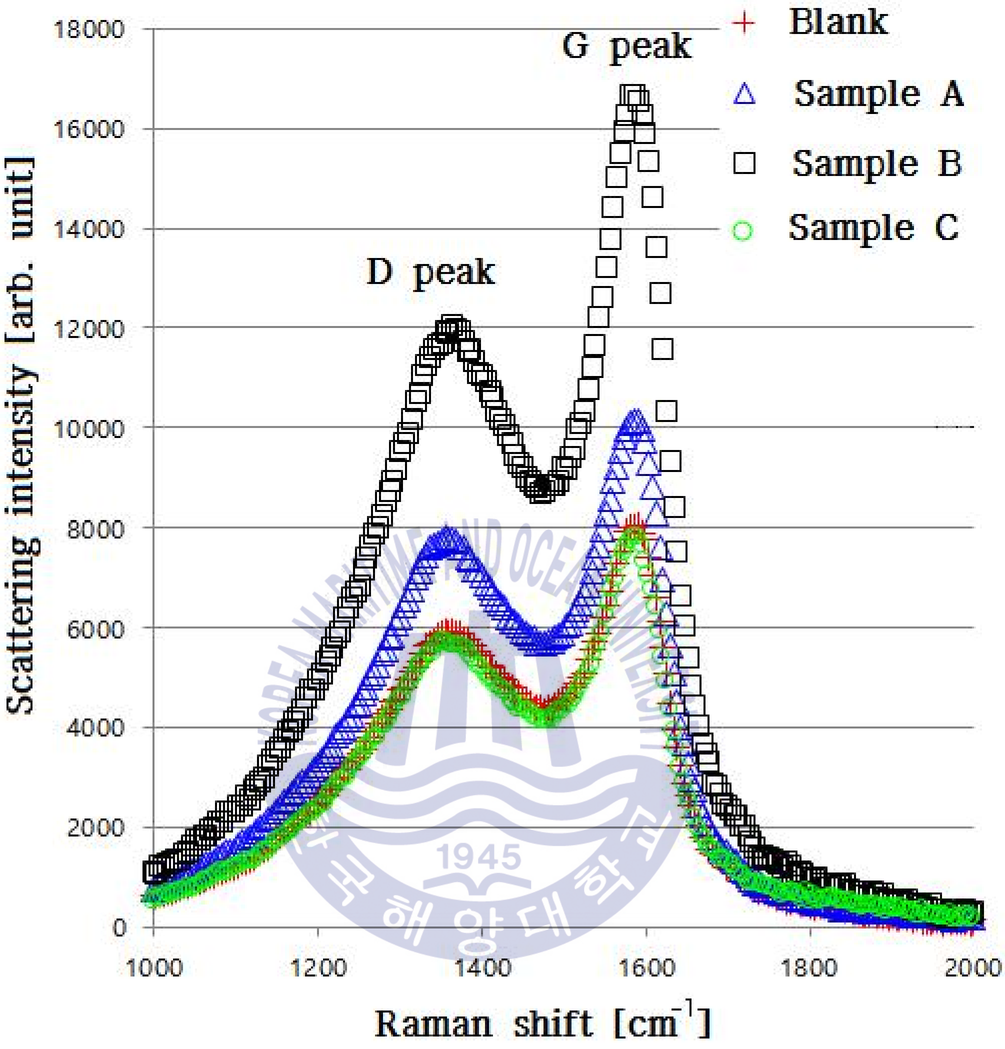


Fig.4-31 Scattering intensity comparison by raman spectroscopy

Table 4-9 Scattering intensity data for the samples

	Blank	Sample A	Sample B	Sample C
G peak	7,956.232	9,994.721	16,429.2	7,642.038
D peak	5,913.315	7,756.594	11,796.18	5,655.34
G/D	1.345478	1.288545	1.392755	1.351296

4.8.2 Energy Dispersive X-Ray Spectroscopy

Energy Dispersive X-ray Spectroscopy (EDS) was applied to this analysis. **Table 4-10** summarizes EDS result.

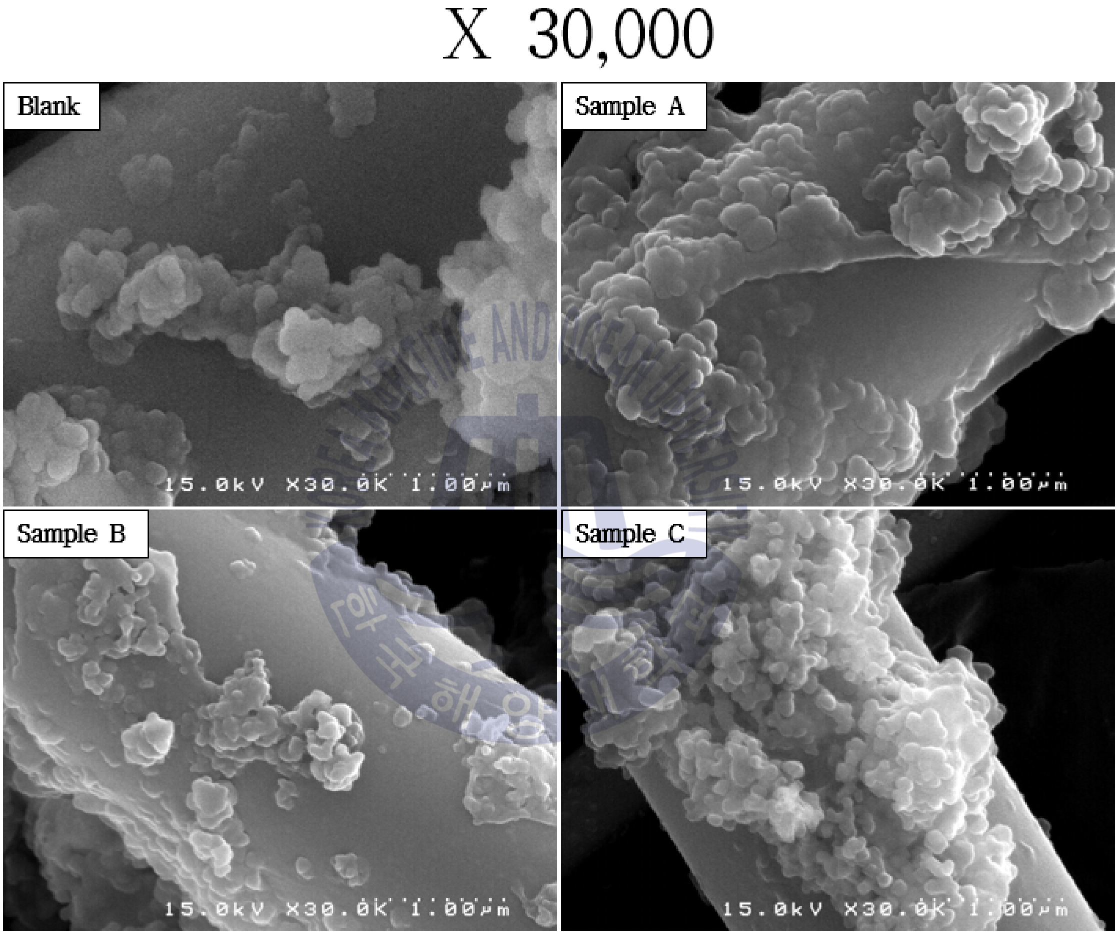


Fig.4-32 Raman spectroscopy image with 30,000 magnification

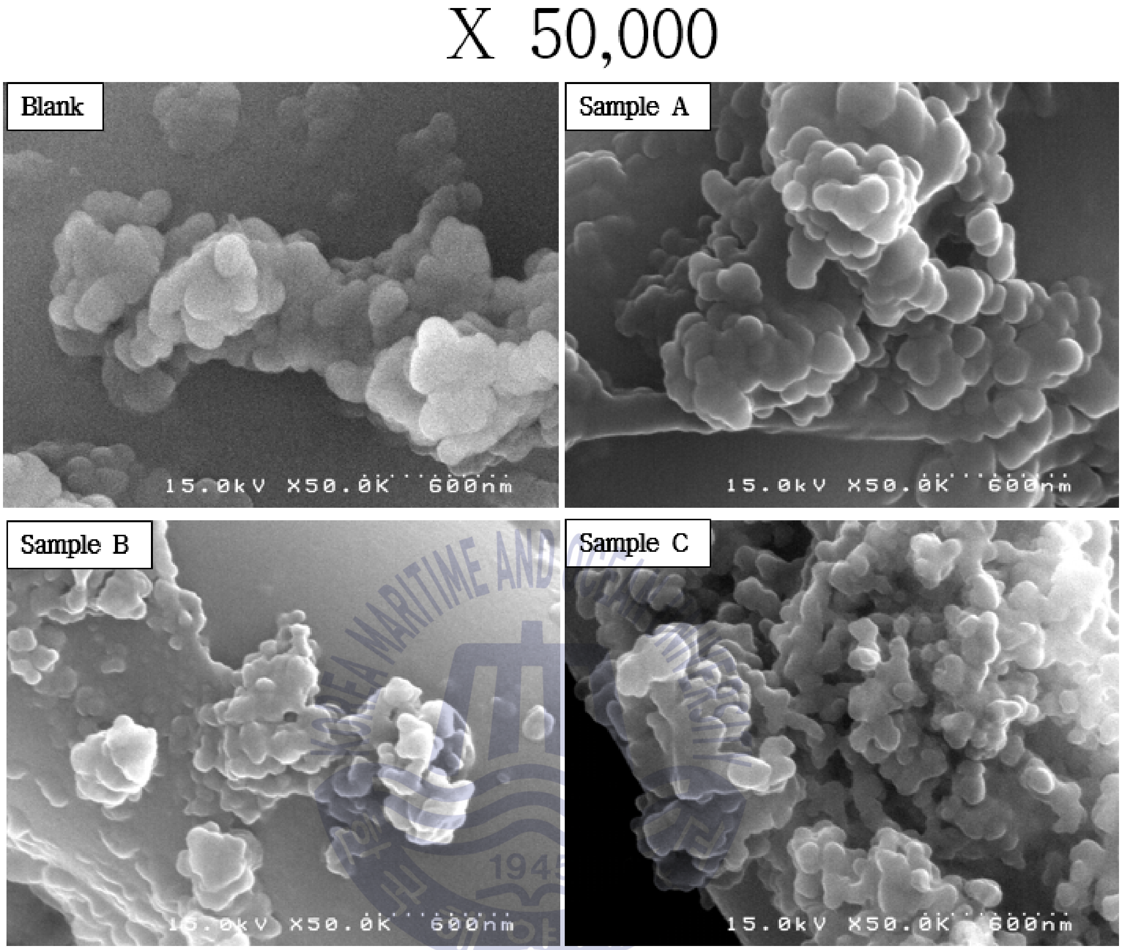


Fig.4-33 Raman spectroscopy image with 50,000 magnification

Table 4-10 EDS analysis results for the samples

Weight(%)	Blank	Sample A	Sample B	Sample C
C	81.89	71.57	70.75	75.13
O	9.57	16.77	11.02	15.81
Na	0.97	1.61	0.64	1.78
Mg	-	0.22	-	0.15
Al	0.73	1.56	1.2	1.62
S	2.94	3.11	4.66	1.49
Ti	-	-	0.78	-
Cu	0.99	0.87	5.32	-
Zn	1.25	1.62	2.49	0.95
K	0.32	0.49	0.75	0.60
Ca	0.50	0.82	0.92	1.04
Ba	0.59	0.95	-	1.43
Ni	-	0.42	0.9	-
Fe	0.23	-	0.57	-

The result shows that carbon content was commonly decreased with additives. Oxygen content was increased and sample A has the highest oxygen content and sample C has the second highest oxygen content. Comparing with blank fuel oil, additive was effective to make heavy fuel to more lighter than blank.

Transmission Electron Microscopy(TEM) was employed to see sample more precisely. **Fig.4-34** shows the result of TEM and **Table 4-11** shows TEM data for every sample.

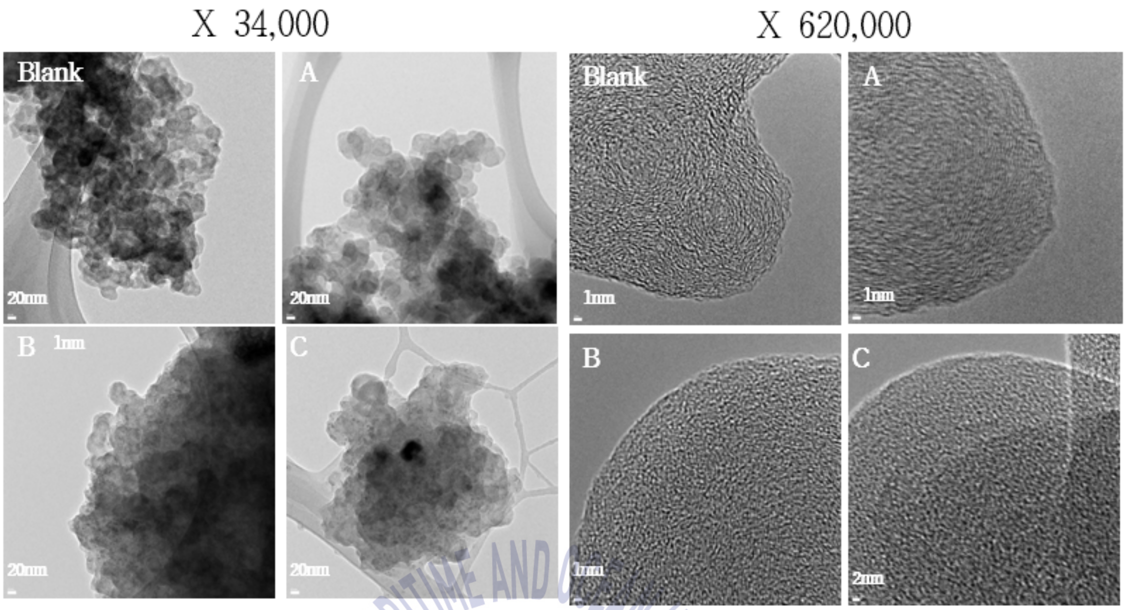


Fig.4-34 TEM images with 34,000 and 620,000 magnification

According to analyst, black spot which is generally represent for the heavy metal, has been investigated on every sample. Blank and sample A shows graphite structure which is consisting the black carbon. However, sample B and C do not show graphite but amorphous structure has been found. The TEM result is not identical to Raman spectroscopy. Because, sample A shows low black carbon fraction and blank, sample B and C show graphite on the raman analysis. In case of raman, the result was within tolerance, therefore, it has less reliability. The study decide to believe the result on TEM. On the data stated on the **Table 4-11**, carbon content decreased at every additive sample. Oxygen content increased at every sample comparing with blank. Sample C shows some metals such as Ni, Si, V and Fe. Sample C was aimed to increase iron content as high as possible but, the iron content was not found at TEM analysis.

Table 4-11 TEM analysis results for the samples

	C(%)	O(%)	Na(%)	Al(%)	S(%)	Ni(%)	Si(%)	V(%)	Fe(%)	Sum
Blank	98.4	1.16		0.1	0.33	-	-	-	-	100
Sample A_1	93.93	5.21	0.3	0.17	0.13	0.27	-	-	-	100
Sample A_2	96.89	2.83		0.15	0.24	-	-	-	-	100
Sample B	97	1.85		0.21	0.45	0.16	0.13	0.14	0.08	100
Sample C_1	95.87	3.63		0.07	0.43	-	-	-	-	100
Sample C_2	93.44	6.11		0.00	0.36	-	0.08	-	-	100

Chapter 5 Conclusions

This study was conducted to verify the effect of fuel oil additives on real engines. Verification of reaction mechanism on the real engine has constraints. Therefore the study has tried various approaches such as laboratory fuel analyzers and optical analyzers to find the reaction mechanism. Many kinds of fuel additives are in the market and the study focused on the investigation of dispersant and fuel combustion improvers. The mentioned types of additives were investigated on other studies. However, the former additives were mainly distillated diesel oil and rarely on residual marine fuel oil. The results attained from the study are summarized in this chapter as follows.

5.1 Dispersability

Long-term dispersability analysis shall be the fundamental analysis for the evaluation of dispersability. The ASTM D7061-12 of dispersability evaluated through the 3-day long-term dispersability analyses needs to be modified to reflect long-term dispersability.

Samples A, B, and C can be distinguished to have good dispersabilty at the initial analysis. Dispersability number of blank fuel oil was 6.2, which is over the limit of 5, and so it could be stated that the original residual fuel oil has poor dispersability. Dispersability number followed the order of blank fuel oil, sample A, and sample B and C in the descending order.

The analysis and simulation show that fuel dispersants are effective in the short term, but the effectiveness may vary with time. Therefore, special attention is required if the fuel is stored for a long time.

5.2 Dispersant mechanism

The dispersant mechanism is consisting of 3 basic properties and the mechanism is quoted from other study.

The first mechanism is wetting. The wetting is referred to a compound added to a liquid in small quantities in order to enhance the spreading of the liquid on a surface or the penetration of the liquid into the solid particles in the liquid or/and the solid substrate that gets in contact with the liquid.

The second is dispersing. Dispersing is an act to move and separate an agglomerate particle to smaller particles.

The last is stabilization. Stabilization is the most complex process and a good wetting and dispersing agent should have these properties.

A dispersant molecule consists of three distinct structural features: a hydrocarbon group, a polar group, and a connecting group or a link

5.3 Fuel oil combustion characteristics by FIA/FCA

Sample B shows a superior pre-combustion delay, while sample C shows superiority in the parameters of ignition delay, main combustion delay, end of main combustion, end of combustion, main combustion period, and after burning period. Based on the IP541/06 analysis, sample C shows superior characteristics for improving combustion.

Sample C shows the highest ECN and CCAI values, which are compatible with other ignition and combustion parameters. Although the CCAI is widely used, the deviated order cannot be easily compared with each sample, and the FIA/FCA analysis gives more coherent information to evaluate fuel ignition quality for the purpose of this study. The value of ECN is 19.4/18/19.4/19.74 as per the order.

ECN is more reliable than CCAI. However, this conclusion is based only on available laboratory tests. The effect of increased ECN on actual engine performance has not been verified.

The maximum heat release rate was 0.216 MPa/ms in sample C and the position of maximum heat release rate was 8.16 ms which is the fastest position among samples. The maximum heat release for sample A was the second highest value. However, the position of maximum heat release for sample A was delayed later than blank fuel oil. These cases explain that combustion occurred most vigorously in sample C with high combustion energy.

Sample C was the most effective at improving ignition and combustion characteristics of the fuel oil. Sample B also improved the performance up to some extent compared with blank fuel oil; however, sample C was more superior than sample B.

The improvement in combustion characteristics has been explained in other studies as the effect of increased radical pool due to the fuel additive at the initial stage of auto ignition.

Combustion characteristics were evaluated by calculating the value of (EC-ID). This value refers to the entire flame propagating period of the analysis and the result is 14.87/15.4/15.79/13.19. Sample C finalize the combustion at the earliest, implying that combustion happens the fastest in Sample C.

ABP of sample C is the shortest as 6.19ms followed by blank and sample A. Sample B recorded the longest ABP. Hence, the tendency to emit black smoke can be given by Sample B > Sample A > Blank > Sample C. But this expectation is purely based on the test at CVCC and the result could be different if the fuel combustion take place inside a real reciprocating engine. This is because the piston is continuously in motion inside the engine, keeping the temperature high and creating various orders of vibrations. These factors will affect the emission of black smoke, possibly causing the actual result to deviated from expectations.

M.ROHR is the highest for sample C at 2.16 bar/ms and the values for the other samples can be given by: Sample A > Blank > Sample B. The position of M.ROHR displays the time at which maximum ROHR was reached, indicating that the shortest position with a value of 8.16ms is found in Sample C. The order for the remaining samples is once again given by: Sample B > Blank > Sample A. The tendency of these values implies that the M.ROHR can be varied with different fuel oils and the P.ROHR, which is the index of combustion speed, can also be varied accordingly.

The AR of sample B is the highest at 7.45 and the order for the remaining sample is given as Sample A > Blank > Sample C with the values being 7.4, 7.38 and 7.32 respectively. These values are related to the energy conversion of fuel oil and sample C shows the least amount of fuel-to-energy conversion.

The study assumes that the ROHR analysis does not consider the combustion efficiency. The analysis is focused solely on time and the amount of energy produced. The actual combustion continues after P.ROHR and until EC. Hence, combustion characteristics after P.ROHR should also be considered to determine the combustion efficiency.

This simple method is derived from the concept that the ROHR and the Position of ROHR shall simultaneously be considered. Therefore, it could be theorized that stronger combustion occurs at larger angles of θ_1 and θ_2 than at smaller angles of θ_1 and θ_2. In case of θ_3, a smaller angle can be indicative of more active combustion.

However, it is important to note that vigorous combustion is not always good for the internal combustion engine. This is because vigorous combustion will lead to high combustion temperature and subsequently higher emission of NOx.

5.4 Thermogravimetric Analysis

An arch-shaped loss in mass from the beginning to up to 500℃ for samples A, B and C. A remarkable mass loss in mass cannot be seen from 500℃ to 900℃. On the other hand, blank maintains an arch-shaped mass loss from the beginning to the end of the analysis, i.e., up to 900℃.

The mass conservation ratio of samples A, B, C drop to 10% up to 500℃ with an arched shape. Even after 500℃, the mass conservation ratio has not decreased noticeably. On the other hand, the mass conservation ratio of Blank steadily arched down from the initial value until the final value at 900 ℃. Finally, mass conservation ratio at 900℃ is about 25 %.

The effects of the constituents of the additive are reducing the surface tension of the fuel oil. These phenomena can be caused by the fuel additive, which acts as a dispersant and combustion improver, because the ultimate purpose of both is to enhance the availability of residual fuel. They are also specifically designed to make the fuel droplets smaller, and in order to achieve this, reduction of surface tension takes priority.

The iron-based fuel additives have a greater effect on reducing thermo gravimetric characteristics. However, it is interesting to note that the concentration of iron itself was not a criteria for the additive's performance. Although the additive does not contain iron, the dispersant alone has also shown a similarly good thermo gravimetric performance.

In case of FIA/FCA analysis, the pressure trace and ROHR tendency were not very clear except in Sample C. Otherwise, the distinguished result of additive effects can be found in the TGA analysis.

5.5 Fuel oil consumption evaluation

5.5.1 Fuel oil consumption at low engine load

Sample A consumed the highest fuel oil, surpassing that of blank fuel oil. Sample C showed a contrasting tendency. Samples C and A had a break point on 750rpm, above which more or less fuel was consumed. Sample C recorded the lowest fuel oil consumption. Sample B recorded the lowest fuel oil consumption at every engine rpm except at 900rpm.

5.5.2 Fuel oil consumption at full engine load

Reference fuel oil is non-additive fuel oil and it recorded the highest fuel consumption. Sample C recorded highest SFOC among fuel additives at every engine load. Samples B and A recorded the lowest SFOC but sample B recorded more higher SFOC at 25% engine load. 3.87%~16.09% SFOC saving recorded every fuel additive comparing with non-fuel additive case.

The study did not measure HC and PM concentration which can be used as combustion criteria. Combustion status was assumed via investigation of CO, SO_2 and water concentration in the exhaust. Blank sample consumed much higher fuel oil and it could be emitted as increased portion of PM at the exhaust. It is well corresponding with other studies that the fuel additives can reduce PM emissions.

5.6 Investigation of fuel combustion improver effect to engine combustion

The combustion improver mechanism is anticipated to be consisted with two stages. The one is pre-combustion stage and the next one is post-combustion stage. The pre-combustion can be described that ferrocene or iron catalysts add on residual fuel. Fine particle of Fe is able to adhesive to fuel molecule. The Fe atom has high oxidation characteristics and the oxidation will be resulted in after

Fe atom attached to fuel molecule. Oxidation of Fe can result in fuel with oxygen content which is capable of leading to fuel lean combustion and it will also help to become closer to complete combustion.

The post-combustion can be described that ash, unburned metal and carbon is contained in the exhaust gas flue. When the exhaust gas flue has sufficient heat energy to overcome activation energy, the remained metal can do additional catalyst reaction. Therefore, it can make more lighter carbon, and ash by oxidation. However, after exhaust gas lose heat energy the metal can be adhered on the surface of carbon or ash and water. It will make agglomerated particulate matters.

5.7 Emission characteristics

5.7.1 Emission characteristics at low engine load

The highest concentration of NOx emitted at every engine rpm while operating with blank fuel oil. Sample A recorded the lowest NOx concentration at 600rpm and 900rpm. NOx concentration with sample B was almost constant. Sample C recorded the lowest NOx emission at 750rpm. At 900rpm, NOx emission was about 500ppm except for sample A. NOx emission followed the order Blank > Sample C > Sample B > Sample A.

Emission characteristics of PM, which normally decreased as engine rpm increased except in the blank sample during the test. The blank sample showed increased PM emission as engine rpm increased. The blank sample emitted the lowest PM at 600rpm and emitted the highest PM at 900rpm. Sample A emitted the highest PM at 600rpm and PM emission decreased as engine rpm increased and it emitted the second highest PM at 900rpm. Sample B showed the lowest PM emission throughout the PM measurement and the load point was 900rpm.

Emission characteristics of fatty acid contain additive showed that the dispersant only additive was not effectively react with residual fuel oil.

5.7.2 Emission characteristics at full engine load

Blank fuel emitted the minimum NOx among sample fuels and the NOx emission increases as engine load increases. It could be explained that the engine combustion temperature rises as engine load increase. The additive dosed fuels show more active combustion than blank fuel oil.

High O_2 and low CO_2 concentration can be explained that the fuel was not effectively reacted during the combustion with O_2. Therefore, the O_2 emission which was not reacted with fuel oil increased. On the other hand, fuel additive samples show commonly low O_2 and high CO_2 concentration. It means O_2 had well reacted with fuel during combustion.

5.8 Optical analyses

5.8.1 Raman spectroscopy

According to the G/D ratio, sample B can be told that it had most efficient combustion. On the other word, sample A showed the least efficient combustion. Sample B shows well dispersed particles. Sample A shows agglomerated condition of particles which is comparatively large. Sample C shows agglomerated condition of particles. The agglomeration is consisting of fine particles with each other.

Sample B has fine particles which are well dispersed on the surface. Sample A and C shows agglomeration of particles and sample A is normally with bigger particles than sample C. Due to the small intensity gap, the analysis result is within the tolerance range.

5.8.2 Energy Dispersive X-Ray Spectroscopy

Carbon content was commonly decreased with additives. Oxygen content was increased and sample A has the highest oxygen content and sample C has the second highest oxygen content. Comparing with blank fuel oil, additive was effective to make heavy fuel to more lighter than blank.

Blank and sample A shows graphite structure which is consisting the black carbon. It could furtherly be explained that the useful hydrocarbon species well reacted during combustion and only useless carbon species remained.

The TEM result is not identical to Raman spectroscopy. Because, sample A shows low black carbon fraction and blank, sample B and C show graphite on the raman analysis. In case of raman, the result was within tolerance, therefore, it has less reliability.

Carbon content decreased at every additive sample. Oxygen content increased at every sample comparing with blank. Sample C shows some metals such as Ni, Si, V and Fe. Sample C was aimed to increase iron content as high as possible but, the iron content was not found at TEM analysis.

The study tried to find reaction mechanism of the residual fuel additives especially combustion catalyst and dispersants. The study can make a conclusion that the additive can react positively to fuel and engines. The experiments on the study are based on the 4-stroke cycle diesel engine and 2-stroke cycle diesel engine has less effects on a reference. Therefore, it needs further verification to find the effects on 2-stroke cycle diesel engine.

The additives verified on the study can be helpful to the engines which uses heavy residual fuel and have short stroke and 4-stroke cycle engine. Mean piston speed can comparably increase when the engine configured in the case.

Unburned carbon, particulate matters can be decreased by the effects of fuel additives but, NOx reduction can not be remarkably reduced according to the mechanism suggested by fuel additive makers.

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