

BLENDING RATIO OF LOW SULPHUR DIESEL A KEY TO LOWER EMISSIONS

A. ADILAKSHMI ^{1*}, V. VENKATESAN ² AND V. TAMILMANI ¹

¹ Department of Chemistry ² Department of Civil Engineering, University College of Engineering,
(A Constituent College of Anna University Chennai), Ariyalur 621 704, India

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ABSTRACT

Sulphur content is one of the key properties of fossil fuels that are related to combustion characteristics including generation of pollutant emission. It is impossible to clean the air, or in particular to reduce air pollution from the transportation sector, without getting Sulphur out of fuels. Sulphur is a pollutant directly, but more importantly, Sulphur prevents the adoption of all major pollution control technologies. No significant air pollution reduction strategy can work without reducing Sulphur to near-zero levels. Sulphur is a naturally occurring component of crude oil and is found in diesel. When this fuel is burned, Sulphur is emitted as Sulphur dioxide (SO₂) or sulphate particulate matter. Sulphur fouls conventional and advanced technologies to control vehicle emissions, including carbon monoxide (CO), particulate matter (PM), nitrogen oxides (NO_x) and hydrocarbons (HC). Low-Sulphur fuels are the key to reducing emissions from existing vehicles and enabling advanced control technologies and fuel-efficient designs for new vehicles. This paper addresses the need to reduce Sulphur in transportation fuels by blending of High Speed Diesel (HSD) with Low Sulphur Heavy Stack (LSHS) and Raw Diesel (RD) with Low Sulphur Heavy Stack (LSHS) to meet the specification of Light Diesel Oil (LDO) and the benefits that can be realized in terms of total pollutant emissions. The blending ratio of for the HSD: LSHS do not meet the required specification and RD: LSHS meeting the specification of LDO in 80:20 ratios.

INTRODUCTION

Sulphur is naturally present in small quantities in petroleum and coal. Sulphur dioxide (SO₂) has been recognized for decades as a major cause of the "acid rain" and air pollution which affect urban and indus-

trial areas. More recently, it has been recognized that SO₂ emissions contribute to the formation of secondary inorganic aerosol gases, fine particles which are harmful to human health.

International shipping uses heavy fuel oil (residual fuels) with very high Sulphur content. The

marine fuel currently in use is on average 2,700 times dirtier than the fuel used in the road sector where strict limits have applied for many years. Maximum limit values applicable for international shipping are set by International Maritime Organization (IMO) in the Annex VI of the international convention for the prevention of pollution from ships, the so called MARPOL Convention.

Impact of Sulphur on Vehicle Emissions

Low Sulphur fuel allows for the further benefit of advanced control technologies for diesel vehicles. Diesel particulate filters can be used with low Sulphur fuel but only achieve approximately 50% control efficiency. Selective catalytic reduction can be used for over 80% control of NO_x emissions.

Near-zero Sulphur fuel allows for the use of NO_x absorbers, increasing NO_x control to over 90% in both diesel and gasoline vehicles. This enables more fuel-efficient engine designs, designs that are incompatible with current emissions control systems. Particulate filters achieve the maximum efficiency with near-zero Sulphur fuels, approaching 100% control of PM. Measures to reduce the sulphur concentrations in light and heavy fuel oils used in stationary facilities are included as part of the key strategies in the department's comprehensive planned actions. Reduction of sulphur in on-road and off-road diesel fuels is also considered since the adverse effects of sulphur derived emissions from combustion sources on the environment has been widely documented (Lee, *et al.* 2000 and Tushingham *et al.*, 2001)

Emissions of sulphur dioxide (SO₂), sulphur trioxide (SO₃), nitrogen oxides (NO_x) and particulate emissions are of prime environmental and health concern and the fuels' performance can be measured in terms of these emissions. One of the potential emission benefits of using low sulphur fuels may be in the reduction of particulate matter (PM) including fine particulate emissions. Fine PM is generally defined as the materials that are less than 2.5 µm aerodynamic diameter and those whose aerodynamic diameter is less than 10 µm. Control or reduction of fine PM from various combustion processes is of particular interest to the departments since they have been linked to adverse health effects (Bates, 1992; Lee, 1992; Dockery *et al.*, 1992 & 1994 and Pope, 1995).

For diesel vehicles with no controls, the amount of Sulphur in the fuel is directly related to SO₂ and PM emissions; some SO₂ emissions are converted in the atmosphere to Sulphate PM. This is shown in figure

1. According to US EPA (Rao, 1997) approximately 2% of the Sulphur in the diesel fuel is converted to direct PM emissions which are basis of the Figure 2.

Global Trends on Low-Sulphur Fuels

In the developed world, auto makers and fuel refiners have had to apply their impressive technical and organizational capabilities to meet increasingly strict environmental regulations. The result has been reduced Sulphur levels and ratcheted-down emissions standards for all types of vehicles. Meanwhile, long-term environmental challenges and prospect of still stricter requirements in the future are spurring further research and technology development.

In developing countries, where vehicle numbers are increasing exponentially, high-Sulphur fuels continue to be the norm and to inhibit the introduction of new vehicle technologies. By instituting early policies to lower Sulphur levels and set strict emissions standards, these countries can allay the mounting human health impacts of increasing vehicle numbers and reduce the burden associated with cleaning up existing vehicles. In doing so, countries relatively new to Sulphur regulation may wish to build on the experience of countries that have achieved and taken advantage of, low-Sulphur fuels.

Further, countries should be increasingly willing to help each other overcome the fuel quality barrier and move to low emission vehicles. Local health and environmental benefits, though themselves sufficient reason to require cleaner fuels, are no longer the only issue: vehicle emissions are of increasing global significance. Pollutants traditionally of local concern such as PM and ground-level ozone now appear to impact the global climate.

The heavy fuel oil used in marine vessels can become a "dumping ground" for very high-Sulphur feedstock's. Due to the poor quality of the cheap bunker fuels used in maritime transport, SO₂ shipping emissions are projected to increase and by 2020 exceed SO₂ emissions from all land-based sources such as power plants in the EU, which over the past several decades have been reduced dramatically at great cost to industry.

In July 2011 the European Commission published a proposal to revise Directive 1999/32/EC (the "Sulphur in fuels directive") that regulates the maximum level of Sulphur permitted for fuels used in the shipping sector. The International Maritime Organization (IMO) has already set standards for this and this EU directive is set to turn these international limits into

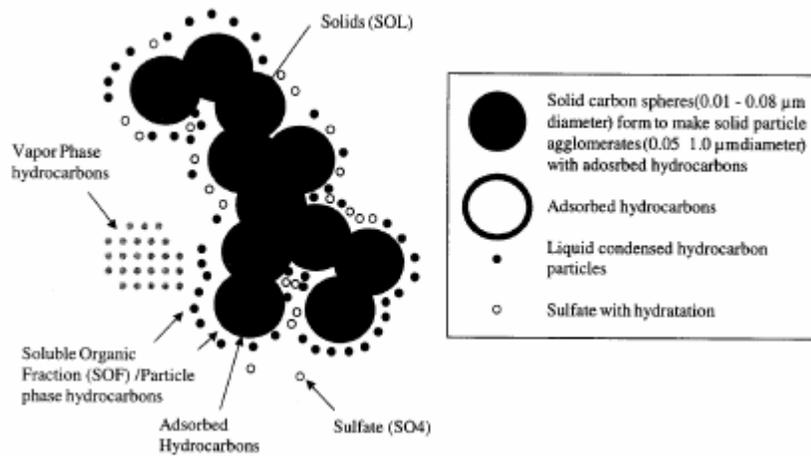


Fig. 1 Change of SO₂ emission into Sulphate PM

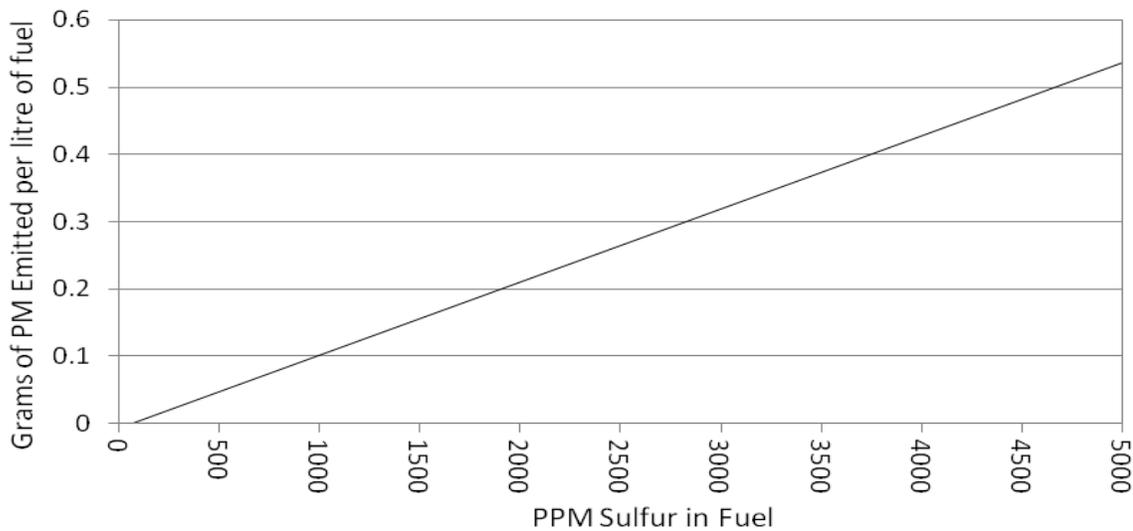


Fig. 2 Direct PM Emissions as a Function of Diesel Fuel Sulphur Level

EU law and probably extend the requirements in some areas.

The heavy fuel oil used in international shipping contains on 2700 times more Sulphur than road fuel. Sulphur contained in fuel causes emissions of Sulphur dioxide (SO₂) and also contributes to the formation of secondary particulate matter (PM) that is particularly harmful both to humans and the environment. These emissions have a major health impact, with shipping air pollution estimated to cause around 50,000 premature deaths per year in Europe. SO₂ emissions also cause environmental problems such as acid rain affecting soil and water and damage to biodiversity.

Location Description

The experiment was carried out at Chennai petroleum Corporation Limited in Cauvery Basin Refinery (CBR), a Public Sector situated at Panangudi, Nagapattinam district. This Refinery is a part of Chennai Petroleum Corporation Limited Manali; Chennai. This Refinery is the first to get ISO-9002 among the Refineries. CPCL-CBR is setup to refine the crude which is available from the oil well situated in and around the Cauvery delta places. A few promising oil wells are located at Narimanam Kovilkalappar, Kamalapuram, Adiakkamangalam, Bhuvanagiri, CPCL- CBR. Capacity to distillate is promoted from 0.5 million to 1

million metric tons of crude per annum. Due to lack of sufficient crude in Narimanam, some amount of Crude is being imported from Nigeria and Malaysia. The Crude used by CPCL-CBR is light crude and the following are main products.

1. Liquefied Petroleum gas (LPG)
2. Light Naphtha (LN)
3. Heavy Naphtha (HN)
4. Superior Kerosene (SK)
5. High Speed Diesel (HSD)
6. Low Sulphur Heavy Stack (LSHS)

Process Description

Crude Distillation Unit (CDU)

Crude supplied by ONGC contains Hydrocarbons like paraffin's, olefins, Naphthenes and Aromatics and some other impurities like water, salts, Sediments Sulphur, Nitrogen compounds etc., Table 1 shows fractions obtained from Crude Distillation and Boiling range and their uses.

Crude received from ONGC is stored in tanks and allowed to settle for some time. By the way of Density difference water and Sediments are removed as much as possible. Then the Crude is pre-heated by exchangers and sent through the desalting along with DM water which contains a high potential grid. Here the water particles get charged and collapsed to form bigger particles and settled due to Density difference at the bottom. Desalted Crude is heated slowly to high temperature by different heat exchangers. This Crude is again heated up to 360 Degree Celsius and gets evaporated. Hydrocarbons having higher boiling point (heavier product) are in a liquid state which are named as Reduced Crude oil and cooled in tempered water and sent to storage tank at 80 degree Celsius.

The vaporised mixture is flashed in the AD column where the lighter vapours goes to the top of the column and heavier vapour goes to the middle of the column. In the top of the column the hydrocarbon mixture named as Light Naphtha and Liquefied Petroleum Gas get cooled and sent to stabilizer. At the middle of the column the middle pump around mixture is fed to the stripper. Here the products HN, SK and HSD are separated out by stripping steam.

METHODOLOGY

To reduce the Sulphur in transportation fuels by blending of High Speed Diesel (HSD) with Low Sulphur Heavy Stack (LSHS) and Raw Diesel (RD) with Low

Sulphur Heavy Stack to meet the specification of Light Diesel Oil (LDO) and the benefits that can be realized in terms of total pollutant emissions. Light diesel oil whose specifications are within limit prescribed by IMO. This can't be obtained directly from fractional distillation. These LDO can be obtained by blending final waste product LSHS obtained from distillation of crude oil with raw diesel. Table 2 gives the required specifications of the Light Diesel Oil.

LSHS though having Low sulphur content can't be used directly as fuel since at normal room temperature it act as solid. Raw diesel in spite of having low Sulphur content because of its heavy cost can't be offered in ships and barges. So with the view to have a fuel having low cost, and low sulphur content Blending between Raw diesel and LSHS was done under various ratio. For each blending ratio the Quality parameters were analysed.

According to American Society for Testing and Materials (ASTM) the required specifications for the High Speed Diesel, Raw Diesel were studied with the standard procedures. The Density, Flash Point (Abel and Pensky method), Pour Point, Viscosity, Carbon Residue, Water Content, Sediment, Ash and Sulphur were analyzed for the blending ratio and compared to the standards of LDO.

Determination of Sulphur by Bomb Method

The Sample is oxidized by combustion in a bomb containing oxygen under pressure. The Sulphur as sulphate in the bomb washing is determined photometrically in a spectrophotometer.

Preparation of bomb and Sample

Cut a piece of firing wire 100 mm in length coil the middle section and attach the two ends of negative and positive terminals. Arrange the oil cup in it above the one side of Sample cup. Insert between the two loops of the coil a wisp of cotton or nylon thread of such length that one end will dip into Sample cup. Place about 5 mL of sodium carbonate solution in the bomb and rotate the bomb in such a manner that the interior surface is moistened by the solution. Place the Sample cup in position and arrange the cotton wisp or nylon thread so that the end dips into the Sample. Assemble the bomb and lighten the cover securely. Admit Oxygen slowly until pressure is reached as indicated in Table 3.

Immerse the bomb in a cold distilled water bath connect the terminals to the open circuit. Close the circuit to ignite the Sample. Remove the Bomb form

Table 1. Fractions obtained from Crude Distillation and Boiling range and their uses

Sl.No.	Fraction	Boiling Range	Uses
1.	Gas	Below room temperature	Fuel of gasoline (by polymerization) and rubber
2.	Naphtha on further refraction		
	a) Petroleum ether	50-70 °C	As solvent in varnish and rubber industries for dry cleaning.
	b) Petrol (or) gasoline	70-90 °C	Motor Fuel dry cleaning, for making petrol, air gas
	c) Ligroin (or) Light Petrol	90-120 °C	As solvent in dry cleaning.
	d) Benzene	120-150 °C	In vanish and dry cleaning
3.	Kerosene	150-300 °C	As Fuel and illuminate for making oil gas
4.	Gas oil (or) heavy oil	Above 300°C	As Fuel in diesel engine, cracked to yield more gasoline
5.	Residue from evaporation fractionation by vacuum distillation is separated in to		
	a) paraffin wax		For making candles and book polish.
	b) lubrication oil	On cooling	For lubrication.
	c) Vaseline		In toilet goods ointments and for lubrication.
	d) pitch	On redistilation	In paints and varnishes.
	e) petroleum ether		As Fuel.

Table 2. Specification of Light Diesel Oil

S.No.	Characteristics	Requirement
1.	Flash point (Pensky Martens Closed) Min °C	66
2.	Viscosity, Kinematic at 40°C cst	2.5 to15.7
3.	Carbon Residue Percent by Weight Max.	1.5
4.	Water Content, Percent by Volume, Max	0.25
5.	Sediment, Percent by Weight, Max	0.10
6.	Ash, Percent by Weight, Max	0.02
7.	Sulphur, total Percent by Weight, Max	1.8
8.	Pour Point, °C Max	12°C in winter & 21°C in summer
9.	Density at 15°C kg/m ³	820-870

Table 3. Pressure level for admitting the Oxygen

Capacity of Bomb (mL)	Minimum Gauge Pressure (Atm.kg/cm ³)	Maximum Gauge Pressure (Atm.kg/cm ³)
300-350	38(39)	40(41)
350-400	35(36)	38(38)
400-450	30(31)	32(23)
450-500	27(28)	29(30)

the bath after immersion for at least 10 min. Release the pressure, open the bomb and examine the contents. If traces of unblended oil (or) sooty deposits are found, discard the determination. Thoroughly clean the bomb before putting in it to use again.

Collection of Sulphur solution

Raise the interior of the bomb, the oil cup and the inner surface of the bomb cover with a fire jet of distilled water and collect the washing in a 600 mL beaker. Having a mark to indicate 75 mL. Remove any precipitate in the bomb by means of rubber policeman and wash the base of the terminals indicators. Add 10 mL of saturated Bromine water to the washing in the beaker. Place the Sample in 50 mL beaker. Add 5 mL of saturated Bromine water, 2 mL of HCl and enough distilled water just to cover the cup. Heat the contents of the beaker to just below its boiling point for three or four minutes and add it to the beaker containing the bomb washings, wash the Sample cup and the 50 mL beaker is thoroughly washed with distilled water. Do not filter any of the washing since filtering would remove any Sulphur present as insoluble material.

Determination of Sulphur

Take the absorption solution in 50 mL Nessler cylinder and make up to 50 mL by using DM water and 10 mL of conditioning reagent, a pinch of BaCl₂ shake well after 10 min. Read the absorbance at 420 nm do

Table 4. Parameters of High Speed Diesel

Parameter	Std. Specification	Unit	HSD	RD	LSHS
Density	820-870	g/mL	826	855	907
Flash point	Min 35	°C	43	90	206
Carbon Residue	Max 1.0	%Wt	0.08	0.12	4.2
Water Content	Max 0.05	%Vol	0.01	0.01	0.05
Sediment	Max 0.05	%Wt	0.01	0.01	0.02
Ash	Max 0.01	%Wt	Nil	Nil	0.02
Sulphur	Max 0.05	%Wt	0.02	0.03	0.15
Pour Point	Max + 12(w)				
Max + 15(s)	°C	+3	+12	+48	
Viscosity	2.0-5.0	Cst	2.5	3.9	12.3

Table 5. Parameters of Blended fuel (HSD with LSHS)

Parameters	Ratio's				
	90:10	80:20	75:25	60:40	50:50
Flash point °C	47	51	52	54	58
Pour point °C	+15	+18	+21	+24	+27
Kinematic Viscosity cst	3.32	4.73	5.29	7.2	15.14
Sulphur	0.18	0.17	0.15	0.18	0.09

Table 6. Parameters of Blended fuel (RD with LSHS)

Parameters	Ratio's		
	90:10	80:20	70:30
Flash point °C	92	96	98
Pour point °C	+12	+15	+23
Kinematic Viscosity cst	4.9	5.6	9.1
Sulphur	0.03	0.026	0.038

the blank simultaneously.

RESULTS AND DISCUSSION

Flash point, Viscosity, Carbon Residue, Water Content, Sediment, Ash, Acidity, Sulphur, Pour Point, Density measurement of High Speed Diesel, Raw Diesel and Low Sulphur Heavy Stack were analyzed and is presented in the Table 4.

Blending of High Speed Diesel and Low Sulphur Heavy Stack

Blending of HSD and LSHS were done for various ratios 90:10, 80:20, 75:25, 60:40, 50:50 and Flash point, Viscosity, Pour Point and Sulphur contents were measured and are presented table 5. From the table 5 it is observed that none of the ratios meets the specifications of Light Diesel Oil. The blending ratio 75:25 themselves attains the maximum Pour Point limit of Light

Diesel Oil. But the Flash Point is not meeting the specification limit. Further blending of HSD and LSHS, the Pour Point will not meet the specification. Since the above Parameters, has not been meeting specification of LDO, other Parameters need not be analyses. Hence blending of High Speed Diesel with Low Sulphur Heavy Stack won't be suitable as the fuel for the engines. If the blended fuel is used the emissions from the fuel is higher than the standards.

Blending of Raw Diesel and Low Sulphur Heavy Stack

Blending of RD and LSHS were done for various ratios 90:10, 80:20, 75:25, 60:40, 50:50 and Flash point, Viscosity, Pour Point and Sulphur contents were measured and are presented in Table 6.

The blending ratio 90:10 and as well as 80:20 ratio's are well within the specification limit of LDO were as further blending of LSHS to Raw Diesel 70:30 is not within the specification limit. The other Parameters were analyzed and found to be within the specification limit of LDO given in Table 2. The blending of Raw Diesel and LSHS was done mainly for having Fuel LDO which is more economical than Raw Diesel. Hence the ratio 80:20 is more economical than 90:10. The optimum blending ratio of Raw Diesel and LSHS to meet the specification of light diesel oil (LDO) is found to be 80:20. Thus from the above discussion, it was concluded that the blending between LSHS &

HSD do not meet the specification of LDO given in Table 2.

CONCLUSION

Light Diesel Oil is mainly used as a Fuel oil in marine vessels. To meet the specification for the above, HSD & LSHS have been taken for blending for the various ratios like 90:10, 80:20 etc. Being the low Flash point of the blending mixture of HSD which do not meet the specification of LDO. The blending mixture of Raw Diesel and LSHS has been taken for analysis for the various Parameters like Flash point, Pour Point and kin. Viscosity, Sulphur and other such parameters. All the Parameters were meeting with specification in the ratios of 90:10 and also 80:20 (Raw Diesel + LSHS). Hence it is concluded that 80:20 blending ratio is better than 90:10 ratio, as per the standard requirement of Raw Diesel is low and economically viable in 80:20 ratio and also meeting the specification of LDO. With high Sulphur levels, diesel catalysts produce high levels of hazardous Sulphate. Some advanced catalyst technologies such as NO_x adsorbers are precluded by high levels of Sulphur. Finally, PM filter performance is impaired by higher levels of Sulphur.

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REFERENCES

- American Society for Testing Manuals volume 05-01, 05-02 & 05-03.
- Bates, D.V. 1992. Health indices of the adverse effects of air pollution: The question of coherence. *Environ. Res.* 59 : 336-349.
- BIS 2007. Bureau of Indian standards for testing of petroleum and its products, IS 1448(Part 1/Sec 1 and sec 2, 2002).
- CPCL, Manual of Crude Distillation Unit Operation. Diesel Emissions Control - Sulphur Effects (DECSE) project, 2001, US DOE.
- Dobromir, I. Yordanov, Aleksandar, N. Dimitrov, Zlatotsvet, B. Tsonev and Petko St Petkov, 2010. Flash point correlation with specific gravity, refractive index, and viscosity of base oil fractions. *Asian Chemistry Letters.* 14 (2) : 171-176.
- Dockery, D.W., Schwartz, J. and Spengler, D.J. 1992. Air pollution and daily mortality: Associations with particulates and acid aerosols. *Environ. Res.* 59 : 362-373.
- Dockery, D.W. and Pope, C.A. 1994. Acute respiratory effects of particulate air pollution. *Annu. Rev. Public Health.* 15 : 107-132.
- EIA, the Transition to Ultra-Low-Sulfur Diesel Fuel: Effects on Prices and Supply. 2001, U.S. Department of Energy: Energy Information Administration: Office of Integrated Analysis and Forecasting: Washington, DC.
- George, V. Dyroff, 1993. *Manual on Significance of Tests for Petroleum Products.* (Sixth edition).
- Lee, S. Win, 1992. A national round robin program on sulphur analysis test methods for incorporation into the new low sulphur diesel fuel specifications. Confidential client report to Environment Canada and CGSB. Energy Research Laboratories. Energy, Mines & Resources Canada, Division Report ERL 92-69 (CF).
- Lee, S. Win, Pomalis, R. and Kan, B. 2000. Methodology development for measuring fine particulate emissions from fossil-fuel stationary combustion systems. Phase II, Report CETC 00-09 (CF).
- Pope, C.A. 1995. Combustion-source particulate air pollution and human health: Casual associations or confounding? Particulate Matter: Health and Regulatory Issues. *Air and Waste Management Association VIP-49:* 60-77.
- Rao T. 1997. *Effects of Sulphur on Exhaust Emissions*, US EPA.
- Shaha, A.K. 1974. *Combustion Engineering and Fuel Technology*, Oxford & IBH Publishing Company.
- Tushingham, M. and Bellamy, J. 2001. Potential to reduce emissions of sulphur dioxide through reducing sulphur levels in heavy and light fuel oils. *Discussion paper, Environment Canada*, March 22.