

DIESEL PRODUCTION BY FAST PYROLYSIS OF *MISCANTHUS GIGANTEUS*, WELL-TO-PUMP ANALYSIS USING THE GREET MODEL

by

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*In this paper “well-to-pump” environmental analysis of pyrolytic diesel from *Miscanthus giganteus* is performed. The average annual yield of *Miscanthus* from III-V year of cultivation on 1 ha of chernozem soil in Serbia (23.5 t) is considered as an input for the process. Two pyrolytic diesel pathways are considered: distributed pyrolytic pathway with external hydrogen production (from natural gas) and integrated pyrolytic pathway with internal hydrogen production (from pyrolytic oil). and are compared to a conventionally produced diesel pathway. The results of the analysis reveal that integrated-internal pyrolytic diesel pathway has lowest resources consumption and lowest pollutant emissions. Compared to conventionally produced diesel, integrated-internal pyrolysis pathway consumes 80% less of fossil fuels, and 92% more of renewables, has 90% lower global warming potential, 30% lower terrestrial acidification potential but 38% higher particulate matter formation potential. Compared to the distributed-external pathway, 88% less fossil fuels, and 36% less renewables are consumed in the integrated-internal pathway, global warming potential is 97% lower, terrestrial acidification is 20% lower, and particulate matter formation is 49% lower. Nevertheless, this pathway has high coal and hydroelectrical power consumption due to electricity production and high emissions of particulate matter, CO₂, SO_x, and N₂O. Another drawback of this production pathway is the low yield of diesel obtained (38% lower than in distributed-external pathway). With this regard, it is still hard to designate production of diesel from fast pyrolysis of *Miscanthus* as a more environmentally friendly replacement of the conventional production diesel pathway.*

Key words: diesel, pyrolysis, *Miscanthus*, life cycle assessment

Introduction

In terms of climate change mitigation, production of biofuels and their use as a substitution for fossil fuels have become even more appealing in the last few decades. These fuels, are mainly derived from biomass: *first generation biofuels* were produced from sugar-starch

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crops and oil crops, and *second generation biofuels* from lignocellulosic biomass such as crop residues, woody crops or energy grasses [1]. For second-generation biofuels two different production technologies can be applied: biochemical conversion, which includes biomass fermentation process and thermochemical conversion, which includes gasification and pyrolysis of a biomass feedstock [1].

Pyrolysis of a biomass represents a thermal decomposition in the absence of oxygen, in which three main products are obtained: liquid fuel (crude bio-oil), biochar and non-condensable gasses (CH_4 , CO) [2-4]. For pyrolytic diesel production, it is important to ensure high yields of the liquid phase. This can be obtained if the following conditions are met: finely ground biomass feedstock for increased heat transfer rates at the reaction interface, carefully controlled pyrolysis reaction temperature of around 500 °C and vapour phase temperature of 400-450 °C, short vapour residence times of typically less than 2 seconds (fast pyrolysis) and rapid cooling of the pyrolysis vapours (quenching) [3]. Obtained pyrolytic crude bio-oil is a dark brown liquid composed of a very complex mixture of oxygenated hydrocarbons and a significant amount of water which originates from both the original moisture and reaction product [5]. In order to be used as a biofuel, high amount of oxygen in crude bio-oil has to be reduced in a process called *hydrotreating* (stabilization), and heavy molecules (30 or more C atoms) of the oil has to be broken down to smaller chains similar to diesel (C12) or gasoline (C8), in a process called *hydrocracking* (upgrading) [2]. Both *hydrotreating* and *hydrocracking* processes are taking place in a hydrogen-rich environment. Hydrotreating is performed within pressure range of 7-10 MPa and temperature range of 300-400 °C, using a cobalt-molybdenum catalyst and hydrocracking is performed within pressure range of 10-14 MPa and temperatures range of 400-450°C, using a nickel-molybdenum catalyst [2]. Hydrogen used in these processes may come from an external source (*e. g.*, steam methane reforming of natural gas) or from an internal source by reforming co-produced fuel gas or a fraction of the pyrolysis oil [6]. Burning of pyrolytic co-products, biochar, and non-condensable gasses can provide heat and electricity for the pyrolysis process itself.

Most used feedstock for pyrolytic oil production are rape and sunflowers, herbs residue, rice husk, cotton stalk, corn stalk, sugarcane bagasse and coconut shell, wheat straw, switchgrass (*Panicum virgatum*), *Miscanthus* (*Miscanthus x giganteus* Greef et Deu.), willow (*Salix viminalis*), beech wood (*Fagus sylvatica*) and recently, microalgae [7, 8]. Environmental assessment of pyrolytic bio-oil (diesel and gasoline) production and/or use has been discussed in several studies [6, 9-15]. Available data on production of pyrolysis bio-oil (yields of pyrolysis products, required energy, GHG emissions, *etc.*) mainly refer to the corn stover [6, 9, 11, 14] or wood and forest residues [6, 9, 10, 12, 13, 15, 16] which represent the most studied biomass feedstock for pyrolysis.

In this paper, production of diesel from fast pyrolysis of *Miscanthus giganteus* in a fluidized-bed reactor is considered. *Miscanthus giganteus* is a perennial grass, widely used as a bioenergy crop due to high biomass yields, good biomass quality for the combustion and low GHG emissions compared to fossil fuels [17-22]. Cultivation of *Miscanthus* in Serbia has started on only several experimental plots with different types of soil, such as chernozem and eutric cambisol [23] providing high biomass yields. Several studies have shown that the cultivation of *Miscanthus* for energy purposes has great potential in Serbia [23-26]. So far, use of *Miscanthus* for fast pyrolysis process has been discussed in several papers which are mostly focussing on the identification of optimal conditions for obtaining high crude bio-oil yields [8, 27-36] where stabilization and upgrading phases of crude *Miscanthus* bio-oil are omitted. Also in these studies, no environmental analysis of *Miscanthus* bio-oil is performed.

This study represents a life cycle assessment of pyrolytic diesel production from *Miscanthus* which is cultivated on 1 ha of agricultural land in Serbia. According to ISO 14040, the definition of the goal and scope of the study, the life cycle inventory analysis phase, the life cycle impact assessment phase and the life cycle interpretation phase are defined and described.

Goal and scope of the study

The main goal of this study is to quantify relevant environmental impacts occurring from the production of pyrolytic diesel from *Miscanthus giganteus* crops and to examine if the production of *Miscanthus* pyrolytic diesel is a more environmentally favourable option than the conventional production of diesel. Another goal is to quantify how much pyrolytic diesel can be obtained from 1 ha of *Miscanthus* plantation in Serbia in order to approve or disapprove cultivation of *Miscanthus* for energy purposes in Serbia. A *well-to-pump* life cycle analysis is performed, considering all potential environmental threats, from raw materials extraction (*well*) to the production and transportation of diesel fuel from the plant to the pump [37]. Well-to-pump analysis of *Miscanthus* diesel starts with land preparation for rhizomes planting, cultivation, harvesting and balling of *Miscanthus* crops, considers transport of bales to the pyrolysis plant where biomass feedstock is prepared for the pyrolysis process, and after the pyrolysis, transport of produced diesel to the pump. The analysis is conducted by using data on *Miscanthus* yields cultivated on chernozem experimental field in the northern part of the Serbia [23, 26], by analysing secondary data (from relevant publications) and by employing, expanding and modifying the corn stover pyrolytic distributed-external diesel pathway integrated in GHG, regulated emissions, and energy use in transportation (GREET) model (developed by Argonne National Laboratory, USA) [6, 38]. Cultivation of *Miscanthus* on chernozem is chosen due to the availability of data for cultivation on this type of soil [23, 25, 26] and to the fact that in Serbia large area of set-aside arable land covered with chernozem (60000 ha in the northern part) are available, where cultivation of *Miscanthus* in one part of this land is considered not to jeopardize the food supply [39, 40]. Corn stover pyrolytic pathway is chosen due to the similar morphology of the biomass feedstock. For the comparison with conventionally produced diesel, the corresponding pathway from GREET model is used [38]. For sensitivity analysis, the integrated-internal pyrolytic pathway is considered, where lower emissions and resources consumption is expected.

Functional unit

In order to quantify how much pyrolytic diesel can be produced from the annual yield of *Miscanthus* cultivated on 1 ha, the functional unit in distributed-external diesel pathway is average annual *Miscanthus* yield from III-V year of cultivation on 1 ha of chernozem soil in Serbia, *i. e.*, 23.5 t (85% d.m.) [41]. In comparison with conventional diesel pathway, the functional unit is the energy content of the produced pyrolytic diesel obtained from 23.5 t (85% d.m.) of *Miscanthus*, 406.75 GJ (LHV/HHV = 34373.78 MJ/m³ of 9.85 t of pyrolytic diesel, see Section *Miscanthus pyrolytic diesel pathway (Distributed, external H₂ source)*). In integrated-internal pyrolytic diesel pathway the functional unit is lower, 252.12 GJ (LHV/HHV = 34373.78 MJ/m³), since less pyrolytic diesel is obtained from average *Miscanthus* yield compared to the distributed-external pathway. This functional unit is used for the comparison with the conventionally produced diesel pathway.

Inventory analysis

Miscanthus pyrolytic diesel pathway (Distributed, external H₂ source)

Miscanthus life cycle is divided into several operations: *Miscanthus* cultivation phase, transportation of *Miscanthus* biomass from the field to the pyrolysis plant, grinding of biomass, drying of biomass, pyrolysis and stabilization (hydrotreating) of crude bio-oil, hydrocracking and formation of stable pyrolysis product – pyrolytic fuel, and transportation of fuel from plant to pump. Detailed input/output matrix is presented in tab. 1.

According to own unpublished results for cultivation of *Miscanthus* on 1 ha of chernozem in Northern Serbia, 3 kg/ha per year of herbicide is needed, same as 333 kg/ha per year of fertilizer, 180 m³ per year of water (for irrigation) and around 120 kg/ha per year of diesel for agricultural operations (harrowing, plowing, planting, fertilization, irrigation, harvesting and balling). These inputs are included in the *Miscanthus* cultivation phase.

After harvest, balling and drying in the field, *Miscanthus* bales are transported to the pyrolysis plant by a truck. The distance between the field and the plant is assumed to be 50 km since the transportation by truck is profitable for distances up to 100 km [42]. Fast pyrolysis is considered to take place in a bio-refinery plant (which is not part of the existing oil refinery) where processes of stabilization and upgrading are separated (Distributed Refinery Scenario). The first step in biomass processing in the bio-refinery plant is grinding. Considering common assumption of 50 kWh of energy needed for grinding one ton of biomass [43], 4.23 GJ is needed for grinding 23.5 t of *Miscanthus* bales, tab. 1. Grinded *Miscanthus* biomass is then dried (from 85% d. m. to 93% d. m.) and the final *Miscanthus* biomass weight is 21.4 t, tab 1.

Drying of biomass is performed in a steam dryer where the amount of heat used for drying is calculated according to a study published by Wright *et al.*, [2], tab 1.

After grinding and drying, *Miscanthus* biomass is sent to a fluidized bed reactor for fast pyrolysis conversion. Data on yields of pyrolysis products are taken from the only available paper, published by Kim *et al.* [36] where detailed analysis of *Miscanthus* pyrolysis is performed. Considering the optimum case for *Miscanthus* crude bio-oil yield of 57.2 %, on the temperature of around 350 °C and vapour retention time of 2 second, from 23.5 t (85% d. m.) 12.24 t of crude bio-oil is obtained, 4.47 t of biochar and 4.71 t of fuel gas, tab. 1. Due to the absence of data regarding stabilization and upgrading phases of crude *Miscanthus* bio-oil [27, 30-32, 36, 44], data for corn stover are considered and modified [6]. Based on the energy and mass balance of processes in a corn stover pathway, the appropriate inputs and outputs of the corresponding processes in a *Miscanthus* pathway are calculated considering different functional unit. Hydrogen used for both hydrotreatment and hydrocracking is obtained by reforming of natural gas. Heat for pyrolysis, stabilization and upgrading processes is obtained from combustion of pyrolysis co-products, biochar, and fuel gas [2, 6]. Finally, 9.85 t of pyrolysis fuel is obtained and further transported by a truck to the pump, considering 50 km of distance.

Conventional diesel pathway

For the comparison with the conventional diesel fuel production, GREET pathway *Conventional Diesel from Crude Oil* is chosen [38]. The GREET pathway considers the entire production process of diesel, from the pet coke, bitumen, shale oil, synthetic crude oil and crude oil together with all transportation processes (by rail, barge, pipeline and ocean tanker) and the use of natural gas, electricity, and diesel. After being produced, diesel is exported to Serbia. With this regard, the final transportation process has been modified and considers transoceanic transport by a tanker between the USA and Europe (from Portland, Maine till the Rotterdam,

Table 1. Input-output relation and for pyrolysis of *Miscanthus* obtained on 1 ha of land in the northern part of Serbia

Particulars	Units	Amount	Comments/remarks
<i>Input</i>			
Herbicide	kg	3	Production and transport of herbicide is integrated into the model
Miscanthus rhizomes			Production and transport of rhizomes is out of the scope of the study
Fertilizer	kg	333	NPK 15:15:15 (50 kg N/ha + 50 kg P ₂ O ₅ 1/ha + 50 kg K ₂ O 1/ha) Production and transport of fertilizer is integrated in the model
Water	m ³	180	For irrigation of <i>Miscanthus</i> crops [ha ⁻¹ yr ⁻¹]
Diesel	kg	120	Used in agricultural machinery [ha ⁻¹ yr ⁻¹]
<i>Output</i>			
Miscanthus bales (85% d. m.)	t	23.5	Mass of harvested <i>Miscanthus</i> after drying in the field [41]
<i>Input</i>			
Miscanthus bales (85% d. m.)	t	23.5	
Grinding	GJ	4.23	Electricity for the mill (supplied from the grid)
Drying	GJ	8.63	Heat obtained from combustion of pyrolysis bio-char (heating appliance efficiency is 0.90)
<i>Output</i>			
Miscanthus (93% d. m.)	t	21.4	Mass of <i>Miscanthus</i> after drying
<i>Input</i>			
Miscanthus (93% d. m.)	t	21.4	Miscanthus biomass feed for pyrolysis
Fluidised bed pyrolysis			
– crude bio-oil	t	12.24	yield 57.2% (temp 350 °C, vapour retention time 2 s) [36]
– bio-char	t	4.47	yield 20.9%, HVV/LHV = 22000.47 MJ/t [36]
– fuel gas	t	4.41	yield 22%, HVV/LHV = 19920 MJ/m ³ [36]
<i>Hydrostabilization</i>			
<i>Input</i>			
– gaseous hydrogen	GJ	103.35	Produced from Natural Gas
– natural gas	GJ	321.65	
– electricity	GJ	70.88	
<i>Output/Input</i>			
Liquid fuel	t	9.85	Density:0.78t m ⁻³ ; LHV/HHV = 33200.35 MJ/m ³
<i>Hydrocracking</i>			
– gaseous hydrogen	GJ	0.27	Produced from natural gas
– natural gas	GJ	14.21	
– electricity	GJ	0.24	
<i>Output</i>			
– pyrolysis diesel	t	9.85	Density:0.83 t/m ³ ; LHV/HHV = 34373.78 MJ/m ³
Transport by truck	tkm	9.85x50	Distance between pyrolysis plant and fuel pump is 50 km

The Netherlands) with a distance of 3175 nmi. From Rotterdam till the Belgrade, transportation of diesel by railway is considered (distance 1800 km).

Miscanthus pyrolytic diesel pathway (Integrated, internal H₂ source)

In order to lower the impact of the diesel production, sensitivity analysis is done and another production scenario is created. This scenario considers the integrated production of pyrolytic diesel, in which the reactions of stabilization and cracking are occurring together, on the same location, and the internal hydrogen production. Namely, hydrogen for the pyrolysis can also be obtained from the bio-oil itself. Pyrolytic bio-oil consists of a lighter fraction, aqueous phase, and a heavier fraction consisting mostly of lignin [4]. The heavier fraction is separated by gravity and the remaining, lighter fraction is being mixed with the steam and sent to a *high-temperature pre-reformer* where it converts into *syngas* or synthetic gas. Synthetic gas, together with methane, is further sent to the reformer where the hydrogen is formed [4].

The drawback of this pathway is the lower yield of pyrolytic oil obtained compared to external hydrogen production pathway. Considering estimations given by Wright *et al.* [2] where 38% of the bio-oil has to be reformed into hydrogen in order to upgrade the remaining bio-oil, in the internal hydrogen production scenario, 6 t of pyrolytic oil is obtained.

Impact assessment

Environmental analysis in well-to-pump life cycle considers quantification of pollutant emissions, such as: CO₂, volatile organic compounds (VOC), CO, NO_x, particulate matter 10 and 2.5 micrometres in diameter (PM₁₀, PM_{2.5}), SO_x, CH₄, and N₂O. Based on these emissions three impact categories are calculated: GWP, TA, and PMF potential. Characterization factors for GWP for 100 years time scale (CO₂ eq) : CO₂=1, CH₄ = 25 kg CO₂, N₂O = 298 kg CO₂ are taken from IPCC (AR4) [45], characterization factors for terrestrial acidification potential for 100 years time scale (SO₂ eq) for NO_x = 0.56 kg SO₂ and characterization factors for PMF (PM₁₀ eq): NO_x = 0.21 kg PM₁₀; SO₂ = 0.19 kg PM₁₀ are taken from ReCiPe impact assessment method [46]. The environmental analysis also quantifies depletion of resources along the production pathways such as: crude oil, natural gas, coal, forest residue, pet coke, hydro electrical power, nuclear energy, geothermal energy, wind energy, bitumen and shale oil. For better transparency, resources consumed are grouped into fossil fuels and renewables.

Results and discussion

The results of well-to-pump analysis quantifying emissions and resources depletion from *Miscanthus* pyrolytic diesel production in Distributed Refinery Scenario with an external source of hydrogen are presented in the tab. 2 and on figs. 1 and 2.

The most environmentally burdensome operation in *Miscanthus* pyrolysis diesel pathway is the hydrostabilization process, due to the high amount of natural gas used for hydrogen production, around 322 GJ, tab.1. The highest impact comes from the natural gas life cycle itself, since modified GREET pathway for corn stover considers the entire life cycle of the diesel used for non-road applications (in commercial boiler, stationary reciprocating engine, turbine, *etc.*) and the entire life cycle of the electricity (distributed – U.S. mix) consumed in natural gas pathway. For both cases, the highest contribution comes from the use of non-RES. Since the natural gas used in the analysed pathway is produced in the USA, electricity mix for this country is considered, where 34.30% of electricity is being produced from coal, 31.92% from natural gas, 20.38% from nuclear power, 6.35% from hydro energy, 4.79% from wind energy, 0.62% from oil-fired systems, 0.57% from solar energy, 0.5% from biogenic waste, 0.43% from geothermal energy and 0.16% from biomass. Electricity used for the mill in *Miscanthus* grinding operation is considered to be produced in Serbia (standard Serbian electricity mix is considered) where 70% of electricity is produced from coal and 30% from hydro energy.

Table 2. Pollutant emissions and resource depletion occurring along distributed-external H₂ Miscanthus pyrolytic diesel pathway

Emissions:	P1	P2	P3	P4	P5	P6	P7	Total:	Units
CO ₂	790	70.23	981.04	450.45	12924.24	136.75	60.97	15413.68	kg
VOC	0.60	0.02	0.08	0.11	3.98	0.13	0.45	5.37	kg
CO	1.41	0.06	0.09	0.3	11.24	0.4	0.05	12.14	kg
NO _x	3.45	0.17	0.54	0.77	25.91	0.53	0.15	28.07	kg
PM10	0.31	0	0.17	0.11	4.65	0.02	0	5.26	kg
PM2.5	0.27	0	0.07	0.06	2.93	0.01	0.01	3.38	kg
SO _x	3.87	0.02	2.46	0.92	31.01	0.27	0.02	34.7	kg
CH ₄	1.94	0.15	1.45	2.23	96.1	3.6	0.13	103.66	kg
N ₂ O	1.05	0.000261	0.019739	0.010261	0.67	0.02	0	0.72	kg
SO ₂	2.25E-03	3.3E-10	5.64E-10	8.36E-10	2.02E-08	6E-10	3E-10	2.25E-03	kg
Resources:									
Water total	183	0.07	8.67	3.14	102.5	0.66	0.06	298	m3
Crude oil	4542	602.49	207.39	758.47	2998.40	48.57	517.68	9675	MJ
Natural gas	4529	109.62	44.99	6457.77	321651	14208.23	109.41	347110	MJ
Coal average	497	12.18	10082.93	3472.45	114412	560.86	16.18	129053.6	MJ
Forest residue	4	0.09	0.16	0.24	5.74	0.18	0.08	10.49	MJ
Pet coke	9	1.16	0.40	1.46	5.75	0.09	0.99	18.85	MJ
Hydroelectric power	33	0.81	1510.35	518.15	17094.43	82.07	1.55	19240.36	MJ
Nuclear energy	107	2.68	4.59	6.79	164.41	5.26	2.31	293.04	MJ
Geo thermal power	2	0.06	0.10	0.14	3.44	0.11	0.05	5.9	MJ
Solar	3	0.07	0.13	0.19	4.56	0.15	0.06	8.16	MJ
Wind power	25	0.63	1.08	1.60	38.65	1.24	0.54	68.74	MJ
Bitumen	736	97.63	33.60	122.90	485.74	7.87	83.88	1567.62	MJ
Shale oil	1095	145.33	50.02	182.95	723.06	11.71	124.87	2333	MJ

P1 – Miscanthus cultivation phase, P2 – Transport from the field to the plant, P3 – Grinding, P4 – Drying, P5 – Pyrolysis + hydrotreatment (stabilization) of bio-oil, P6 – Hydrocacking (upgrading) of bio-oil, P7 – Transport from the plant to the pump

Second most burdensome operation in *Miscanthus* pyrolysis diesel pathway is the production, *i. e.*, cultivation phase of *Miscanthus* crops where the highest impact comes from production and transportation of herbicide and fertilizer, in which high amount of crude oil, pet coke, bitumen and shale oil are consumed, together with high consumption of renewables. Since *Miscanthus* crop has to be irrigated, highest consumption of water is registered in this phase of a pathway (60% of total water used in the pathway). Pyrolysis and stabilization phase has the highest emissions of pollutants except for the N₂O and SO₂, which are highest in the *Miscanthus* production phase. This is due to high consumption of diesel with high sulfur content for non-road applications such as agricultural machinery, commercial boiler, stationary reciprocating engine, turbine, *etc.* As a consequence of fossil fuels consumption in the pathway, high emissions of CO₂ occur, around 15.4 t, tab. 2. This can be diminished if carbon sequestration potential from *Miscanthus* cultivation is considered, tab 3. Data for the carbon sequestration

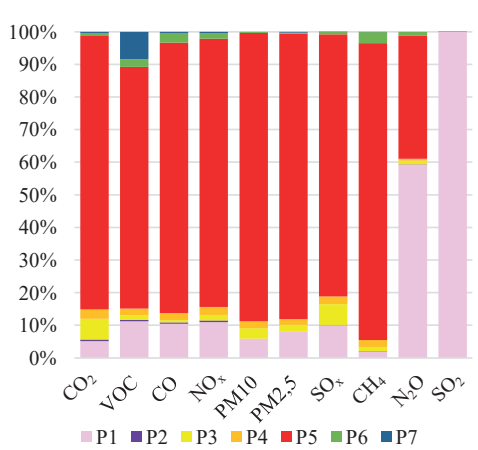


Figure 1. Pollutant emissions during the production of pyrolytic diesel from *Miscanthus giganteus* [kg]
(for color image see journal web site)

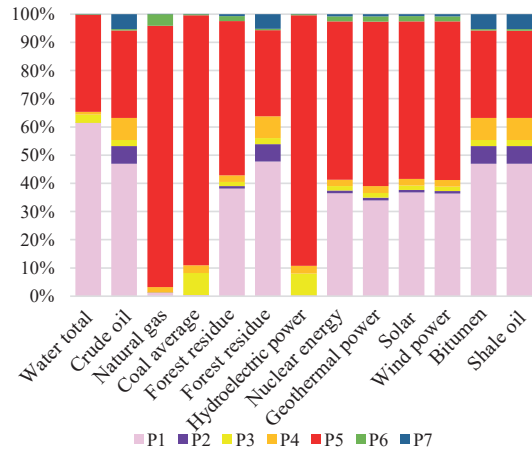


Figure 2. Resources depletion during the production of pyrolytic diesel from *Miscanthus giganteus* [MJ]
(for color image see journal web site)

potential is taken from the unpublished research of the same authors, where 5 t of CO₂ is considered to be sequestered from the 23.5 t of *Miscanthus*.

The results of the comparative well-to-pump analysis of distributed-external H₂ diesel production pathway and conventional diesel pathway are presented in tab. 3 and figs. 3 and 4.

All considering pollutant have higher emissions in distributed pyrolytic diesel pathway. In the conventional pathway: 63% less CO₂, 60% less VOC, 63% less CO, 55% less NO_x, 78% less PM₁₀, 72% less PM_{2.5}, 73% less SO_x and 87% less N₂O are emitted compared to the distributed pyrolytic pathway, fig. 3. Considering the emissions of SO₂ they are almost 100% higher in distributed pathway due to high consumption of diesel with high sulfur content (for

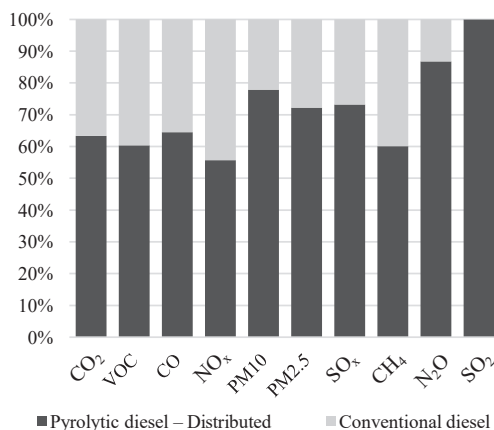


Figure 3. Comparison of pollutant emissions for distributed – external H₂ pathway and conventional diesel pathway [kg]

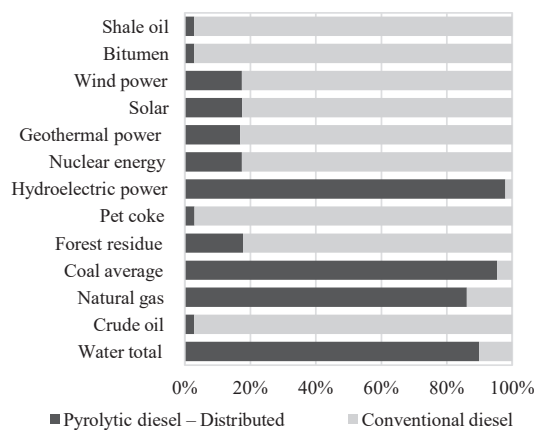


Figure 4. Comparison of resource depletion for external distributed – external H₂ pathway and conventional diesel pathway [MJ]

Table 3. Pollutant emissions and resource depletion occurring from the production of diesel in the distributed-external H₂ pathway, integrated-internal H₂ pathway and conventional pathway, calculated per functional unit

Emissions:	f.u. = 406.75 GJ		f.u. = 252.12 GJ		Units
	Pyrolysis diesel-distributed	Conventional diesel-SER	Pyrolysis diesel-integrated	Conventional diesel-SER	
CO ₂	10413.68 ^a	6022.8	396.82 ^b	3733.02	kg
VOC	5.37	3.53	1.44	2.19	kg
CO	12.14	6.67	1.61	4.13	kg
NO _x	28.07	22.32	9.74	13.83	kg
PM10	5.26	1.49	3.19	0.92	kg
PM2.5	3.38	1.29	2.23	0.8	kg
SO _x	34.7	12.72	11.34	7.88	kg
CH ₄	103.66	68.71	6.93	42.59	kg
N ₂ O	0.72	0.11	0.16	0.07	kg
SO ₂	2.25E-03	1.69e-07	2.25E-03	1.05e-07	kg
GWP _(CO₂ eq) ^c	13580	7773.33	467.75	4818.63	kg
TA _(SO₂ eq) ^d	15.72	12.50	5.45	7.74	kg
PMF _(PM10-eq) ^e	14.53	7.47	7.47	4.62	kg
Resources:					
Water total	298	33.69	223.00	20.88	m3
Crude oil	9675	309485.82	6317.30	191824.00	MJ
Natural gas	347110	56157.97	4885.37	34807.56	MJ
Coal average	129053.6	6247.70	46889.83	3872.42	MJ
Forest residue	10.49	48.09	4.87	29.80	MJ
Pet coke	18.85	593.85	12.41	368.08	MJ
Hydroelectric power	19240.36	414.74	6980.92	257.06	MJ
Nuclear energy	293.04	1376.51	131.79	853.18	MJ
Geothermal power	5.9	28.78	2.52	17.84	MJ
Solar	8.16	38.19	3.69	23.67	MJ
Wind power	68.74	323.62	30.83	200.59	MJ
Bitumen	1567.62	50148.93	1023.66	31083.07	MJ
Shale oil	2333	74650.64	1523.20	46269.60	MJ
Fossil fuels:	489.76	497.28	60.65	308.22	GJ
Renewables:	19.63	0.85	7.15	0.53	GJ

a – net CO₂ emissions = total CO₂ emissions (15413.68kg) minus carbon sequestration potential (5000kg); *b* – same calculation as for *a*; total CO₂ emissions in integrated pathway are 5396.82 kg; *c* – Characterization factors for GWP for 100 years time scale (CO₂ eq): CO₂ = 1; CH₄ = 25 kg CO₂; N₂O = 298 kg CO₂; IPCC(AR4); carbon sequestration is also considered; *d* – Characterization factors for TA potential for 100 years time scale (SO₂ eq) for NO_x = 0.56 kg SO₂ [46]; *e* – Characterization factors for PMF (PM₁₀ eq): NO_x = 0.21 kg PM₁₀; SO₂ = 0.19 kg PM₁₀ [46].

non-road applications such as a commercial boiler, stationary reciprocating engine, turbine, *etc.*), tab. 2. In both pathways, emissions of CO₂ are the highest: 10.4 t and 6 t, for pyrolytic diesel production and conventional diesel production, respectively. In all three investigated

impact categories, conventional diesel production pathway expresses lower impact: in GWP 43% lower, in TA 20% lower, and in PMF 49% lower. On the contrary, this production pathway has the highest resource consumption, fig. 4. Almost 97% lower consumption of crude oil, pet coke, bitumen and shale oil and also 78% lower consumption of forest residues, nuclear, geothermal, solar and wind energy are detected in pyrolytic pathway compared to the conventional pathway. The only exceptions are consumption of natural gas, coal and hydroelectric power which are less consumed in the conventional production of diesel, 84%, 95% and 98%, respectively. As previously stated, a huge amount of natural gas is needed for hydrogen production for upgrading and stabilization process and high amount of coal and hydroelectric power are used for electricity production in Serbia, 75.35 GJ, tab.1. Shale oil, bitumen, pet coke and crude oil are used as a feedstock for conventional diesel production which explains their high consumption in the conventional diesel pathway. On the other hand, in this pathway, renewable energy resources (wind power, solar, geothermal, and nuclear) are more consumed due to electricity production mix of the USA. But when considering the total amount of fossil fuels consumed [MJ], only 4% less fossil fuels are consumed in distributed-external pyrolytic diesel production pathway and 96% less RES [MJ] is consumed for conventional production of diesel. Although conventional diesel pathway has higher consumption of biomass, wind, solar and geothermal energy, the pyrolytic pathway has a high amount of hydroelectric power consumed, 19206.55 MJ, compared to 414.74 MJ, tab. 3. Irrigation of *Miscanthus* crops has a high influence on water consumption in the pyrolytic pathway.

Comparison of the *Miscanthus* integrated-internal pyrolytic diesel production with conventionally produced diesel is presented in the tab. 2, and figs. 5 and 6. Utilization of coal, hydroelectrical power and water are still highest for the integrated-internal pathway, *i. e.*, 92%, 96% and 92%, lower in the conventionally diesel production pathway, respectively. All other resources are less consumed in this pathway: around 85% less nuclear, biomass, wind, solar and geothermal energy and 97% less crude oil, pet coke, bitumen, shale oil and natural gas. Considering emission of pollutants, VOC, CO, NO_x, CH₄ and SO₂ are still less emitted in integrated-internal diesel pathway, 62%, 61%, 30%, 84% and 97%, respectively, and unlike in the previous case, CO₂ emissions are 90% lower compared to the conventional diesel pathway,

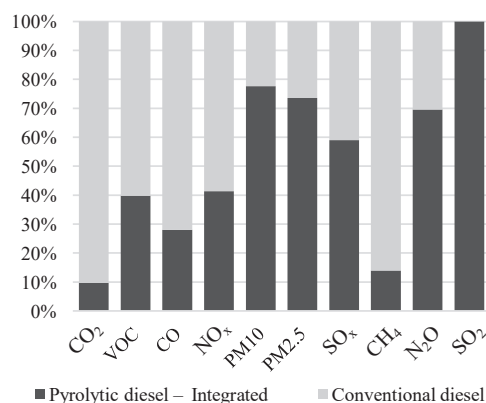


Figure 5. Comparison of pollutant emissions for integrated-internal H₂ pathway and conventional diesel pathway [kg]

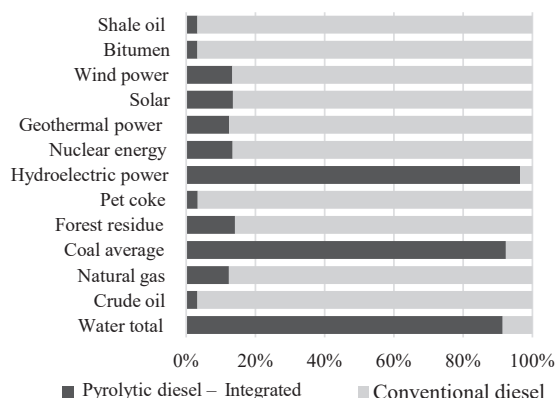


Figure 6. Comparison of resource depletion for integrated-internal H₂ pathway and conventional diesel pathway [MJ]

resulting in 90% lower GWP. Emissions of PM10, PM2.5, SO_x, and N₂O are lower in conventional pathway: 19%, 68%, 59%, 30%, and 56%, respectively, resulting in 38% lower PMF, but the emissions of SO₂ are almost 100% higher in integrated-internal pathway, resulting in 30% lower TA for this pathway. In total, 80% less fossil is consumed in the integrated-internal pathway, while 92% less renewables are consumed in conventional diesel pathway.

Comparison of the *Miscanthus* integrated-internal H₂ production pathway, with distributed-external H₂ production pathway, is presented in tab. 3 and on figs. 7 and 8. As stated before, the drawback of the internal H₂ production is the lower yields of diesel, but the advantage is in lower resources consumption and in lower pollutant emissions, tab. 2. Since no natural gas is needed for stabilization and upgrading phases, almost 100% less of natural gas is used in integrated-internal diesel pathway, which also leads to 64% less consumption of coal, hydroelectric power and water, 61% less consumption of crude oil, pet coke, bitumen and shale oil and 86% less consumption of forest residues, nuclear, geothermal, solar and wind energy compared to distributed-external diesel pathway. Considering emission reduction, in integrated-internal pathway 96% less CO₂, 73% less VOC, 87% less CO, 65% less NO_x, 40% less PM10, 33% less PM2.5, 67% less SO_x, 93% less CH₄, 78% less N₂O, where SO₂ is equally emitted in both pathways. The GWP, TA, and PMF are lower in the integrated-internal pathway, 97%, 65% and 49%, respectively. Consumption of fossil fuels is 87% less in integrated-internal diesel pathway and consumption of renewable energy sources is 64% less.

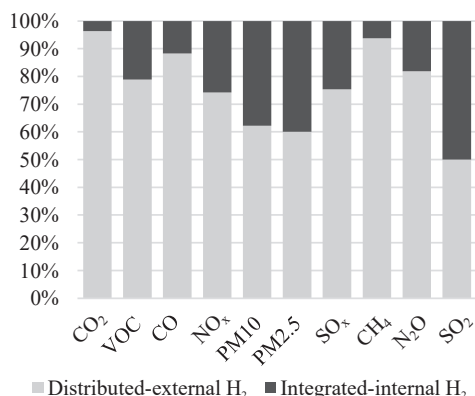


Figure 7. Comparison of pollutant emissions for distributed-external H₂ and integrated-internal H₂ diesel pathway [kg]

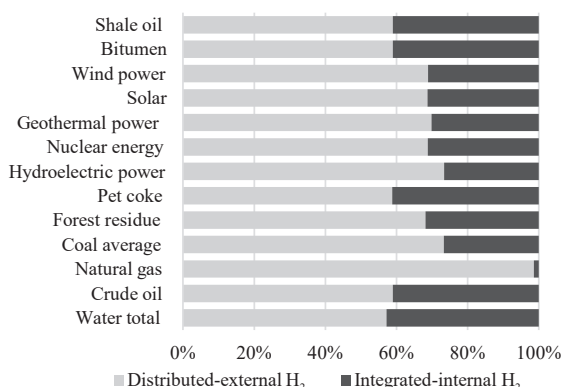


Figure 8. Comparison of resource depletion for distributed-external H₂ and integrated-internal H₂ diesel pathway [MJ]

Conclusions

In this paper, production pathway of pyrolytic diesel is constructed and the environmental analysis is performed by using GREET model. As an input, 23.5t ha⁻¹ of *Miscanthus giganteus* annual yield is considered. Two different pyrolytic diesel production pathways are considered: distributed-external H₂, where processes of stabilization and upgrading of fuel are separated and hydrogen is obtained from natural gas, and integrated-internal H₂, where stabilization and upgrading of fuels are occurring together and hydrogen is obtained from the fraction of pyrolytic oil. Each one of these pathways is compared to a conventionally produced diesel pathway.

Results from three *well-to-pump* analysis show that the conventional diesel production pathway has the highest resource consumption and distributed-H₂ external pathway has the

highest pollutant emissions. The main environmental impact in distributed-H₂ external pathway is caused by high consumption of natural gas (347 GJ) for the production of hydrogen which is used for upgrading and stabilization of diesel. In conventionally produced diesel pathway, the highest impact comes from utilization of crude oil, pet coke, shale oil, and bitumen, which are raw materials for diesel production. On the other hand, the advantage of this production pathway is high consumption of renewable energy resources (used for electricity production). Results of the analysis indicate integrated-H₂ internal pyrolytic pathway has the lowest specific environmental impact per consumed power unit. Even though emitting 90% less of CO₂ and 84% less of CH₄, this production pathway has higher emissions of particulate matter (around 60%), SO_x (30%), and N₂O (56%) compared to the conventional production pathway due to high total power consumption. Likewise, the pyrolytic diesel yield is 38% lower than in distributed-H₂ external pathway. With this regard, it is hard to state that the production of diesel from *Miscanthus giganteus* by fast pyrolysis will soon be able to replace conventional diesel production.

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References

- [1] Larson, E. D., *Biofuel Production Technologies: Status, Prospects and Implications for Trade and Development*, UN Reports, New York and Geneva, 2008, UNCTAD/DITC/TED/2007/10
- [2] Wright, M. M., et al., *Techno-Economic Analysis of Biomass Fast Pyrolysis to Transportation Fuels*, *Fuels*, 89 (2010), Supp. 1, pp. S2-S10
- [3] Bridgwater, A. V., et al., *An Overview of Fast Pyrolysis*, in: *Prog. Thermochem. Biomass Convers.*, (Ed. A. V. Bridgwater), Wiley, New York, USA, 2008
- [4] Brown, T. R., et al., *Techno-Economic Analysis of Biomass to Transportation Fuels and Electricity via Fast Pyrolysis and Hydroprocessing*, *Fuel*, 106 (2013), Apr., pp. 463-469
- [5] Bridgwater, A. V., *Upgrading Fast Pyrolysis Liquids*, in: *Thermochemical Processing of Biomass: Conversion into Fuels Chemicals and Power* (Ed. Brown, R. C.), Wiley, New York, USA, 2011, Chapter 6
- [6] Han, J., et al., *Well-to-Wheels Analysis of Fast Pyrolysis Pathways with GREET*, ANL/ESD/11-8 Reports, Argonne National Lab., Argonne, Ill., USA, 2011
- [7] Isahak, W. N. R. W., et al., *A Review on Bio-Oil Production from Biomass by Using Pyrolysis Method*, *Renew. Sustain. Energy Rev.* 16 (2012), 8, pp. 5910-5923
- [8] Greenhalf, C. E., et al., *A Comparative Study of Straw, Perennial Grasses and Hardwoods in Terms of Fast Pyrolysis Products*, *Fuel*, 108 (2013), June, pp. 216-230
- [9] Han, J., et al., *Life Cycle Analysis of Fuel Production from Fast Pyrolysis of Biomass*, *Bioresour. Technol.*, 133 (2013), Apr., pp. 421-428
- [10] Peters, J. F., et al., *Simulation and Life Cycle Assessment of Biofuel Production Via Fast Pyrolysis and Hydroupgrading*, *Fuel*, 139 (2015), Jan., pp. 441-456
- [11] Dang, Q., et al., *Environmental Life Cycle Assessment of Bio-Fuel Production Via Fast Pyrolysis of Corn Stover and Hydroprocessing*, *Fuel*, 131 (2014), Sept., pp. 36-42

- [12] Jones, S., *et al.*, Production of Gasoline and Diesel from Biomass Via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case, PNNL-18284 Reports, US Department of Energy, Washington DC, 2009
- [13] Steele, P., *et al.*, Life-Cycle Assessment of Pyrolysis Bio-Oil Production*, *For. Prod. J.* 62 (2012), 4, pp. 326-334
- [14] Kauffman, N., *et al.*, A Life Cycle Assessment of Advanced Biofuel Production from a Hectare of Corn, *Fuel.*, 90 (2011), 11, pp. 3306-3314
- [15] Hsu, D. D., Life Cycle Assessment of Gasoline and Diesel Produced Via Fast Pyrolysis and Hydroprocessing, *Biomass and Bioenergy.* 45 (2012), Oct., pp. 41-47
- [16] Iribarren, D., *et al.*, Life Cycle Assessment of Transportation Fuels from Biomass Pyrolysis, *Fuel*, 97 (2012), July, pp. 812-821
- [17] Lewandowski, I., Schmidt, U., Nitrogen, Energy and Land Use Efficiencies of *Miscanthus*, Reed Canary Grass and Triticale as Determined by the Boundary Line Approach, *Agric. Ecosyst. Environ.* 112 (2006), 4, pp. 335-346
- [18] Smeets, E. M. W., *et al.*, The Economical and Environmental Performance of *Miscanthus* and Switchgrass Production and Supply Chains in a European Setting, *Renew. Sustain. Energy Rev.*, 13 (2009), 6-7, pp. 1230-1245
- [19] Morandi, F., *et al.*, *Miscanthus* as Energy Crop: Environmental Assessment of a *Miscanthus* Biomass Production Case Study in France, *J. Clean. Prod.*, 137 (2016), Nov., pp. 313-321
- [20] Aravindhakshan, S. C., *et al.*, Economics of Switchgrass and *Miscanthus* Relative to Coal as Feedstock for Generating Electricity, *Biomass and Bioenergy.*, 34 (2010), 9, pp. 1375-1383
- [21] Parajuli, R., *et al.*, Environmental Performance of *Miscanthus* as a Fuel Alternative for District Heat Production, *Biomass and Bioenergy.*, 72 (2015), Jan., pp. 104-116
- [22] Mantineo, M., *et al.*, Biomass Yield and Energy Balance of Three Perennial Crops for Energy Use in the Semi-Arid Mediterranean Environment, *F. Crop. Res.*, 114 (2009), 2, pp. 204-213
- [23] Dželetović, Ž., *et al.*, Prinos *Miscanthus* × *giganteus* gajenog na dve lokacije u Srbiji (Yield of *Miscanthus* × *giganteus* during crop establishment at two locations – in Serbian), *J. Process. Energy Agric.*, 18 (2014), Apr., pp. 62-64
- [24] Dželetović, Ž., *et al.*, Water Supply and Biomass Production of *Miscanthus* × *Giganteus*, *Proceedings, 1st Int. Congr. Soil Sci. XIII Natl. Congr. Soil Sci.*, Soil Science Society of Serbia/Soil Science Institute, Belgrade, Serbia, 2013, pp. 435-450
- [25] Dželetović, Ž., *et al.*, Prospects of Using Bioenergy Crop *Miscanthus* × *Giganteus* in Serbia, in: *Mater. Process. Energy Commun. Curr. Res. Technol. Dev.* (Ed. Mendey-Vilas, A.), Formatex Research Center, Badajoz, Spain, 2013, pp. 360-370
- [26] Dželetović, Ž. S., Мискантус (*Miscanthus* × *Giganteus* Greef et Deu.) – производне одлике и продуктивност биомасе (*Miscanthus* – Production Quality and Biomass Productivity – in Serbian), *Zadužbina Andrejević*, Belgrade, 2012
- [27] Hodgson, E. M., *et al.*, *Miscanthus* as a Feedstock for Fast-Pyrolysis: Does Agronomic Treatment Affect Quality?, *Bioresour. Technol.*, 101 (2010), 15, pp. 6185-6191
- [28] Greenhalf, C. E., *et al.*, The Influence of Harvest and Storage on the Properties of and Fast Pyrolysis Products from *Miscanthus* X *Giganteus*, *Biomass and Bioenergy.* 56 (2013), Sept., pp. 247-259
- [29] Hodgson, E. M., *et al.*, Variation in *Miscanthus* Chemical Composition and Implications for Conversion by Pyrolysis and Thermo-Chemical Bio-Refining for Fuels and Chemicals, *Bioresour. Technol.*, 102 (2011), 3, pp. 3411-3418
- [30] Corton, J., *et al.*, Expanding the Biomass Resource: Sustainable Oil Production Via Fast Pyrolysis of Low Input High Diversity Biomass and the Potential Integration of Thermochemical and Biological Conversion Routes, *Appl. Energy.* 177 (2016), Sept., pp. 852-862
- [31] Banks, S. W., *et al.*, Fast Pyrolysis Processing of Surfactant Washed *Miscanthus*, *Fuel Process. Technol.*, 128 (2014), Dec., pp. 94-103
- [32] Mos, M., *et al.*, Impact of *Miscanthus* x *Giganteus* Senescence Times on Fast Pyrolysis Bio-Oil Quality, *Bioresour. Technol.*, 129 (2013), Feb., pp. 335-342
- [33] Yorgun, S., Fixed-Bed Pyrolysis of *Miscanthus* x *Giganteus*: Product Yields and Bio-Oil Characterization, *Energy Sources*, 25 (2003), 8, pp. 779-790
- [34] Heo, H., *et al.*, Influence of Operation Variables on Fast Pyrolysis of *Miscanthus Sinensis* Var. *Purpurascens*, *Bioresour. Technol.*, 101 (2010), 10, pp. 3672-3677
- [35] Melligan, W., *et al.*, Pressurised Pyrolysis of *Miscanthus* Using a Fixed Bed Reactor, *Bioresour. Technol.*, 102 (2011), 3, pp. 3466-3470

- [36] Kim, J. Y., *et al.*, Assessment of *Miscanthus* Biomass (*Miscanthus Sacchariflorus*) for Conversion and Utilization of Bio-Oil by Fluidized Bed Type Fast Pyrolysis, *Energy*, 76 (2014), Nov., pp. 284-291
- [37] Perić, M., *et al.*, Best Practices of Biomass Energy Life Cycle Assessment and Possible Applications in Serbia - Review Paper, *Croat. J. For. Eng.*, 37 (2016), 2, pp. 375-390
- [38] ***, GREET®, Argonne Natl. Lab. IL, USA. (n. d.). <https://greet.es.anl.gov>.
- [39] Oljača, S., *et al.*, Ekološke Posledice Upotrebe Biljaka za Dobijanje Energije (Environmental Consequences of Plant Utilization for Energy – in Serbian), *Agric. Eng.*, 32 (2007), 4, pp. 91-97
- [40] Ševarlić, M. M., Popis Poljoprivrede 2012 – Poljoprivredno Zemljište u Republici Srbiji (Census of Agriculture 2012 – Agriculture Land in the Republic of Serbia – in Serbian), Belgrade, 2015
- [41] Dželetović, Ž. S., Miskantus (*Miscanthus x giganteus* Greef et Deu.) – Proizvodne odlike i produktivnost biomase, Zadužbina Andrejević, Belgrade, 2012
- [42] Smeets, E., *et al.*, The Economical and Environmental Performance of *Miscanthus* and Switchgrass Production and Supply Chains in European Setting, *Renewable and Sustainable Energy Reviews*, 13 (2009), 6-7, pp. 1230-1245
- [43] Mani, S., *et al.*, Grinding Performance and Physical Properties of Wheat and Barley Straws, Corn Stover and Switchgrass, *Biomass and Bioenergy*, 27 (2004), 4, pp. 339-352
- [44] Acaroglu, M., Aksoy, A. S., The Cultivation and Energy Balance of *Miscanthus × Giganteus* Production in Turkey, *Biomass and Bioenergy*, 29 (2005), 1, pp. 42-48
- [45] ***, IPCC, Climate Change 2007 Synthesis Report, 2007
- [46] Goedkoop, M., *et al.*, ReCiPe 2008. A LCIA Method which Comprises Harmonised Category Indicators at the Midpoint and the Endpoint Level, Report I: Characterisation, 2013. doi:<http://www.lcia-recipe.net>.