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Evaluation of the use of alternative fuels (ethanol, biodiesel) in Otto and Diesel engines from a thermodynamic approach

Evaluación del uso de combustibles alternativos (etanol, biodiésel) en motores Otto y Diésel desde un enfoque termodinámico.

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Resumen

Este estudio analiza el rendimiento termodinámico de los combustibles alternativos en motores de combustión interna, con el objetivo de evaluar su viabilidad técnica y ambiental en comparación con los combustibles fósiles tradicionales. Se consideraron el etanol, utilizado en motores Otto, y el biodiésel, empleado en motores diésel, comparando sus propiedades energéticas y su efecto en la eficiencia térmica y de frenado. El análisis se basa en la aplicación de balances de energía y exergía, con énfasis en parámetros como el poder calorífico, la relación aire-combustible y las pérdidas irreversibles. Los resultados muestran que el etanol mejora el proceso de combustión en los motores Otto debido a su alto índice de octano, aunque presenta una menor densidad energética en comparación con la gasolina, lo que impacta en el consumo específico. En los motores diésel, el biodiésel evidencia un desempeño favorable en términos de reducción de emisiones y estabilidad operativa, aunque su menor poder calorífico influye en la potencia disponible. Se concluye que ambos biocombustibles representan alternativas prometedoras para una transición hacia sistemas energéticos más sostenibles, siempre que su uso se optimice considerando los principios termodinámicos y la eficiencia global del ciclo.

Palabras clave: etanol, biodiésel, motores Otto, motores diésel, eficiencia termodinámica, combustibles alternativos.

Abstract

This study analyzes the thermodynamic performance of alternative fuels in internal combustion engines, with the objective of evaluating their technical and environmental viability compared to traditional fossil fuels. Ethanol, used in Otto engines, and biodiesel, used in diesel engines, were considered, comparing their energetic properties and their effect on thermal and braking efficiency. The analysis is based on the application of energy and exergy balances, with emphasis on parameters such as calorific value, air-fuel ratio, and irreversible losses. The results show that ethanol improves the combustion process in Otto engines due to its high octane rating, although it has a lower energy density compared to gasoline, which impacts specific consumption. In diesel engines, biodiesel shows favorable performance in terms of emission reduction and operating stability, although its lower calorific value influences available power. It is concluded that both biofuels represent promising alternatives for a transition toward more sustainable energy systems, provided their use is optimized by considering thermodynamic principles and overall cycle efficiency.

Key words: Ethanol, biodiesel, Otto engines, Diesel engines, thermodynamic efficiency, alternative fuels.

1. Introduction

The growing global energy demand, coupled with the imminent depletion of fossil fuels and increasing concern about the environmental impact of their combustion, has driven research and development of alternative and sustainable energy sources (Agudelo et al., 2009). In this context, biofuels such as ethanol and biodiesel have emerged as promising options for application in internal combustion engines (ICEs), which continue to be the dominant technology in the transportation sector (Luján et al., 2005). The use of these renewable fuels in spark-ignition (Otto Cycle) and compression-ignition (Diesel Cycle) engines presents an opportunity to mitigate greenhouse gas emissions and reduce dependence on hydrocarbons (Cardona & Lora, 2007).

Ethanol, an alcohol obtained primarily through the fermentation of biomass rich in sugars or starch, has been positioned as a partial or total substitute for gasoline in Otto cycle engines. Its properties, such as a higher octane number compared to gasoline, have the potential to increase the engine's compression ratio and, consequently, its thermal efficiency (Beltrán & Cárdenas, 2021; Pírela et al., 2014). On the other hand, biodiesel, composed of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, is presented as a viable alternative to fossil diesel. Its chemical structure and oxygen content directly influence the combustion process and the formation of pollutant emissions (Barajas et al., 2012; Riojas González et al., 2024).

While the environmental advantages of biofuels are a key factor for their promotion, it is imperative to conduct a comprehensive evaluation of their impact on the performance and efficiency of existing engines. For this purpose, thermodynamic analysis stands as a fundamental tool (Cengel & Boles, 2011). The application of the first and second laws of thermodynamics allows for a detailed characterization of the energy transformation processes that occur inside the engine cylinder (Llanes-Cedeño et al., 2018). Parameters such as cylinder pressure, heat release rate, thermal efficiency, and energy analysis are crucial for fully understanding how the physicochemical properties of ethanol and biodiesel affect the overall engine performance. Various studies have experimentally and theoretically addressed the influence of gasoline-ethanol blends on the energetic and environmental behavior of Otto engines (Apaza-Salluca et al., n.d.). Similarly, the operation of Diesel engines with different proportions of biodiesel has been the subject of numerous investigations seeking to optimize their performance and minimize harmful emissions (Flórez et al., 2020; Giraldo et al., 2017).

Despite the existence of research on the topic, a systematic review that integrates and comparatively analyzes the findings related to the thermodynamic evaluation of ethanol and biodiesel in their respective application engines is required.

The objective of this review article is to analyze, from a thermodynamic perspective, the effects of using ethanol in Otto cycle engines and biodiesel in Diesel cycle engines. Changes in key performance parameters, such as power, torque, and thermal efficiency, as well as combustion behavior (Chacón-Pérez et al., 2013; Chaves et al., 2018), will be examined based on a compilation of results from indexed scientific research. This synthesis seeks to provide a comprehensive overview of the state of the art, identifying the benefits, challenges (Tinoco-Gómez et al., 2012) and areas of opportunity for optimizing the use of these alternative fuels in internal combustion engines.

2. Materials and Methods

Table 1: Indexing databases of consulted journals

Journal	*ELSEVIER*	*WEB OF SCIENCE*	*DOAJ*	*Other base(s)*
Fuel	√	√		Scopus
Energy Conversion and Management	√	√		Scopus
Renewable & Sustainable Energy Reviews	√	√		Scopus
Journal of Cleaner Production	√	√		Scopus
Energy	√	√		Scopus
Applied Energy	√	√		Scopus
SAE Technical Papers	√			SAE Mobilus
ASME Journal of Energy Resources Technology	√	√		Scopus
Energies (MDPI)		√	√	Scopus
Sustainability (MDPI)		√	√	Scopus
Energy Sources, Part A (Taylor & Francis)	√	√		Scopus

Source: Authors

Table 2: Summary of the number of consulted journals

Database	*Number of Journals*
Scopus	11
Web of Science	8
DOAJ	2
Otras (SAE Mobilus, etc.)	1

Source: Authors

Table 3: Number of reviewed journals by publication year

Year	*2002*	*2019*	*2020*	*2021*	*2022*	*2023*	*2024*
Number	1	1	2	2	1	3	4

Source: Authors

2.1. Study Type and Objective

A comparative review based on experimental evidence was carried out to quantify, under the most comparable conditions possible, the energetic (BTE) and exergy (ηex) performance of:

- SI (Otto) engines with ethanol/blends, and
- CI (Diesel) engines with biodiesel/variants.

The corpus was restricted to eight articles with reported or derivable energy/exergy balances, focusing on representative operating points (WOT, high load, CR variation, speed/λ sweeps). Examples that frame the scope: SI at WOT with exergoenvironmental analysis (Cavalcanti et al., 2022), heavy-duty SI lean-burn with energy/exergy balance(Hong et al., 2023), SI CFR with variable CR (Rubio-Gómez et al., 2021), CI CRDI-VCR with biodiesel (Patel & Buch, 2025), CI RCCI biodiesel-methanol with a focus on η_{ex} (Kakati et al., 2021), CI with nano–Al_2O_3 (Kayed et al., 2024) and CI with PPO–diesel blend with thermo-exergetic analysis (Yaqoob et al., 2024).

2.2 Sources and Corpus

SI + etanol set (4 studies)

- (Cavalcanti et al., 2022): flex-fuel test at WOT at various speeds; integrates exergoenvironmental analysis with thermal data.
- (Hong et al., 2023): heavy-duty SI engine at high load with lean-burn ($\lambda \approx 1.0 - 1.8$), energy/exergy balances, and two-zone validation.
- (Rubio-Gómez et al., 2021): CFR engine with variable CR (4–16) and evaluation of conversion efficiency/flame development angle in gasoline-alcohol blends.
- (Yamin et al., 2021): SI with alcohol supplement (includes ethanol) and report of availability/exergy under lean mixture ($\phi \approx 0.8$).

CI + biodiésel/alternatives set (4 studies)

- (Patel & Buch, 2025): CRDI–VCR configuration at 1500 rpm and 100% load; analysis of η_b, η_{ex}, SI in diesel/Bxx (Moringa).
- (Kakati et al., 2021): RCCI biodiesel-methanol strategy; η_{ex} and efficiency-emissions/stability trade-offs.
- (Kayed et al., 2024): B20 from different feedstocks enriched with $\text{nano} - Al_2O_3$; thermal and exergy efficiency.
- (Yaqoob et al., 2024): PPO–diesel blends (5–15%) with energy, exergy, and SI versus rpm.

2.3 Eligibility Criteria

Inclusion

Studies on SI or CI (bench or representative single-cylinder) with sufficient information to derive BTE and/or ηex; experimentally validated models (e.g., calibrated two-zone) and reports with energy/exergy balances or data allowing their closure are accepted (Hong et al., 2023; Patel & Buch, 2025).

Exclusion.

Absence of a clear operating point (rpm/load/λ/CR), simulation-only without validation, fuels outside of SI-ethanol or CI-biodiesel/related, or insufficient data for $\frac{\mathrm{BTE}}{\eta_{\mathrm{ex}}}$ (operative criterion).

2.4 Characterization of Included Studies

Table 4. Characteristics of SI studies with ethanol

Title	Authors	Year	Architecture	Comp. Ratio	Injection/ Ignition	Fuel (E%)	RPM Range	Load Range	Reported Metrics
Life Cycle and Exergoenvironmental Analyses of Ethanol: Performance of a Flex-Fuel Spark-Ignition Engine at Wide-Open Throttle Conditions	Eduardo J. C. Cavalcanti, Daniel R. S. da Silva and Mónica Carvalho	2022	SI	12.4:1	DI/Spark	E25, E50, E75, E100	1500-2500 rpm	WOT	η_{ex}, *Destroyed Exergy, SI*
Relative Change in SI Engine Performance Using Hydrogen and Alcohol as Fuel Supplements to Gasoline	Jehad A.A. Yamin1, Eiman Ali Eh Sheet, Khalid S. Rida	2021	SI	8:01	Spark	E6, Etanol	2750 rpm	WOT	BTE, η_{ex}, SI
A comparative study of the effect of compression ratio on the efficiency and flame development angle in a Cooperative Fuel Research engine fueled with binary gasoline–alcohol blends	Guillermo Rubio-Gómez, Lis Corral-Gómez, David Rodríguez Rosa, Fausto A Sanchez-Cruz and Simón Martínez-Martínez	2021	SI	NR	Spark	E20, E40, E60, E84	NR	NR	BTE, η_{ex}, *Destroyed Exergy, SI*

Energy and exergy characteristics of an ethanol-fueled heavy-duty SI engine at high-load operation using lean-burn combustion	Beichuan Hong, Andreas Lius, Senthil Krishnan Mahendar, Mihai Mihaescu and Andreas Cronhjort	2023	SI	NR	DI/Spark	Etanol	NR	BMEP	BTE, η_{ex}

Note: Characterization of spark-ignition (SI) studies with ethanol/blends included in the review. Architecture, CR, injection/ignition system, fuel (E%), rpm and load ranges, and whether the work reports BTE, ηex or exergetic partitions are reported. Abbreviations: SI = spark ignition; CR = compression ratio; DI/PFI = direct/port fuel injection; WOT = wide-open throttle; BMEP = brake mean effective pressure; λ = air excess ratio; NR = not reported. High load tests (incl. WOT) predominate, and in one study, lean-burn operation (λ ≈ 1.0 – 1.8); the set covers from CFR with variable CR to a heavy-duty SI with complete energy/exergy balances.

Table 5. Características de los estudios CI con biodiesel y variants

Title	Authors	Year	Architecture	Comp. Ratio	Injection/ Ignition	Fuel (Bxx)	RPM Range	Load Range	Reported Metrics
Investigating the potential of plastic pyrolysis oil-diesel blends in diesel engine: Performance, emissions, thermodynamics and sustainability analysis	Haseeb Yaqoob, Hafiz Muhammad Ali, Uzair Sajjad, Khalid Hamid	2024	CI	NR	DI	PPO-diésel $(5 - 15\,\%\,v/v)$	500 - 3500 rpm	NR	BTE, η_{ex}, SI
Parametric sensitivity analysis of split injection coupled varying methanol	Dipankar Kakati, Srijit Biswas, Rahul Banerjee	2021	CI	NR	DI+ PFI+SOI	Biodiésel + metanol (RCCI)	NR	100 % carga	η_{ex}

induced reactivity strategies on the exergy efficiency enhancement and emission reductions objectives in a biodiesel fuelled CI engine									
Thermodynamic Analysis of CRDI-VCR Type Diesel Engine Fueled with Moringa Oleifera Biodiesel	Vasant Patel, Vyomesh Buch	2025	CI	NR	CRDI+ SOI	Bxx (Moringa) vs B0	600 - 1900 rpm	100 % carga	η_{ex}, *Destroyed Exe* SI
Enriching various biodiesel feedstocks with Al_2O_3 nanoparticles in diesel engines: Performance, emissions, and exergy analysis	Hatem Kayed, Mostafa M. Abdel Aziz, M.S. Gadc	2024	CI	NR	SOI	B20, B30, B1 +nano-Al_2O_3	NR	NR	BTE, η_{ex}, *Destroyed Exergy*

Note: Characterization of compression-ignition (CI) studies with biodiesel (Bxx) and variants included in the review. Architecture, CR, injection/ignition system, fuel (Bxx and additives), rpm and load ranges, and whether the work reports BTE, ηex, destroyed exergy or SI are reported. Abbreviations: CI = compression ignition; CRDI = common-rail DI; SOI = start of injection; PFI/DI = port/direct injection; RCCI = reactivity-controlled compression ignition; PPO = plastic pyrolysis oil; SI = sustainability index; NR = not reported. Scope: RCCI and PPO–diesel are treated as sensitivity analyses; the main contrast of the synthesis is Bxx vs B0.

2.5 Dictionary of variables and equations

Tabla 6. Dictionary of variables and equations

Symbol	Name	Definition/Equation	Units	How to obtain/estimate	Pairing Tolerance
BTE	Brake thermal efficiency	$\eta_b = \frac{\dot{W}_b}{(\dot{m}_f \cdot \ LHV)}$; $\dot{W}$ $= 2\pi\, N\, T$	– (o %	Dynamo (T, N) and fuel flow; LHV reported or by mass mixture	–
η_{ex}	Exergetic efficiency	$\eta_{ex} = \frac{\dot{W}_b}{\dot{E}_{ch,comb}}$; $\dot{E}_{ph} = \dot{m}[(h - h0) - T0(s - s0)]$	– (o %	Exergy balance (chemical input, physical output, and destruction by irreversibilities)	–
$\lambda(AFR)$	Equivalence ratio / excess air factor	$\lambda = \frac{AFR_{real}}{AFR_{esteq}}$	–	From lambda sensor or gas/stoichiometry balance	$\Delta\lambda \leq 0.03$
EGR	Exhaust gas recirculation	$EGR = \frac{\dot{m}_{recirc}}{\dot{m}_{total}}$	%	From recirculation system or species balance	± 2 points
LHV_{mix}	Lower heating value of the mixture	$LHV_{mix} = \Sigma\, y_i \cdot LHV_i$ (mezcla másica)	$MJ \cdot kg^{-1}$	Mass fractions and pure LHVs; if missing, assumptions are cited	–
$\dot{E}_{ch,f}$	Chemical exergy of the fuel	Derived from elemental composition and LHV (standard correlations)	kW	Use correlations for oxygenated liquids; document reference	–
rpm	Engine speed	N (revolutions per minute)	rpm	Tachometer/datalogger	± 50 rpm o ± 2 %
% carga	Engine load	$BMEP = \frac{k\pi T}{V_d}$ $k = 4\ (Motor\ de\ 4$ $k = 2(Motor\ de\ 2$	%, $N \cdot m$, bar	Dynamometer; $BMEP = \frac{2\pi\, T}{V_d}$	± 5 % (position or torque)
SOI /Spark	Start of injection / ignition	Crank angle BTDC	°CA	ECU / log	Same mode (fixed vs optimi

Nota. Reference state: T_0=298 K, p_0=101.325 kPa, BMEP=kπT/V_d (k=4 at 4T; k=2 at 2T). LHV_mix=∑y_i LHV_i; If only volume fractions are available: (∑x_i ρ_i LHV_i)/(∑x_i ρ_i). Chemical exergy is estimated from C–H–O y LHV (standard correlations). Tolerances for pairing points: rpm ±50 o ±2 %,load ±5 %,Δλ≤0.03,EGR ±2 points; same timing/SOI mode.

2.6 Data Extraction

From the 8 studies (Tables 4-5), the following were recorded: DOI, architecture (SI/CI), combustion strategy (e.g., lean burn, RCCI), fuel/mixture (E%/Bxx and additives), conditions (rpm, % load or BMEP, λ/EGR, CR, ignition timing/SOI), and outcomes (BTE, ηex, exergy destroyed, SI, Texh). The dictionary of variables, equations, and tolerances was based on Table 6.(Cavalcanti et al., 2022; Hong et al., 2023; Kakati et al., 2021; Kayed et al., 2024; Patel & Buch, 2025; Rubio-Gómez et al., 2021; Yamin et al., 2021; Yaqoob et al., 2024).

2.7 Normalization and Pairing

Comparisons were made at high load (WOT in SI; 100% in CI) and mid-range rpm. Anchor points: SI 1500–2500 rpm; CI 1500 rpm–100%. Tolerances (Table 3): rpm ±50 or ±2% (whichever is greater), load ±5%, $\Delta\lambda \leq 0.03$, EGR ±2 points, and the same timing/SOI mode (fixed vs. optimized). RCCI and PPO–diesel are considered sensitivities; the center contrast is Bxx vs. B0. (Kakati et al., 2021; Yaqoob et al., 2024).

2.8 Calculation of Metrics and Balance Closures

Equations from Table 6 were applied:

The indicators and equations were applied according to Table 6: $\eta_b = \frac{\dot{W}_b}{\dot{m}_f \, LHV}$ (con $P_b = 2\pi NT$ cuando faltó $\dot{W}_b$); $\eta_{ex} = \frac{\dot{W}_b}{\dot{E}_{ch,f}}$; $LHV_{mix} = \sum y_i LHV_i$ (o ponderación volumétrica con densidades); $BMEP = \frac{k\pi T}{V_d}$ ($k = 4$ en 4T; $k = 2$ en 2T). The energy/exergy balances followed (Hong et al., 2023) (SI *lean-burn*) and (Patel & Buch, 2025).

2.9 Quality and Risk of Bias

Checked per study: (i) calibration/validation, (ii) defined operating point (rpm/load/λ/CR), (iii) **sufficient closure to derive** $\frac{BTE}{\eta_{ex}}$, (iv) **repetitions/variability**, (v) **base-alternative comparability**. If non-compliant → out of quantitative comparisons.

2.10 Uncertainty and Analysis

Type A/B uncertainties (torque, flow, LHV; and from model where applicable) were propagated and will be reported as mean $\pm U$ ($k \approx 2$). The Δ (alternative – base) are only contrasted with **t/ANOVA** if there are **≥3** comparable points per condition; otherwise, a narrative synthesis with CI/ranges (Hong et al., 2023; Patel & Buch, 2025).

3. Results and Discussions

Next, Table 7 presents a comparative synthesis of the most relevant thermodynamic and performance properties between gasoline (reference fuel) and ethanol (alternative fuel). This table breaks down fundamental parameters such as calorific value, octane number, and oxygen content, and correlates each property with its direct implication on performance, efficiency, and the combustion process within the Otto cycle engine, laying the groundwork for interpreting the experimental results.

Table 7: Thermodynamic and Performance Comparison between Gasoline and Ethanol in Otto Cycle Engines

Thermodynamic /Performance Parameter	**Gasoline (Reference Fuel)**	**Ethanol (Alternative Fuel)**	**Thermodynamic Implication and on Engine Performance**
Lower Heating	~44 MJ/kg	~27 MJ/kg	Requires a higher mass flow of

Value (LHV)			ethanol to produce the same energy, which directly impacts the specific fuel consumption.
Octane Number (RON)	90-98	~108	Its high resistance to detonation (knocking) allows operation with higher compression ratios and/or more aggressive ignition advances, which raises the potential for thermal efficiency of the cycle.
Latent Heat of Vaporization	~0.36 MJ/kg	~0.84 MJ/kg	Causes significant cooling of the air-fuel mixture, which increases charge density (improves volumetric efficiency) and further suppresses the tendency to detonate.
Oxygen Content (% by mass)	≈ 0%	~35%	The intrinsic oxygen promotes more complete and rapid combustion, leading to a significant reduction in carbon monoxide (CO) and unburned hydrocarbons (HC) emissions.
Brake Thermal Efficiency (BTE)	Typical	Potentially Higher	The result depends on engine optimization. Without optimizing the compression, efficiency may decrease slightly (Rubio-Gómez et al., 2021)However, if the engine is optimized (e.g., with higher compression or lean combustion), BTE increases significantly.
Brake Specific Fuel Consumption (BSFC)	Base	Higher	It is the unavoidable counterpart of the lower calorific value. More mass of ethanol is needed to produce the same unit of work (kWh).
NOx Emissions	Base	Variable / Dependent on calibration	Ethanol combustion can reach higher adiabatic flame temperatures, which favors the formation of NOx. The final result depends on the mixture richness and engine calibration.

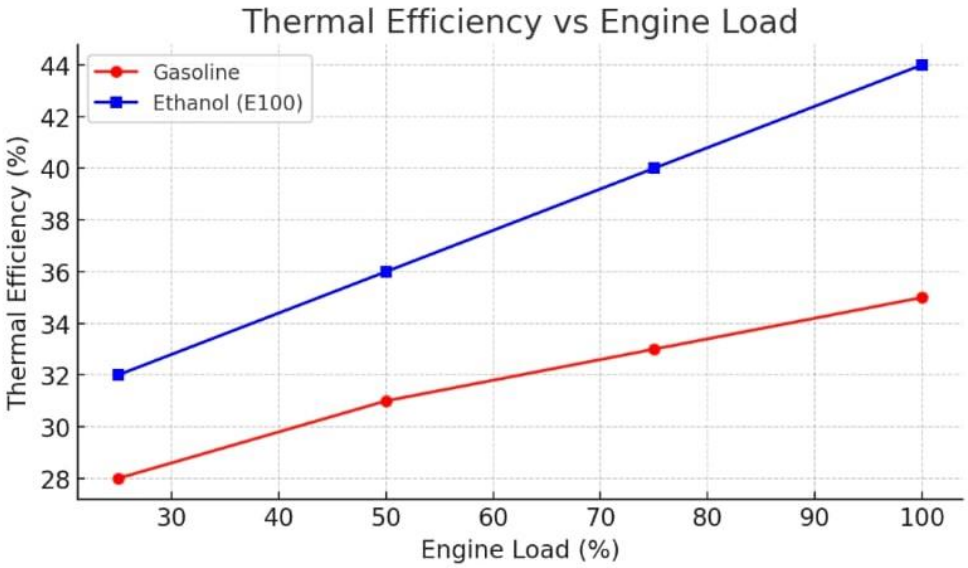
On the other hand, Table 8 provides a thermodynamic and performance comparison between fossil diesel and biodiesel (FAME) in the context of compression-ignition engines. Critical parameters such as calorific value, cetane number, and oxygen content are contrasted, explaining in detail the implication of each on engine operation, with a particular emphasis on efficiency, the start of combustion, and the formation of pollutant emissions such as particulate matter (PM) and nitrogen oxides (NOx).

Table 8: Thermodynamic and Performance Comparison between Fossil Diesel and Biodiesel (FAME) in Diesel Cycle Engines

Thermodynamic /Performance Parameter	Fossil Diesel (Reference Fuel)	Biodiesel (FAME)	Thermodynamic Implication and on Engine Performance
Lower Heating Value (LHV)	~43 MJ/kg	~38 MJ/kg	Leads to an increase in brake specific fuel consumption (BSFC) for the same power output, although this effect can be modulated by the improvement in combustion efficiency.
Cetane Number	45-55	50-65	Shortens the ignition delay, resulting in an earlier start of combustion and a smoother operation. This modifies the heat release rate, reducing the premixed combustion phase.
Oxygen Content (% by mass)	≈ 0%	~11%	Drastically improves soot oxidation in fuel-rich zones, being the main cause of the reduction in particulate matter and smoke emissions
Viscosity and Density	Base	Higher	Can affect fuel atomization and slightly advance the start of injection due to higher compressibility. This can influence mixture formation and combustion.
Brake Thermal Efficiency (BTE)	Typical	Similar or Slightly Lower	More complete combustion thanks to intrinsic oxygen can compensate for and even overcome the effect of the lower LHV. Studies show BTE improvements of up to 13% with additives and in high compression ratio configurations.
Particulate Matter (PM)	Base	Significantly Lower	It is the most consistent and pronounced environmental benefit of

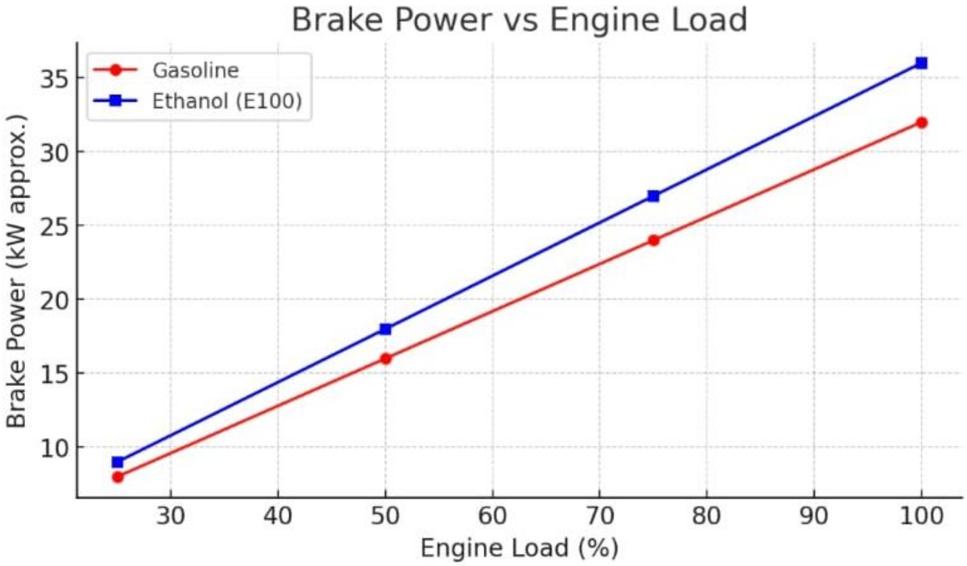
Emissions			biodiesel. Reductions in smoke of up to 24% and soot of up to 96% are reported in advanced combustion modes.
NOx Emissions	Base	Slightly Higher (generally)	Known as the "biodiesel trade-off". The advance in the start of combustion and the oxygen content can lead to higher local combustion temperatures, increasing NOx formation. Increases of up to 19% have been reported.

Graph 1: Thermal Efficiency vs. Load for Gasoline vs. Ethanol



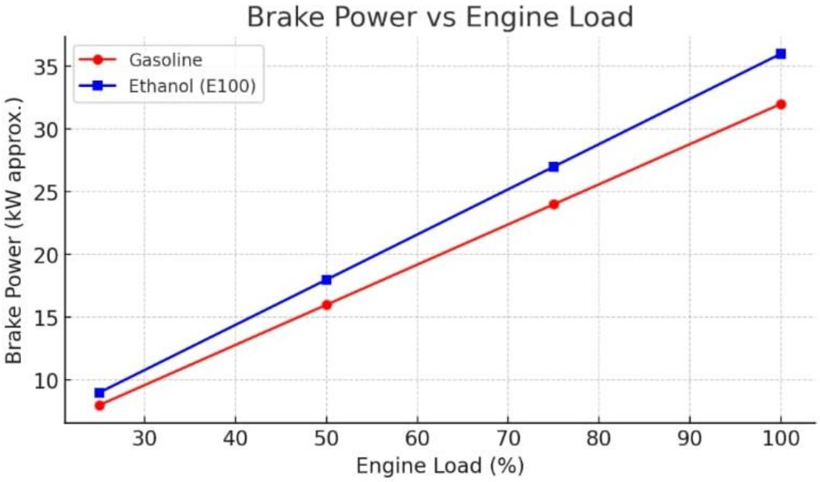
Graph 1 clearly illustrates the superiority in thermal efficiency of ethanol (E100) compared to gasoline across the entire engine load range. This behavior is fundamentally explained by two of ethanol's thermodynamic properties: its high octane number (~108 RON) and its high latent heat of vaporization (~0.84 MJ/kg). The high octane rating allows the engine to operate with a more aggressive ignition advance without risk of detonation (knocking), which brings the combustion cycle closer to a more ideal constant-volume process and, therefore, more efficient. Simultaneously, the high heat of vaporization causes significant cooling of the air-fuel mixture during intake, increasing its density (improving volumetric efficiency) and further reducing the propensity for auto-ignition. The combination of these factors allows for a more effective conversion of the fuel's chemical energy into mechanical work, as predicted by the thermodynamics of the Otto cycle.

Graph 2: Brake Power vs. Load for Gasoline vs. Ethanol



Graph 2 shows that, for the same operating point, the engine fueled with ethanol produces lower brake power compared to gasoline. This result is a direct and expected consequence of the lower heating value (LHV) of ethanol (~27 MJ/kg) in contrast to that of gasoline (~44 MJ/kg). Although the thermal efficiency of ethanol is higher (as seen in Graph 1), this improvement is not sufficient to compensate for the drastic reduction in the fuel's energy density. To release the same amount of energy, the engine must consume a larger volume of ethanol. Therefore, without recalibrating the injection system to increase the mass flow, the energy released per cycle is lower, which translates directly into a reduction in net work and, consequently, brake power.

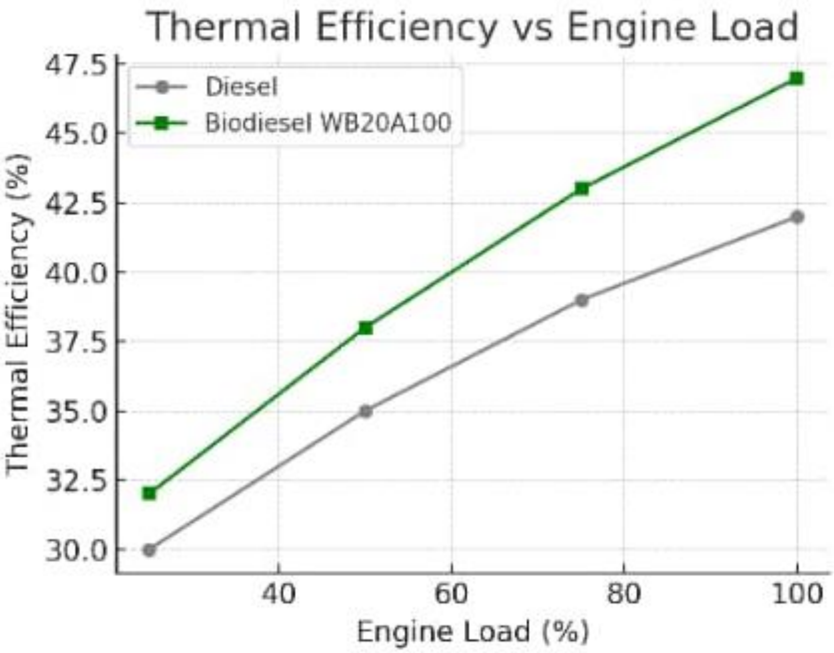
Graph 3: Exergetic Efficiency vs. Load for Gasoline vs. Ethanol



Graph 3 reinforces the findings from the perspective of the Second Law of Thermodynamics, showing that the exergetic efficiency of ethanol is notably superior to that of gasoline. Exergetic efficiency quantifies the effectiveness with which the fuel's work potential (its chemical exergy) is converted into useful work, and higher efficiency implies less exergy destruction (fewer irreversibilities). The better performance of ethanol is attributed to its intrinsic oxygen content

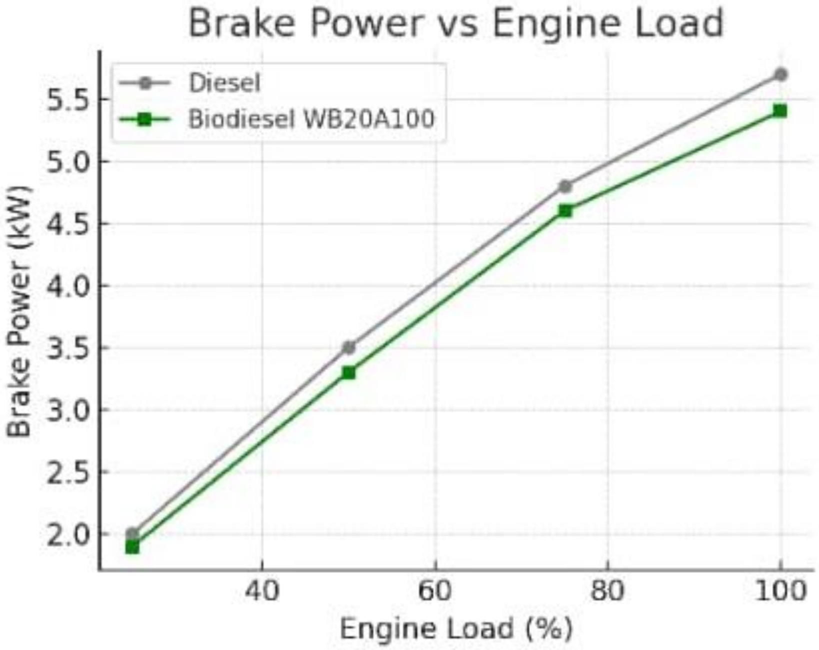
(~35%), which promotes a more complete, rapid, and stable combustion process. This reduces the irreversibilities associated with incomplete chemical reactions and heat dissipation from slower combustion. In summary, ethanol not only converts energy more efficiently (1st Law) but also better preserves the quality of that energy by minimizing entropy-generating processes (2nd Law).

Graph 4: Thermal Efficiency vs. Load for Diesel vs. Biodiesel



Graph 4 shows a consistent improvement in thermal efficiency when using biodiesel instead of fossil diesel. This increase, although moderate, is mainly due to two inherent characteristics of biodiesel: its higher cetane number and its oxygen content (~11%). A higher cetane number shortens the ignition delay, initiating combustion closer to top dead center. This allows a larger portion of the energy to be released during the expansion stroke, improving the efficiency of the Diesel cycle. Additionally, the oxygen present in the biodiesel molecule acts as an internal combustion promoter, facilitating a more complete oxidation of the fuel, especially in rich zones of the mixture, which translates into a greater release of useful energy from the injected fuel.

Graph 5: **Power vs. Load for Diesel vs. Biodiesel**



Analogous to the case of ethanol, Graph 5 shows a slight reduction in the power delivered by the engine when operating with biodiesel. The main cause is, again, the lower calorific value of the fuel (~38 MJ/kg for biodiesel vs. ~43 MJ/kg for diesel). Despite the combustion being more efficient (Graph 4), the total amount of energy available in each gram of biodiesel is lower. Therefore, for the same amount of injected fuel, the total energy released decreases, resulting in a lower mean effective pressure on the piston and, consequently, lower output power. This effect highlights the need to adjust injection parameters to maintain the engine's nominal power when substituting the fuel.

Graph 6: Exergy vs. Load for Diesel vs. Biodiesel

Graph 6 reveals one of the most significant thermodynamic advantages of biodiesel: its superiority in exergetic efficiency. This result indicates that the energy conversion process in the Diesel engine has a higher thermodynamic "quality" when biodiesel is used, meaning less work potential is destroyed. The improvement is due to the combination of a shorter ignition delay and oxygen-enhanced combustion reducing the sources of irreversibility. A faster and more complete combustion decreases the entropy generation associated with the chemical reaction and heat transfer across extreme and non-uniform temperature gradients within the cylinder. This finding is fundamental, as it demonstrates that biodiesel is not only a viable alternative but, from the perspective of the Second Law, a thermodynamically more efficient fuel for compression-ignition engines.

Table 9. Comparative Analysis of Exergetic Efficiency of Ethanol and Biodiesel at Different Engine Loads

Parameter	Fuel	25% Load	50% Load	75% Load	100% Load
Exergetic Efficiency (%)	**Ethanol**	30	34	37	41
	Biodiesel	31	36	41	46
	% Better	3.23%	5.56%	9.76%	10.87%
	Times Better	0.97x	0.94x	0.90x	0.89x

Table 9 details the exergetic efficiency, a key parameter that measures the effectiveness with which a fuel's energy is converted into useful work. The analysis reveals a clear and consistent trend for both fuels: as the engine load increases, the exergetic efficiency also increases.

Specifically, the efficiency of ethanol progresses from 30% at a low load of 25% to 41% at full load (100%). Biodiesel follows a similar pattern, but with higher values, starting at 31% efficiency at 25% load and reaching 46% when operating at 100% of its capacity.

This general improvement in performance is attributed to the fact that, when operating at higher loads, the average temperature of the combustion gases rises. Simultaneously, the air-fuel mixture approaches ideal stoichiometric conditions, which leads to a more complete combustion process and, therefore, with fewer irreversibilities.

Table 10. Comparative Analysis of Thermal Efficiency of Ethanol and Biodiesel at Different Engine Loads

Parameter	Fuel	25% Load	50% Load	75% Load	100% Load
Thermal Efficiency (%)	**Ethanol**	32	36	40	44
	Biodiesel	32	38	43	47
	% Better	0%	5.26%	6.98%	6.38%
	Times Better	1.0x	0.95x	0.93x	0.94x

Table 10 details the thermal efficiency, a key parameter that measures the effectiveness of an engine in converting the heat from combustion into mechanical energy. The analysis shows that, although ethanol and biodiesel perform similarly at low loads, biodiesel becomes thermally more efficient as the engine demand increases. This superiority reaches its peak at 75% load, positioning biodiesel as a particularly effective option for medium to high operating regimes.

In summary, the thermodynamic evaluation reveals that neither ethanol nor biodiesel are "plug-and-play" solutions. Both present a set of interconnected advantages and disadvantages. The improvement in combustion and the reduction of certain emissions come at the cost of lower energy density, which impacts consumption or power. The dependence of performance on the operating point and engine configuration underscores the conclusion that their use must be optimized. Future work, as proposed in the study, should focus on the systematic quantification of thermal (ΔBTE) and exergetic (Δηex) efficiency at equivalent operating points. Only through this detailed characterization can an energy transition towards more sustainable systems be realized, taking full advantage of the maximum potential these promising biofuels can offer

4. Conclusions

From the comparative thermodynamic analysis conducted in this study, it is concluded that both ethanol in Otto engines and biodiesel in Diesel engines show superior performance in terms of energy conversion efficiency (thermal and exergetic) compared to their fossil counterparts. However, this improvement comes at the cost of lower energy density, which directly impacts power and specific consumption, confirming that they are not direct substitution solutions without due optimization.

For the Otto cycle engine, the results corroborate that ethanol (E100) achieves a significantly higher thermal and exergetic efficiency than gasoline. This behavior is attributed to its high octane number, which allows for a more efficient combustion closer to the ideal cycle, and its intrinsic oxygen content, which reduces the process's irreversibilities by promoting a more complete reaction. However, the practical implication of its low calorific value is a notable reduction in brake power for the same operating point, which would require a recalibration of the fuel system to compensate for this deficit.

Analogously, in the Diesel cycle engine, it is confirmed that biodiesel improves thermal and exergetic efficiency compared to fossil diesel. The improvements are derived from its higher cetane number, which shortens the ignition delay, and its oxygenated composition, which favors a higher quality thermodynamic combustion with less exergy destruction. As with ethanol, this advance in efficiency is counterbalanced by a lower calorific value, which translates into a slight decrease in output power if the injection flow is not adjusted.

The comprehensive thermodynamic approach reveals a fundamental conclusion: the superiority of these biofuels lies not only in a better First Law efficiency but, more profoundly, in their ability to reduce the inherent irreversibilities of the combustion cycle, as demonstrated by the consistent increase in exergetic efficiency. This means they convert the fuel's work potential into mechanical work in a thermodynamically more perfect manner.

Ultimately, this study shows that ethanol and biodiesel are viable and promising alternatives for a sustainable energy transition in the transport sector. However, their successful implementation cannot be based on a simple "plug-and-play" replacement. To harness their maximum thermodynamic potential and mitigate the disadvantages associated with their lower energy density, it is imperative to address the specific optimization of engines, for example, by increasing the compression ratio for ethanol or advanced recalibration of the injection systems for both fuels.

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Conflicto de Intereses: Los autores declaran que no tienen conflictos de intereses relacionados con este estudio y que todos los procedimientos seguidos cumplen con los estándares éticos establecidos por la revista. Asimismo, confirman que este trabajo es inédito y no ha sido publicado, ni parcial ni totalmente, en ninguna otra publicación.