POTENTIAL EMISSIONS OF KYOTO AND NON-KYOTO CLIMATE ACTIVE COMPOUNDS IN THE PRODUCTION OF SUGARCANE ETHANOL

EUGENIO SANHUEZA

SUMMARY

Sugarcane ethanol is the most commercially developed liquid biofuel. The potential emissions of Kyoto and non-Kyoto Protocol climate active compounds in the production of sugarcane ethanol in agricultural lands are evaluated herein. Various scenarios are considered, such as low or high N_2O emission from Nfertilizers, inclusion or not of pre-harvest burning, uncontrolled or controlled emissions in bagasse based boilers, and 20 or 100 years time horizons in GWPs. The CO_2 emitted in ethanol fuel combustion is recycled during sugarcane "re-growing" and does not count as greenhouse gas. However, even though many uncertainties remain, the available information allows estimating that CO_2 -eq emissions are very large when ethanol production is based on pre-harvest burning and there is non-controlled particle emission in boilers. In these scenarios, compared with the combustion of equivalent amounts of gasoline, higher CO_2 -eq emission would take place. Halting sugarcane field burning would not be sufficient to revert the situation, especially in a 20-years time horizon. Only when more environmental friendly procedures are applied, a significant saving of CO_2 -eq emissions occurs at 20 and 100-years horizon scenarios. In all scenarios, non-Kyoto Protocol compounds make an important net contribution. Therefore, if a real evaluation of climate active compounds emissions is to be reached, it would be crucial to include these compounds in life cycles studies. To reduce uncertainties, especially of non-Kyoto compounds, additional research is needed.

he negative environmental consequences and concerns about the supply of fossil fuels have led to the search

of renewable sources of energy. At present, fossil fuels represent ~80% of the total world energy supply. However, the presently known reserves of oil, natural gas and coal will only last around 41, 64 and 155 years, respectively (BP, 2006). The remaining ~20% is supplied by nuclear energy (~6.3%) and renewable (~13.7%). The renewable sources correspond to traditional biomass (~8.5%), hydropower (~1.7%) and to the growing "new renewable sources" (~3.4%), which include modern biomass (1.9%), geothermal (0.23%), wind (0.32%), solar (0.53%), and small hydropower (0.41%) (Goldemberg, 2004, 2007). The largest new renewable source, modern biomass, refers to biomass produced in a sustainable way and used for electricity generation, heat production, and liquid fuels for transportation.

Although CO₂ is emitted during the combustion of bio-ethanol, this is removed afterwards from the atmosphere to re-grow the crop used to produce the fuel. However, this environmental advantage would be cancelled if large quantities of fossil fuels are needed for the growth process of the bio-fuel crop and/or large quantities of climate active compounds (not coming from fossil fuel) are released to the atmosphere during the production process. It is important to point out that in the present evaluation it is assumed that sugarcane plants are grown in already existent agricultural lands. Several authors (Righelato y Spracklen, 2007; Fargione et al., 2008; Searchinger et al., 2008) have reported that changing native soils to agricultural fields will emit large amounts of CO_2 to the atmosphere, which is not re-captured for decades.

Bio-ethanol is mainly produced from corn and sugarcane. Most of bio-fuel life cycle analysis (LCA) studies have been undertaken in European or North American contexts, mainly dealing with the evaluation of corn-ethanol. These studies have been reviewed by Larson (2005), Wang (2005), Farrell et al. (2006), Fleming et al. (2006) and Hammerschlag (2006). In general, they indicate that current corn ethanol technologies are less petroleum-intensive than gasoline but greenhouse gas (GHG) emissions are quite similar to those of gasoline. Only two "independent" estimates of GHG emissions and energy balances of sugar cane ethanol production are found in the literature (Macedo et al., 2004; De

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Eugenio Sanhueza. Doctor in Sciences, Universidad de Chile. Researcher, Instituto Venezolano de Investigaciones Científicas (IVIC), Venezuela. Address: Laboratorio de Química Atmosférica, IVIC. Apdo. 22117. Caracas 1020A, Venezuela. e-mail: esanhuez@ivic.ve

Oliveira *et al.*, 2005); in this case, both net energy output and Kyoto GHG emission are very favorable.

In the future, greater quantities of ethanol are expected to be used as a motor fuel. The European Union (EU) has agreed on an action plan for bio-fuels that comprises at least 10% of the region's transport fuel used by 2020; the Philippines Biofuels Act 2006, requires that gasoline sold in the country must contain at least 5% ethanol by February 2009; Japan is planning to implement a 3% mandatory level of ethanol in cars. Brazil, the mayor producer of sugarcane ethanol, will increase its production for local use and export (Goldemberg, 2007), and there is increasing interest to spread the techniques developed there to other Latin American countries (Lula da Silva, 2007). Therefore, evaluation of climate implications of bio-ethanol production from sugarcane is quite pertinent. In this paper, emissions of Kyoto and non-Kyoto climate active compounds to the atmosphere, during the production of sugarcane ethanol in agricultural lands, are evaluated; emphasis is placed on emissions from pre-harvest burning and bagasse combustion in boilers, which involve biomass combustion that produce significant amounts of semi-oxidized compounds (e.g. CO, BC) not included in the Kyoto Protocol.

Production of Sugarcane Ethanol

Sugarcane ethanol is the most commercially developed liquid biofuel. The production of sugarcane ethanol has two basic steps: sugar production by cultivating cane and industrial ethanol processing.

Sugarcane cultivation and harvest

Sugarcane is one of the most efficient crops regarding photosynthesis, with yields of 70-80tonnes/ ha (Sequera et al., 1984, Ripoli et al., 2000, Yadav, 2003, Macedo et al., 2004, Restuti and Michaelowa, 2007). In general, sugarcane cultivation is based on a ratoon system (after the first cut the same plant is cut several times on a yearly basis). After 12-18 months from planting, the cane is ready for the first cut. In this moment, it is common to burn down the cane-field in order to simplify manual harvesting. After cutting, the cane stalks are transported to the mill. The energy used in this step (agricultural machinery, trucks) is mainly fossil fuel diesel (Macedo et al., 2004).

Industrial production of ethanol

In an industrial area. 5600-6400L of ethanol and 21-28 tonnes of bagasse are produced per ha (Moreira and Goldemberg, 1999; Macedo et al., 2004, de Oliveira et al., 2005). In mills, cane-juice and bagasse are produced. Production of ethanol from cane juice includes microbial (yeast) fermentation of sugars, distillation and dehydration (optional). The energy to achieve the industrial production step would be internally provided by the combustion of ~90% of the bagasse produced (Macedo et al., 2004; Autrey and Chang, 2006; Ho, 2006; Restuti and Michaelowa, 2007). Fermentation time varies from 4 to 12h and chemical efficiencies range 80-90%, resulting in an alcohol content of 7-10°GL, called fermented wine. After fermentation, water is removed from the fermented wine solution by distillation, but the purity is limited to ~96% (hydrated ethanol, 96°GL, Gay-Lussac) due to the formation of a low-boiling water-ethanol azeotrope. It is important to note that the 96°GL ethanol may be used directly as fuel by specially designed Brazilian cars (Moreira and Goldemberg, 1999). Further dehydration to produce anhydrous ethanol (99.7°GL) is achieved by several techniques, such as physical absorption process using a molecular sieve or calcium oxide, or azeotropic distillation after addition of cyclohexane or other compounds (Smeets et al., 2006).

GWPs of Kyoto and Non-Kyoto Climate Active Compounds

One way to compare the climate impact of a compound emitted to the atmosphere is by using the "global warming potential" (GWP), which translates the level of emissions into a common measure in order to compare their relative radiative forcing without directly calculating the changes in atmospheric concentrations. GWPs are calculated as the ratio of the radiative forcing that would result from the emissions of 1kg of a climate active compound to that from emission of 1kg of \overline{CO}_2 over a period of time. Recently, other metrics have been proposed for weighting the climate impact of GHG emissions, like the GTP (global temperature change potential; Shine et al., 2005), the CEF (CO₂ equivalent factor; Delucchi, 2006), and the WI (warming index; Berntsen et al., 2006), which are likely to handle short-lived compounds in a better way. However, since GWPs are used within the Kyoto Protocol and values for practically all the compounds evaluated can be found, GWPs were used in this evaluation. According to Fuglestvedt *et al.* (2003) GWPs would have advantages over other metrics in term of political feasibility.

The GWPs for long lived gases (e.g. CH₄, N₂O) are well established and applied in the Kyoto Protocol. On the other hand, the GWPs of atmospheric short-lived compounds (e.g. CO, black carbon), not included in the Protocol, are more uncertain and their radiative forcing will depend on the location and timing of the emission (Derwent et al., 2001; Fuglestvedt et al., 2003; Bond and Sun, 2005; Berntsen et al., 2006). Significant efforts have been made to produce GWPs of short-lived pollutants (see references in Table I), which give an indication of the impact of their emission on climate. As expected, they have larger GWPs for the shorter time horizon (20 years) and their control would produce quicker responses (Andreae, 2001; Jacobson, 2002; Bond and Sun, 2005). Table I summarizes the GWPs used in this work to evaluate the CO₂-eq emissions in the production of sugarcane ethanol.

Carbon monoxide (CO) has a negligible direct GWP but leads to indirect radiative effects through reduced OH levels, which enhances methane atmospheric lifetime and tropospheric production of ozone, a potent GHG. Variations of GWP values with location are small and Berntsen *et al* (2005) suggested that one global number may be acceptable. GWPs of 5.0 and 2.0 for 20-year and 100-year time horizons, respectively, were used in the calculations of CO_2 -eq emissions.

Non-methane volatile organic compounds (NMVOCs) include a wide spectrum of hydrocarbons with varying lifetimes. Their atmospheric reactions affect ozone and methane concentrations in the troposphere, producing a positive indirect radiative forcing effect. Only 100year horizon GWPs are found in the literature (Table I) and IPCC (2007) gives a weighted average of 3.4, with an estimated uncertainty range of -50% to +100%. Based in the difference of GWPs between 20- and 100-years of other short-lived compounds, the 20-years horizon GWP for NMVOC was assumed to be 10.

Methane, in presence of NO_{x_i} is oxidized in a chain reaction that produces ozone. Therefore, NO_x emissions lead to two indirect radiative effects, methane decrease and ozone increase, which have opposite signs and are evaluated separately. As shown in Table I, very different net GWP values have been reported for different regions of the world, which do not agree even on their sign (note that these studies do not include the effect of nitrate aerosols). In IPCC (2007) there is no indication or suggestion of any

"central" value. Therefore, the contribution of NO_x to the CO₂-eq emissions was not calculated. However, considering that NO_x emissions from biomass combustion (see Tables III and IV) are lower than the ones for organic particles, and that the cooling effect of NO_x suggested by CEF factors (Delucchi, 2006) would be $\sim 10 \times$ lower than that for organic particles, the NO_x contribution to the net CO₂-eq emission is likely to be very low.

Black carbon (BC), formed by incomplete combustion, is a major pollutant that has received inadequate or no attention in the evaluation of bio-fuels impact on climate (Delucchi, 2006; Jacobson, 2006). According with Jacobson (2001), at a global scale BC aerosols may be the second most important component of global warming after CO_2 in terms of direct forcing. BC is the main light-absorbing

component of aerosols. The radiative properties of individual aerosol particles depend on the extent to which BC is mixed with primarily scattering aerosol components, such as sulphates and organics. BC scatters (back to space) and absorbs portions of incoming solar rays, leading to a reduction in solar radiation reaching the Earth's surface. In addition, BC absorbs radiation from the diffuse upward rays of scattered sunlight, reducing the solar radiation reflected back to space (Bond and Sun, 2005; Seinfeld, 2008). The net effect (scattering vs absorption) is a warming of the atmosphere, with an impressive large GWP. BC GWPs found in the literature are presented in Table I. The values from Jacobson (2007) are significantly larger because they refer to fossil fuel BC. Considering that this evaluation mainly involves emissions from biomass combustion, more weight was given to the other estimates, which deal with general BC emissions. Relatively conservative GWPs were used in calculation, 2000 and 500 for the 20- and 100-years time horizons, respectively.

Atmospheric organic carbon (OC) consists of primarily scattering particles that can be white to clear brown. They contribute directly to global cooling because they reflect sunlight back into space. With only one excep-

TABLE I				
GWPS OF CLIMATE ACTIVE COMPOUNDS				

		GWP	Reference
	20-years	100-years	-
Kyoto GHG			
CO_2	1	1	IPCC (2007)
CH_4	72	25	IPCC (2007)
N ₂ O	289	298	IPCC (2007)
Non-Kyoto comj	pounds		
СО	10	3.0	Fuglestvedt et al. (1996)
		2.1	Johnson and Derwent (1996)
	2.8-14	1.6-7.2	Daniel and Solomon (1998)
		1.6	Derwent et al. (2001)
		1.9 Europe ^d 2.4 Asia ^d	Berntsen et al. (2005)
NO _x		-12 NH ^e	Derwent et al. (2001)
		-31 SH ^e 25 to 29 Asia -2.7 to +4.1Europe	Berntsen et al. (2005)
NMVOC		1.1-6.2	Johnson and Derwent (1996)
		1.8-5.5	Collins et al. (2002)
BC-particles	2530ª 4470 ^b	840-1280ª 1500-2240 ^b	Jacobson (2007)
	2200	680	Bond and Sun (2005)
	2000°	500	Hansen et al (2007)
		480 ^f (374-677)	Reddy and Boucher (2007)
OC-particles	[-200]	[-50]	See text

^a Fossil fuel soot, ^b BC in fossil fuel soot, ^c These GWPs are an average for the current distribution of BC sources, ^d Calculated as SWGPs and converted to GWPs, ^e As given by IPCC (2007), ^f Global average (range from different regions).

tion, no values for the GWP for OC-particles were found in the literature. Tami Bond (personal communication in Mac-Carty et al., 2007) estimated a likely negative value of -50 CO₂- eq for OC particles (100-year time horizon). Clearly, this GWP has a very large uncertainty; however, in order to make a comprehensive evaluation of the impact of particles (BC and OC, which have opposite effects) emitted during the production of sugarcane ethanol, this preliminary estimated value was used in the present evaluation. An indirect evidence of the soundness of this estimate is found in the ratio given by Delucchi (2006) of CO₂-equivalence factors (CEFs) between OM (-161) and OC (1410), of 8.7. The ratio BC/OC of the GWPs (100-year) would be ~10 (see Table I). Assuming similar lifetimes for BC and OC particles, the 20-year GWP for OC-particles was set to 200.

Emissions of Climate Active Compounds in Sugarcane Ethanol Production

N_2O from the application of N fertilizer

Nitrous oxide (N₂O) is an important greenhouse gas (GHG), constituting $\sim 6\%$ of the anthropogenic green-

house effect, and also contributed to the depletion of stratospheric ozone. In the last decades a great deal of evidence has accumulated showing that agricultural activities, especially application of N fertilizers, have resulted in increased emissions of N₂O to the atmosphere (IPCC, 2007). Soil release of N₂O occurs during biological nitrification (oxidation of NH4+ to NO2⁻ or NO3⁻ under aerobic conditions) and denitrification (reduction of NO₃or NO₂ to nitrogen oxides and N2 by anaerobic bacteria) (Freney, 1997; Bouwman, 1998). The IPCC estimate that ~2% of the N applied to soils as fertilizer is transformed by soil microbes into nitrous oxide; ~1% direct and ~1% indirect emissions. Results also suggest that N₂O emissions from fertilized soils are not related to the type of fertilizer applied and emissions can be calculated from the N applied.

Even though some sug-

arcane varieties are associated with N fixing bacteria (Boddey, 1995; Baldani *et al.*, 2002) relatively high amounts of N fertilizer are applied, varying largely from country to country (IFA, 1999; Baldani *et al.*, 2002). Application of 75-150kg N/ha, leads to a range of N₂O emissions of 1.5 and 3 kg N₂O-N per ha. Considering that the GWP of N₂O for 100-year horizon is 298, these N₂O emissions correspond to 447-897kg CO₂-eq/ha. These values agree with that estimated by Macedo *et al.* (2004) of 521kg CO₂-eq/ha. The 20-year horizon emissions range is 434-867kg CO₂-eq/ha.

Crutzen *et al.* (2008) suggest that nitrous oxide emissions from N fertilizers have been underestimated, indicating that 3-5% of N fertilizers must be converted to N₂O. In this case, the above CO₂-eq emissions should be 1.5- $2.5 \times$ higher. Therefore, the 20-year horizon emission would be 641-2168kg CO₂eq/ha, and 671-2243kg CO₂-eq/ha for 100-years.

Emissions from sugarcane agricultural operations

The diesel fuel used by machinery and trucks during planting, growing, harvesting and transportation

between sugarcane fields and mills of one ha of sugarcane has been estimated as 5.56GJ/ha (Macedo et al., 2004). On the other hand, de Oliviera et al (2005) give a much larger estimate of 23GJ/ha, which according to the evaluation of Smeets et al. (2006) is most likely erroneous and, therefore, is excluded from this evaluation. The Macedo et al. (2004) estimate corresponds to an average including 35% mechanical and 65% manual harvest. In Table II is given the emission of climate active compounds emitted by the consumption of 5.56GJ of diesel. The larger emission corresponds to CO₂, with an important contribution of BC. The total CO₂-eq/ha emission is 610-700kg for 20-year horizon and 464-486kg for 100-years.

Fossil energy is also consumed in producing N fertilizer, lime, herbicides, seeds, etc. This energy, expended away from sugar cane field operations, was estimated for Brazil as 8.3GJ/ ha by Macedo et al. (2004) and as 10GJ/ ha by de-Oliveira et al (2005). No estimates were found for other countries. The corresponding CO₂-eq emission is 750kg/ha (Macedo et al., 2004). Note that this value does not include non-Kyoto Protocol compounds. Therefore, the CO₂-eq total emission per ha, produced during field operations is 1360-1450kg CO₂-eq/ha and 1214-1236kg CO₂-eq/ha for 20 and 100 years time horizons, respectively.

Pre-harvest trash-cane burning emissions

Sugarcane is burned in almost all countries where produced (Moreira and Goldemberg, 1999; Rípoli et al, 2000). The goal of cane (leaves and stalk tops) burning is to reduce costs and increase safety of manual harvesting. Manual harvesting without cane burning is possible, but this is generally not economically feasible, because harvesting efficiency would decrease around 5 times (Smeets et al., 2006). Open biomass burning emits large quantities of semi-oxidized compounds (i.e. CO, BC) that largely contribute to the CO₂-eq emission. Table III summarizes the emissions from sugarcane trash burning. Most of the emission factors used are those reported for biomass burning (references in table).

The contributions of CH_4 and N_2O (Kyoto gases) to the CO_2 -eq are only ~14% and ~23% for the 20- and 100year horizons, respectively. As shown in Table III, the single larger contribution to the CO_2 -eq is due to BC emissions. Nearby the city of Piracicaba, located in a sugarcane-producing region in Brazil, high BC levels in the atmosphere were corre-

TABLE II
CO2-eq EMISSIONS FROM DIESEL COMBUSTION (MACHINERY AND
TRUCKS) EMITTED IN THE CULTIVATION OF the OF SUGARCANE

	EF (g/MJ)	Emission (kg/ha)	CO ₂ -eq (kg/ha)		
			20-years	100-years	
Kyoto					
CO_2	73.3ª	408	408	408	
CH_4	0.005ª	0.028	2.0	0.7	
N_2O	0.0019ª	0.01	2.9	3.1	
Sub-total			413 (59-68%)	412 (88-85%)	
Non-Kyoto					
СО	0.52ª	2.9	14.9	5.8	
NMVOC	0.10 ^a	0.56	5.5	1.9	
NO	0.38	2.1	?	?	
BC (2.5µm)	0.02-0.03 ^b	0.11-0.17	220-334	55-83	
OC (2.5µm)	$0.04-0.06^{b}$	0.23-0.34	-44 to -683	-11 to -17	
Sub-total			197-287 (32%-41%)	52-74 (12%-15%)	
Total			610-700	464-486	

^a IPCC (1995); ^b Weingartner et al. (1997), Kirchstetter et al. (1999), Streets et al. (2001) and Bond et al. (2004).

lated with sugarcane burning (Lara *et al.*, 2005). However, the contribution to the total CO_2 -eq, due to BC is in part counteracted by the relatively high emission of OC-particles; less than 20% of the organic particles are BC. If mechanical harvesting is applied, cane burning is no longer required and the emission (Table III) would be avoided.

Emissions from bagasse combustion

crushed to extract their juice. A sugar

in boilers

factory produces nearly 30% of bagasse out of its total crushing (Kadam, 2002; Macedo et al., 2004; Ho, 2006; Restuti and Michaelowa, 2007). The combustion of part (~90%) of bagasse provides the energy needed to boil off the water in the cane juice, to promote subsequent fermentation and concentration of the ethanol, and electricity to run the machinery. The resulting CO₂ emissions from bagasse burning are equal to the amount of CO₂ that the sugarcane used up from the atmosphere during its growing phase, which makes the process of cogeneration appear to be GHG neutral. However, the combustion of bagasse

	E	Bagasse	is	the	bion	nass
remaining	after	sugarc	ane	sta	ılks	are

TABLE III

EMISSIONS OF CLIMATE ACTIVE COMPOUNDS FROM THE PRI	E-HARVEST
BURNING OF 7 TO 16 TONNES/ha OF "SUGARCANE-TRASH"	BIOMASS

	Emission factor (kg/tones dry trash)	Reference	Emission (kg/ha)	CO ₂ -eq (kg/ha)	
				20-years	100-years
Kyoto					
CH_4	1.3-2.4	1,2	9.1-38.4	655-2765	227-960ª
N ₂ O	0.15	2	1.05-2.4	303-715	313-710 ^b
Sub-total				958-3480	540-1670
				(15.1-12.5%)	(26-19%)
Non-Kyoto					
CO	30-65	2,3	210-1040	1050-5200	420-2080
NMVOC	2-5	2,3	14-80	140-800	48-272
NO	3.1	2	22-50	?	?
BC	0.7-1.4	2,4,5,6,7,8	4.9-22	9800-44000	2450-11000
OC	4-8	2,5,6,	28-128	-5600 to -25600	-1400 to -6400
Sub-total				5390-24400	1518-6952
Total				(84-88%) 6348-27880	2058-8622

References: 1 Delmas *et al.* (1991), 2 Scholes and Andreae (2000), 3 EPA (1975), 4 Liousse *et al.* (1996), 5 Streets *et al.* (2001), 6 Bond *et al.* (2004), 7 Parashar *et al.* (2005), 8 Andreae *et al.* (1996). ^a Macedo *et al.* (2004) estimated 6.6kg CO₂-eq/tonnes (528 CO₂-eq/ha). ^b Macedo *et al.* (2004) estimated 2.4kg CO₂-eq/tonnes (192 CO₂-eq/ha).

TABLE IV
CO ₂ -eq EMISSIONS FROM THE COMBUSTION OF 19-25tonnes
(0.16-0.21TJ) OF BAGASSE IN BOILERS, WITH AND WITHOUT CONTROL
OF PARTICLE EMISSIONS

	Control	E.F.	E.F. Emission C		O ₂ -eq (kg/ha)	
		(Kg/1J)	(kg/na)	20-years	100-years	
Kyoto						
CH_4		30 ^a	4.8-6.3	48-63	14-19	
N ₂ O		4 ^a	0.64-0.84	185-243	191-250	
Sub-total				233-306	205-269	
				(~1% uncontrolled)	(4% uncontrolled)	
Non-Kyoto						
CO		1706 ^b	273-358	2730-3580	819-1074	
NMVOC		[50]	8-10.5	80-105	27-36	
NO		88 ^b	14-19	?	?	
BC-particle	Uncontrolled	(100-140) ^{c,d}	16-29	32000-58000	8000-14500	
(2.5µm)	90% control ^e	(100-140)x0.1	1.6-2.9	3200-5800	800-1450	
OC-particle	Uncontrolled	(600-840) ^c	96-174	-19200 to -34800	-4800 to -8700	
(2.5µm)	90% control ^e	(600-840)x0.1	9.6-17.4	-1920 to -3480	-480 to -870	
Sub-total	Uncontrolled			15610-26885 (~99%)	4046-6910 (~96%)	
	90% control			4090-6005 (~95%)	1166-1690 (~86%)	
Total	Uncontrolled			15842-27191	4251-7179	
	90% control			4323-6311	1377-1959	

^a IPCC (2006); ^b IPCC (1995); ^c Liousse *et al.* (1996), Street *et al.* (2004), Bond *et al.* (2004) and Parashar *et al.* (2005); ^d a heating value of 8.6MJ/kg bagasse was used; ^ee.g., scrubbers (EPA, 1996).

produces other compounds that will contribute to the greenhouse effect. Table IV summarizes the emissions from the combustion of 19-25 tonnes of bagasse (0.16-0.21TJ), corresponding to 90% of the bagasse produced per ha of harvested sugarcane.

The CO emission factor is much higher than those from conventional fossil fueled plants (IPCC, 1995). This is mainly due to the high moisture content (~50%) of bagasse, which reduces the combustion efficiency in the reaction chamber. This may also explain the relatively high emissions of BC. The

inclusion of equipment to control particles significantly reduces their emissions (see Table IV). Under uncontrolled conditions, for the 100 year time horizon, – non-Kyoto compounds contribute over 85% to the total CO₂-eq emission, and over 95% for the 20 year Ky horizon.

Other emissions from industrial operations

The emission in the industrial sector (e.g. lubricant, building, equipment) was estimated to be ~300kg CO₂eq/ha (Macedo *et al.*, 2004). Note that this value does not include non-Kyoto climate active compounds.

Emissions from an Equivalent Amount of Gasoline

As mentioned above, when ethanol replaces gasoline in motor vehicles, the resulting CO_2 emission is equal to the amount of CO_2 that the sugarcane plant used up from the atmosphere during its growing phase; therefore, this CO_2 does not contribute to global warming. The heating power of ethanol is lower than gasoline and it takes ~1.5L of ethanol to provide the energy of 1L of gasoline (Treanton, 2004). Fuel economy (km/L) for gasoline is 1.3 to $1.4 \times$ higher than that for E85 (85% ethanol + 15% gasoline); the combined cycle (45% highway and 55% city driving) fuel economy of the 2007 Mercedez-Benz C230 is 8.06 and 5.95km/L for gasoline and E85, respectively (Fuel Economy, 2008). Therefore, the 5600-6400L of ethanol produced per ha will replace 3733-4267L of gasoline (2949-3371kg gasoline/ha; gasoline density= 0.79kg/L), corresponding to 128-147GJ/ha.

Methane fugitive emissions from oil activities

The combined CH₄ fugitive emission factor for oil production, transportation, refining and storage ranges between 1.1 and 7.4×10^{-3} kg CH₄/ GJ (IPCC, 1995). Therefore, the methane emissions produced by "processing" 128-147GJ of petroleum, corre-

sponding to the replaced 3733-4267L of gasoline per ha, is $(141-1100)\times10^{-3}$ kg CH₄/ha. The 20 and 100-year horizon emissions are 10-79kg CO₂-eq/ha and 3-27kg CO₂-eq/ha, respectively.

CO₂-eq emissions from gasoline refining

The mayor fuels used in petroleum refineries are still (refinery) gas and natural gas (EIA, 2008; Wang, 2008). Still gas is burned after the removal of NMVOC (to produce LPG) and H_2 ; therefore, this fuel contains mainly methane, as natural gas does. Actually,

resulting

TABLE V

EMISSIONS FROM THE COMBUSTION OF 0.020-0.024TJ OF NATURAL GAS IN OIL REFINERIES TO PRODUCE 3733-4267 LITERS OF GASOLINE WITH AN EFFICIENCY OF 83%*

	Emission factor (kg/TJ)	Emission (k/ha)	CO ₂ -eq (kg/ha)	
			20-years	100-years
Kyoto				
CO_2	57600ª	1152-1382	1152-1382	1152-1382
CH_4	1 ^a	0.02-0.024	1.44-1.73	0.5-0.6
N_2O	0.1ª	0.002-0.0024	0.58-0.69	0.6-0.7
Non-Kyoto				
CO	19 ^b	0.38-0.46	1.9-2.3	0.79-0.92
NMVOC	~0	~0	~0	~0
NO	267 ^b	5.3-6.4	?	?
BC	~0°	~0	~0	~0
OC	0.001°	(2-2.4)×10 ⁻⁵	(4-4.8)×10 ⁻³	(1-1.2)×10 ⁻³
Total			1156-1386	1154-1384

* This replaces the equivalent amount of ethanol produced in 1ha of sugarcane. ^a IPCC (2006), ^b IPCC (1995), ^c Bond *et al.* (2004).

3733-4267L of gasoline, which is equivalent to the ethanol produced from 1ha. Considering that the energy efficiency, or energy use, of gasoline production in oil refineries is ~83% (Wang, 2008), the energy required (from natural gas) to produce this amount of gasoline is 0.020-0.024TJ. The total CO2-eq emission (Table V) is 1156-1386kg for a 20-year horizon and 1154-1384kg for a 100-year horizon; practically only (~99%) CO_2 is emitted.

both fuels have similar pol-

lutants emissions factors

(IPCC, 1995). Table V con-

tains the emissions of Kyoto

and non-Kyoto compounds

from refining

CO₂ emission from gasoline passenger cars

Emissions of climate active compounds from passenger cars, due to the consumption of 3733-4267L of gasoline, that replace the equivalent amount of ethanol produced per ha of sugarcane cultivation, are summarized in Table VI. Total CO₂-eq emission ranges from 10953 to 12517kg/ha No (20 year horizon) and 10097-11539kg/ha (100 years). Over 88% correspond to Kyoto gases.

According to the review by Jacobson (2006), E85 fueled cars emit similar amounts of CO and particles than gasoline cars, 43% more methane and 45% more NMVOC; no informa-

tion is available for N₂O. Considering that CH₄ and NMVOC contribute with <0.6% and <2.3%, respectively, to the total CO₂-eq emission, the differences in emission rates of gases other than CO₂ is negligible (well within the uncertainties). Therefore, the avoided emission of using ethanol instead of 3733-4267L of gasoline is 9354-10693kg CO₂/ha, which entirely corresponds to the CO₂ that will be recycled.

Total CO_2 -eq emission in production and combustion of an equivalent amount of gasoline replaced by ethanol (TEEG)

Adding the CH_4 fugitive emissions from oil exploitation activities, the emissions of climate active compounds in the production of gasoline in refineries, and the CO_2 emitted from gasolinefueled cars, the emissions avoided by the replacement of gasoline by ethanol are 10520-12427 and 10511-12103CO₂-eq/ha for the 20-years and 100-years time horizons, respectively.

Discussion

Sugarcane ethanol energy budget

The energy budget (input vs output) of sugarcane-ethanol is very favorable. The energy required in the industrial production of ethanol is mainly internally supplied by the combustion of bagasse. The external energy input to the agri-

TABLE VI EMISSIONS FROM THE CONSUMPTION OF 3733-4267 LITERS OF GASOLINE* IN PASSENGER CARS** THAT REPLACE THE EQUIVALENT AMOUNT OF ETHANOL PRODUCED PER HECTARE OF SUGARCANE

	EF g/kg	Emission kg/ha	CO ₂ -eq kg/ha	
			20-years	100-years
Kyoto				
CO_2	3172ª	9354-10692	9354-10692	9354-10692
CH_4	0.32ª	0.94-1.08	68-78	23.5-27
N ₂ O	0.30ª	0.88-1.0	254-289	262-298
Non-Kyoto				
СО	49.9ª	147-169	735-840	294-336
NMVOC	10.48 ^a	31-35	310-350	105-119
NO _x	7.94ª	23-27	?	?
BC-particles	0.045 ^b	0.13-0.15	260-300	65-75
OC-particles	0.046 ^b	0.14-0.16	-28 to -32	-7 to -8
Total			10953-12517	10097-11539

* d= 0.79kg/L; 2949-3371kg of gasoline.

** Fuel economy= 11.9km/L; equipped with advanced three way catalyst control. a IPCC (1995), ^b Best estimate for development countries (Battye and Boyer, 2002).

> cultural and industrial activities are ~15GJ/ha and ~3.67GJ/ha, respectively (Macedo et al., 2004). On the other hand, the energy in ethanol that replaces gasoline is 150-161GJ/ha. Therefore, the ratio between output and input of energy is ~8 (returns about 8 units of energy for each unit expended). The input of energy will increase when changing to mechanical harvesting, needed to avoid important emissions of climate active compounds during canetrash burning. Also, in the case that bagasse (160-210GJ/ha) is not used as energy source, the ratio output/input would drastically drop to ~1 (no net energy gain).

Total CO₂-eq emissions from sugarcane ethanol production (TESEP)

The production of sugarcane ethanol could be achieved following various alternative scenarios (e.g. pre-harvesting burning or no burning, particle emission controls in bagasse based boilers), which emit to the atmosphere different amounts of climate active compounds. In addition, at present it is difficult to decide what is the actual emission of N₂O from the application of N-fertilizers. Therefore, scenarios with low and high N₂O emissions were evaluated separately. Table VII presents the total CO₂-eq emissions produced under some selected scenar-

ios; the large ranges reported reflect the large differences that exist in emission factors, sugarcane yields, amount of N fertilizer applied, etc. At present, it is difficult to give a more likely value, but in order to protect the environment, attention should be paid to the upper range values. In the various scenarios, non-Kyoto Protocol compounds make an important contribution to the CO₂-eq. Since these compounds have short atmospheric lifetimes, the amount of CO2-eq is significantly larger at a 20-years horizon, than in a 100-years horizon. It should be emphasized that the short-lived non-Kyoto compounds present larger uncertainties than the long-lived Kyoto GHG and, therefore,

TABLE VII

TOTAL EMISSION OF CO₂-eq IN 20- AND 100-YEARS HORIZONS AND VARIOUS SCENARIOS, AND RATIO OF TOTAL EMISSION FROM SUGARCANE ETHANOL PRODUCTION AND THE TOTAL EQUIVALENT EMISSION FROM GASOLINE REPLACED BY ETHANOL

Scenario ^a	Time horizon	TESEP CO ₂ -eq (kg/ha)	TESEP/TEEG ^b
$\overline{3-5\%}$ N ₂ O from N-fertilizer, pre-harvest burning and no control in particle emission in bagasse based boilers	20-years	24500-58987	2.3-4.7
	100-years	8494-19572	0.81-1.6
$3\text{-}5\%$ N_2O from N-fertilizer, no pre-harvest burning and no control in particle emissions in bagasse based boilers	20-years	18152-31109	1.7-2.5
	100-years	6436-10950	0.61-0.9
$2\%\ N_2O$ from N-fertilizer, no pre-harvest burning and no control in particle emissions in bagasse based boilers	20-years	17936-29808	1.7-2.4
	100-years	6212-9609	0.59-0.79
$2\%~N_2O$ from N-fertilizer, pre-harvest burning and 90% particle emission control in bagasse based boilers	20-years	12765-36808	1.2-3.0
	100-years	5396-13011	0.51-1.1
$2\%~N_2O$ from N-fertilizer, no pre-harvest burning and 90% particle emission control in bagasse based boilers	20-years	6417-8728	0.61-0.70
	100-years	3338-4389	0.32-0.36

^a All scenarios include emissions from agricultural and industrial operations.

 b TEEG= 10520-12427kg CO₂-eq/ha for 20-years and 10511-12103CO₂-eq/ha for 100 years.

results and conclusions should be considered with caution.

Climate effects of replacing gasoline by sugarcane ethanol

The ratios between the total emission produced during the production of ethanol (TESEP) and the total emission from an equivalent amount of gasoline (TEEG) that is replaced by ethanol are given in Table VII. In the scenario with pre-harvest burning and no particle control in boilers (at present, a prevailing condition in Brazil), higher CO₂-eq emissions, compared with the CO₂ saved by burning an equivalent amount of gasoline, are revealed during the production of ethanol. Actually, the 20-year horizon emissions would be more than 2× higher. Under these conditions, the contribution of non-Kyoto compounds is ~87% for a 20 year horizon and 70% for 100 years.

Since cane burning results in emissions that are potentially damaging for human health (Cançado et al., 2006; Amre et al., 1999), this practice is decreasing and being replaced by mechanized harvesting; in Brazil, 35% of cane harvesting is already mechanized (Macedo et al., 2004). In India, fields are not burnt before harvesting; however, after two subsequent harvests, the whole field is burnt and a new crop is sown (Amre et al., 1999). In scenarios without pre-harvest burning, the situation improves slightly. The 100-year horizon estimates indicate a relatively small (10-40%) saving of CO₂-eq emissions (TES-EP/TEEG= 0.9 and 0.59; Table VII). However, the corresponding 20-year ratios indicate a $\sim 2 \times (100\%)$ increase of warming emissions. Therefore, halting sugarcane field burning would not be sufficient to produce a bio-ethanol that will help decrease global warming.

Finally, under the most climate-favorable scenario, non-trashcane burning and 90% control of particle emissions in bagasse based boilers, the results (Table VII) indicate savings of CO_2 -eq emissions; 70% less emissions in a 100-year horizon and 35% for 20 years. Then, if a positive climate effect is to be achieved by replacing sugarcane ethanol for gasoline, its production should consider these friendly environmental conditions. Particle emission control would also contribute to improve regional air quality and health.

Uncertainties and Research Needs

There are many uncertainties in the present evaluation. However, the available published information allows a first preliminary appraisal of the impact on climate of the growing sugarcane ethanol industry, which in certain conditions, especially for a short time horizon, indicates significant negative consequences. The mayor uncertainties are:

N₂O emissions from N-fertilizers. The generic 2% emission of N₂O from N fertilizers recommended by the IPCC (2006) is based on studies made in temperate agricultural fields, whereas sugarcane is cultivated in tropical regions. On the other hand, the 3-5% N₂O production suggested by Crutzen et al. (2008), based in the global balance of atmospheric N₂O, is an average of the use of N fertilizers in agricultural soils all over the world. Furthermore, it is likely that the N fixation in sugarcane plantations promote additional production of N₂O (Baldani et al., 2002). Therefore, to narrow the large uncertainty in N₂O emissions, comprehensive studies in sugarcane fields are needed.

Emission factors. Emissions from sugarcane trash burning and bagasse combustion are crucial in the present evaluation. However, with only few exceptions, generic emission factors, for biomass burning and biofuel combustions in boilers, were used. Clearly, specific emission factors are needed, and special attention should be given to CO, BC and OC from bagasse combustion in boilers.

GWPs: At present, the use of GWPs for short-lived compound (gases and particles) is controversial (Fuglestvedt et al., 2003; Bond and Sun, 2005; Delucchi, 2006). They will depend on the location and timing of the emission. The development of better 3-D global models allowed obtaining regional GWPs for short-lived gases (Table I). However, since no GWPs have been reported for tropical regions, the values used in this work for CO and NMVOC correspond to averages of median values given for other regions. This causes uncertainties in results. In the case of particles, reasonable amount of information is available for BC and it is quite consistent among authors (Table I), but there is an almost complete lack of information on OC and the calculated cooling effect of OC is based on an estimated GWP value. Research improving and expanding GWPs should be pursued and the use of other measurements to compare to the results presented is recommended.

Conclusions

The main purpose of this work was to evaluate possible climate consequences upon replacing gasoline by sugarcane ethanol. In general, results indicate that emissions of climate active compounds (Kyoto plus non-Kyoto) seem to be unfavorable under most scenarios evaluated. If ethanol production is based on pre-harvest burning and no control of particle emission in boilers, a condition prevailing today in Brazil, CO_2 -eq emissions are higher than the combustion of an equivalent amount of gasoline. In no pre-harvest burning scenarios, the 20-year horizon estimates still indicate higher emissions than gasoline. Only under climate-favorable scenarios there would be a significant saving of CO₂-eq emissions, and they should be applied for positive climate effects to be achieved.

The present preliminary evaluation has many uncertainties, especially in relation to non-Kyoto compounds, but the alarming results obtained, finding negative climatic consequences in the growing sugarcane ethanol industry, call for an urgent attention to this matter. Additional research is needed in various fields to reduce uncertainties.

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EMISIONES DE COMPUESTOS, INCLUIDOS O NO EN EL PROTOCOLO DE KYOTO, CLIMÁTICAMENTE ACTIVOS, DURANTE LA PRODUCCIÓN DE ETANOL DE CAÑA DE AZÚCAR

Eugenio Sanhueza

RESUMEN

El etanol producido de caña de azúcar es el biocombustible más desarrollado comercialmente. En este trabajo se evalúan las emisiones de compuestos climáticamente activos, incluidos y no incluidos en el Protocolo de Kyoto. Se consideran varios escenarios, tales como bajas o altas emisiones de N₂O por fertilización con N, inclusión o no de quema pre-cosecha, emisiones controladas o no en las calderas que utilizan bagazo, y horizontes de 20 o 100 años en los GWPs. El CO₂ emitido en la combustión de bioetanol es reciclado en la resiembra de la caña de azúcar y no cuenta como gas de invernadero. Sin embargo, a pesar de muchas incertidumbres, la información disponible permite estimar que las emisiones de CO₂-eq son altas cuando se realiza quema precosecha y no hay control de las emisiones de las calderas. En estos escenarios ocurrirían emisiones de CO_2 -eq mayores que las correspondientes a la combustión de una cantidad equivalente de gasolina. Eliminar la quema precosecha no sería suficiente para revertir la situación, especialmente cuando se considera un horizonte de 20 años. Solo si se realizasen procedimientos ambientales más amigables habría ahorro significativo en emisiones de CO_2 -eq (a 20 y 100 años). En todos los escenarios, los compuestos no incluidos en el Protocolo de Kyoto contribuyen significativamente. Por ello, para evaluar el impacto real de los compuestos climáticamente activos es crucial incluir estos compuestos en los estudios de ciclo de vida. Para reducir las incertidumbres, especialmente las relacionadas con compuestos no incluidos en el Protocolo, se requieren investigaciones adicionales.

EMISSÕES DE COMPOSTOS, INCLUIDOS OU NÃO NO PROTOCOLO DE KYOTO, CLIMATICAMENTE ATIVOS, DURANTE A PRODUÇÃO DE ETANOL DE CANA DE AÇUCAR

Eugenio Sanhueza

RESUMO

O etanol produzido de cana de açúcar é o bio-combustivel mais desenvolvido comercialmente. Neste trabalho se avaliam as emissões de compostos climaticamente ativos, incluídos e não incluídos no Protocolo de Kyoto. Consideram-se vários cenários, tais como baixas ou altas emissões de N_2O por fertilização com N, inclusão ou não de queima pré-colheita, emissões controladas ou não nas caldeiras que utilizam bagaço, e horizontes de 20 ou 100 anos nos GWPs. O CO_2 emitido na combustão de bioetanol é reciclado na replantação da cana de açúcar e não conta como gás de invernadeiro. No entanto, a pesar de muitas incertezas, a informação disponível permite estimar que as emissões de CO_2 eq são altas quando se realiza queima pré-colheita e não há controle das emissões das caldeiras. Nestes cenários ocorreriam emissões de CO_2 -eq maiores que as correspondentes a combustão de uma quantidade equivalente de gasolina. Eliminar a queima pré-colhita não seria suficiente para reverter a situação, especialmente quando se considera um horizonte de 20 anos. Somente si se realizassem procedimentos ambientais mais amigáveis haveria poupança significativa em emissões de CO_2 -eq (a 20 e 100 anos). Em todos os cenários, os compostos não incluídos no Protocolo de Kyoto contribuem significativamente. Por isto, para avaliar o impacto real dos compostos climaticamente ativos é crucial incluir estes compostos nos estudos de ciclo de vida. Para reduzir as incertezas, especialmente às relacionadas com compostos não incluídos no Protocolo, se requerem investigações adicionais.